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Gel point studies for chemically modified biopolymer networks using small amplitude oscillatory rheometry

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Abstract

Solutions of xanthan gum form a strong gel upon the addition of aluminum ions (Al(III)). Previous studies have reported that the addition of chromium and ferric ions induces gelation in xanthan solutions; this study presents a characterisation of the transition from solution to gel for xanthan in the presence of Al(III). Xanthan-Al(III) solutions are shown rheologically to undergo a sol–gel transition upon heating, the extent of gelation is controlled by the temperature at which the system equilibrates. The rapid thermal equilibration of xanthan-Al(III) provides an ideal system to test the applicability of two established gelation criteria [1,2]. At the gel point, congruency in G' and G'' is observed over 2–3 decades of frequency demonstrating the applicability of the method of Winter and Chambon [1]. The difficulties associated with determining an equilibrium relaxation modulus (E) as a criterion for gelation [2] are discussed.

The gelation behaviour of xanthan-Al(III) gels is characterised for a range of polymer crosslinker combinations (stoichiometric ratios) and a limiting stoichiometric ratio below which gelation does not occur is determined. The relaxation exponent (n) is determined at the limiting stoichiometric ratio to be $n = 0.22$. A value of 0.22 for n is not in agreement with previous work for systems at a limiting stoichiometric ratio. The relaxation exponent is found to vary between 0.22 and 0.16 for a 0.5 wt% xanthan and a range of Al(III) concentrations. The temperature at which the gel point is observed, T_g, follows an asymptotic relationship with stoichiometric ratio suggesting the importance of the order–disorder transition of xanthan molecules on the gelation process of xanthan-Al(III) gels.

Keywords: Xanthan; Gelation; Rheology

1. Introduction

Xanthan gum solutions combined with trivalent metal ions have been the subject of significant interest in the gel literature primarily due to industrial applications. Xanthan–chromium gels are commonly used in the drilling industry for tertiary stage oil recovery [3–7] and preliminary investigations into the application of xanthan gum combined with ferric ions for the food industry have been conducted [8]. Xanthan gels formed by the addition of Al(III) offer unique properties compared to other metal ions. Namely, the system has relatively short but controllable kinetics and it is possible to control the extent of gelation solely through manipulation of temperature. The combination of xanthan solutions with aluminum ions has been previously investigated using $Al(NO_3)_3$ as a source $Al^{3+}_{(aq)}$ [9]. Nolte and coworkers [9] observed the gelation rate of xanthan to increase upon the replacement of $Cr^{3+}_{(aq)}$ with an $Al^{3+}_{(aq)}$ however, the equilibrium value of the storage modulus was reported to be lower. No investigation into the stoichiometric and thermal dependence of the gel point for Xanthan-Al(III) has been reported in the literature to date.

The present study investigates the gelation behaviour of xanthan with $Al_2(SO_4)_3{\cdot}16H_2O_{(aq)}$, (Al(III)) at a controlled pH of 3.8–4. The mechanical strength and gel point of the resultant gels are shown to be dependent on polymer concentration, Al(III) concentration, pH and temperature. To investigate the process of gelation and characterise the gel point, it is necessary to first identify what constitutes a gel and applicable rheological techniques to quantify the gel point.

1.1. Definition of a gel

To establish a suitable technique for measurement of the transition to a gel it is necessary to fundamentally define a gel. Several papers discuss the difficulty in defining when a gel is a ‘gel’, highlighting the erroneous use of the term ‘gel’ [10,11]. The majority of prior studies make reference to the

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theoretical work of Flory [12]. Flory states that a gel is a solid like structure that at the instant of gelation, has a structure in the fluid which extends over the entire sample volume. Flory [12] demonstrates that at the gel point, the effective molecular weight of a polymer solution goes to infinity. Physical interpretation suggests that at the gel point the shear viscosity extends to infinity ($\eta_o \rightarrow \infty$) and the equilibrium modulus is 0 ($G_\infty = 0$). In terms of polymer solutions, it is considered that during gelation a material changes from one in which connectivity extends from a single molecular scale to one in which connectivity extends throughout the entire sample [13].

For the application of Flory's [12] definition of a gel, it is necessary that the connectivity throughout the sample is continuous over any timescale and therefore the crosslinking process must be permanent. A concentrated solution of high initial molecular weight polymer is complicated by the presence of molecular entanglements, which contribute to the overall elasticity of the system. Due to the timescale of molecular entanglements being short compared to the permanent crosslinking associations, the relative contribution of molecular entanglements to the elasticity of the xanthan-Al(III) system is negligible.

1.2. Gel point determination

Determination of gel point has been the subject of significant debate in the literature. It is suggested that the definition provided by Flory [12] be used through extrapolation, however, such measurements are difficult to conduct within any close proximity to the gel point [14]. The crossover of G′ and G″ has been suggested as a criterion for gelation [15], however it is frequency dependent in most polymer systems and is observable in polymer fluids where significant molecular entanglements are present but no permanent connectivity extends throughout the solution [16]. Additionally, the study presented in this work is primarily concerned with linear viscoelastic behaviour as opposed to large deformation relationships, suggesting that the previously proposed gel equation is applicable [1]

$$\tau(t) = S \times \int_{-\infty}^{t} (t - t')^{-n} \dot{\gamma}(t')\, \mathrm{d}t' \tag{1}$$

where τ is the excess stress tensor and $\dot{\gamma}$ is the rate of deformation tensor. Winter and Chambon [1] derive Eq. (1) containing two material parameters S, being the strength of the network at the gel point and n being the relaxation exponent, enabling distinction between a range of gel structures. For a crosslinking polymer system it is shown that the loss and storage modulus are congruent (i.e. parallel) at the gel point with a frequency dependence of:

$$G' = S\sqrt{\pi/2}\,\omega^{n} = G''. \tag{2}$$

Eq. (2) demonstrates S is proportional to G′ at $\omega = 1$ Hz at the gel point. Furthermore, at a critical extent of reaction necessary for gelation, a power law relaxation of the modulus is observed to follow:

$$G(t) = St^{-n} \tag{3}$$

Winter and Chambon [1] show their definition of gelation to fulfil criteria described by Flory [12] at the gel point. The authors demonstrated the application of the gel equation (Eq. (1)) to gels of both balanced and imbalanced stoichiometry [17,18]. The relaxation exponent (n) may be calculated directly from the requirement of congruency of G′ and G″ at the gel point resulting in a constant value of tan(δ) where

$$\tan(\delta) = G''/G'. \tag{4}$$

The frequency independent value of the phase angle δ, in radians, is related to n by $\delta = n\pi/2$, for $0 < n < 1$. A gel with n approaching 1 is a purely viscous gel whereas n approaching 0, suggests a purely elastic gel. No solutions exist to Eq. (4) when $n \geq 1$ and a value of $n \leq 0$ would defy principles of thermodynamics [17]. In summary the method developed by Winter and Chambon [17] and Chambon and Winter [18] requires two parameters: the gel strength S, and the relaxation exponent, n to describe both balanced and imbalanced gelling systems.

The initial work of Winter and Chambon [17] showed ideal gels of balanced stoichiometry to have a relaxation exponent of $n = 1/2$. Ideal systems by definition are systems where the crosslinking occurs only at the ends of the molecules, the initial molecular weight of the molecules is low and no intramolecular crosslinking occurs. Intramolecular crosslinking will significantly affect the stoichiometric balance of the system, as they provide no additional contribution to the elasticity of the system. It is proposed that the xanthan-Al(III) studied in this work is non-ideal due to a high initial molecular weight ($M_w \approx 3.4 \times 10^6$), high probability of side-branching reactions and possibility of intramolecular crosslinking making it unlikely that a relaxation exponent of $n = 0.5$ would be observed at balanced stoichiometries.

The criteria of Winter and Chambon has been applied to a wide range of gel systems including chemically crosslinked and physically associating systems [1,17–24]. Winter and Chambon [1,17,18] investigated polydimethylsiloxane (PDMS) networks of balanced and imbalanced stoichiometries showing $n = 0.5$ for balanced and $n = 0.58$ for imbalanced systems. The physical gelation of a crystalising Poly(vinyl chloride) solution was also investigated showing power law relaxation at the gel point [20] suggesting the applicability of the Winter and Chambon method [1,17] to physical gels. Scanlan and Winter [21] varied the stoichiometry, polymer concentration and pre-polymer chain length and report a value of n ranging between 0.19 and 0.92. The authors observed that for an increase in pre-polymer chain length, n decreased, indicating a more elastic gel at the gel point. The physical gelation of a thermoplastic elastomer fulfilled the gelation criteria as defined by Winter and Chambon [17] showing $n = 0.11$ [22]. Cuvelier and Luanay

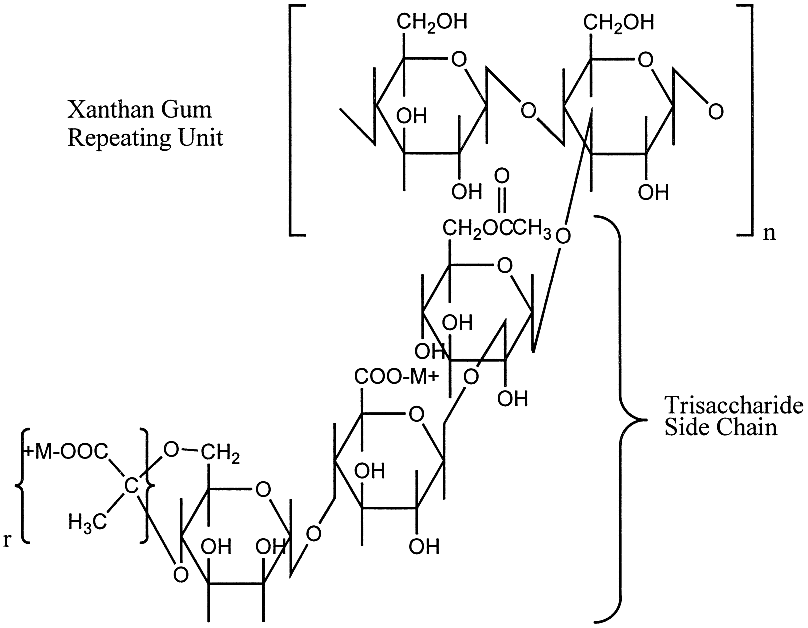

Fig. 1. Repeat unit of Xanthan gum, M represents the counterion predominantly Na^+, K^+ and Ca^{2+} and r represents the degree of pyruvate substitution.

[23] report on the gelation of a range of physical gels and observe a relaxation exponent varying between 0.5 and 0.65. Michon and co-workers [19] reported a relaxation exponent for gelatin gels being as low as 0.2–0.3. Recent work [24] for a non-ideal physically associating gelling system has shown n to vary between 0.14 and 0.5 depending on both polymer concentration and stoichiometry. It has been shown that the stoichiometry of the system as well as the pre-polymer chain length both have a significant effect on the parameters S and n [24].

The application of Winter and Chambon [1] to gels of balanced and imbalanced stoichiometry, in addition to gels with both physical and chemical crosslinks, suggests its applicability is diverse providing a reasonable frequency range in which congruency of G' and G'' at the gel point is observed. A limitation of the use of Winter and Chambon [1] is its applicability in determining a time of gelation, t_g for isothermally gelling systems due to difficulties in establishing the frequency range in which G' and G'' exhibit congruency. Previous work on xanthan chromium gels have illustrated that the gelation process occurs over a long timescale (approximately 40 h at 25°C) and that structure recovers after shear degradation suggesting intuitively the crosslinks to be reversible [5]. Previously xanthan solutions in the presence of a crosslinker have had their gelation measured as a function of time, which introduces difficulties in determining a gel point as a true material parameter.

Xanthan-Al(III) gels provide a thermally activated gelling system with relatively short equilibrium times making them ideal to study through small amplitude oscillatory rheometry, and analysed using the Winter and Chambon [1] gel point criterion. For the xanthan-Al(III) system presented, the polymer to crosslinker ratio (stoichiometric ratio) has been varied to determine the limiting ratio required for gelation as well as the effect on temperature of gelation T_g. This paper describes and discusses linear viscoelastic properties for Xanthan-Al(III) gelling solutions.

2. Sample preparation and experimental techniques

Xanthan gum is a high molecular weight extracellular polysaccharide produced by bacteria of the genus *Xanthomonas* [25]. Commercially xanthan gum is extracted from *Xanthomonas campestris* [26] however for the purpose of most scientific studies, it is extracted from *X. phaseoli*and *X. juglandis*[27]. Fig. 1 illustrates the repeat unit of xanthan gum showing two negative charges on repeat units with a pyruvate substitute and one negative charge on the repeat unit with no pyruvate substitute. Native xanthan (without heat treatment) at room temperature forms an ordered conformation postulated to be a five-fold right-handed double helix responsible for the semi-flexible properties of xanthan gum solutions [28].

Xanthan gum solutions were prepared in 1-litre batches with triple distilled water. The samples were hydrated for 24 h before being stored until use at 4°C to minimise bacterial growth. Aluminum Sulfate was used as a source of Al^{3+} and was combined under constant stirring with xanthan solutions at a controlled temperature. Retaining the temperature below 10°C was shown to retard the crosslinking associations allowing complete mixing of the xanthan and Al(III). The pH was controlled between 3.8 and 4 by the addition of 0.1 M NaOH dropwise with the pH being tested by an Orion 420A pH meter calibrated at 10°C.

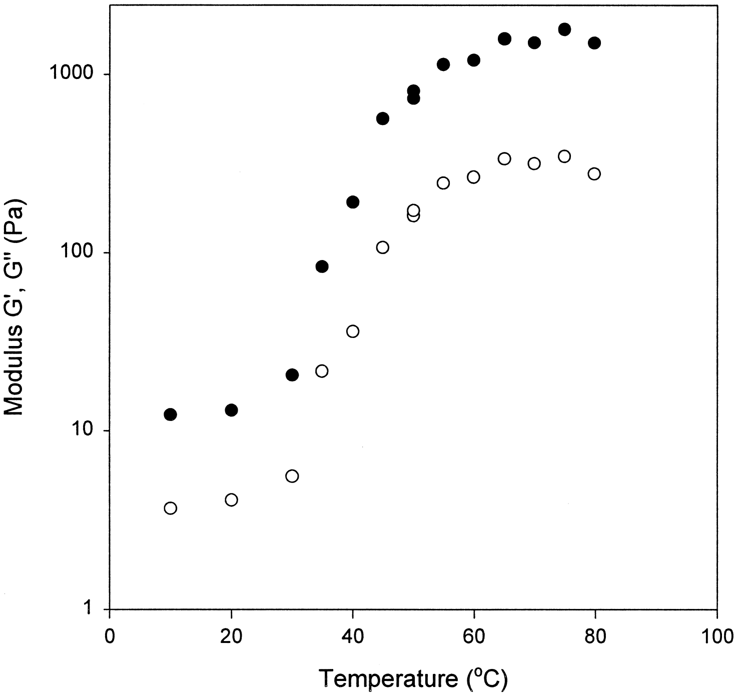

Fig. 2. Evolution of mechanical properties with temperature for 0.5 wt% Xanthan and 1400 ppm Al(III). (X) G′ and (W) G″. All measurements taken at $\omega = 1$ Hz.

Small amplitude oscillatory shear measurements were conducted using a Rheologica Stresstech Rheometer fitted with an extended temperature cell (ETU-10) and a 40 mm 4° cone. Following preparation, the xanthan-Al(III) solutions were transferred directly to the rheometer and allowed to equilibrate at 10°C for 10 min before measurements were taken. For all temperatures and concentrations investigated, measurements were conducted within the linear viscoelastic limit.

Crosslinking was observed to proceed with an increase in temperature. The extent of gelation was controlled by holding the solution at a constant temperature with equilibration of mechanical properties occurring after 10 min. Xanthan-Al(III) solutions were heated from 10–85°C over various timescales with no observable variation in final gel strength. Previous work of xanthan complexing with chromium ions suggests a two stage reaction path with the first stage forming a 1:1 xanthan:ion complex followed by a second stage resulting in a 2:1 xanthan:ion crosslink [29]. No investigation into the kinetics of reaction has been conducted here to establish the validity of a two stage reaction path for xanthan-Al(III) systems as it is postulated that the 1:1 complex will provide no contribution to the overall elasticity. Spectroscopic studies of xanthan complexing with chromium provide evidence for the postulate of 1:1 complexes not contributing to elasticity [9]. Oscillatory tests revealed no mechanical degradation of xanthan-Al(III) after 4 h at 85°C and bench tests showed no synerisis over the polymer and crosslinker concentrations investigated.

3. Linear viscoelastic measurements of the gel point

As discussed above, the gelation of xanthan-Al(III) solutions occurs through the heating from a non-reactive mixing temperature of 10°C up to complete gelation at 85°C. The samples were heated in 10°C increments and an equilibration time of 10 min after each temperature increment ensured no reaction effects were occurring during the frequency sweeps. Frequency sweeps were conducted over the range 0.04–8 Hz. Fig. 2 illustrates the evolution of dynamic properties as measured at a frequency of 1 Hz for 0.5 wt% xanthan and 1400 ppm Al(III). No significant increase in G′ or G″ was observed below 30°C, whilst above 30°C, an inflection in mechanical properties was observed that plateaus above temperatures of 70°C. No crossover in G′ and G″, or maximum in G″ was observed, both of which have been previously used for a gelation criteria [24,30] and both of which have been shown to be frequency dependent measures of the gel point [24].

To characterise the gel point, two frequency independent measures have been investigated. In addition to the technique of Winter and Chambon [1], a more direct criterion for gelation proposed by Djabourov [2] has been considered. Djabourov [2] proposed that the value of the storage modulus as the frequency of oscillation approaches zero, or relaxation time approaches ∞, may be considered a measure of gel rigidity;

$$E = \lim_{\omega \to 0} G'(\omega) \tag{5}$$

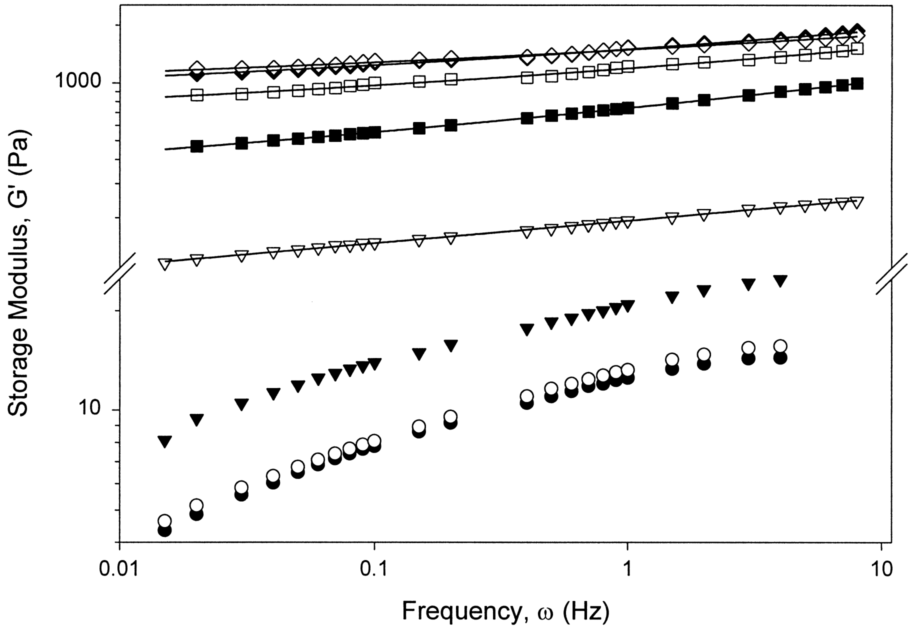

Fig. 3. Frequency dependence of the storage modulus with increasing temperature for 0.5 wt% Xanthan and 1400 ppm Al(III). (X) 10°C, (W) 20°C, (P) 30°C, (L) 40°C, (B) 50°C, (A) 60°C, (V) 70°C and (S) 80°C. Solid lines represent three-parameter power law fits as described in Eq. (7). No regression was possible for data at $T \leq 30$°C.

with E being the 'relaxed shear modulus'. The first point at which E is non-zero is considered to be indicative of the onset of an infinite spanning network or the gel point. The approach adopted by Djabourov [2] is analgous to the proposal of Winter and Chambon [1] in that at the gel point, the response of the transient shear modulus, $G(t)$ to a rapid shear experiment will follow;

$$G(t) = St^{-n} \tag{6}$$

and $G(t)$ will have a finite value at long times beyond the gel point. The key difference between the techniques is that Djabourov [2] argues it is necessary that the plateau

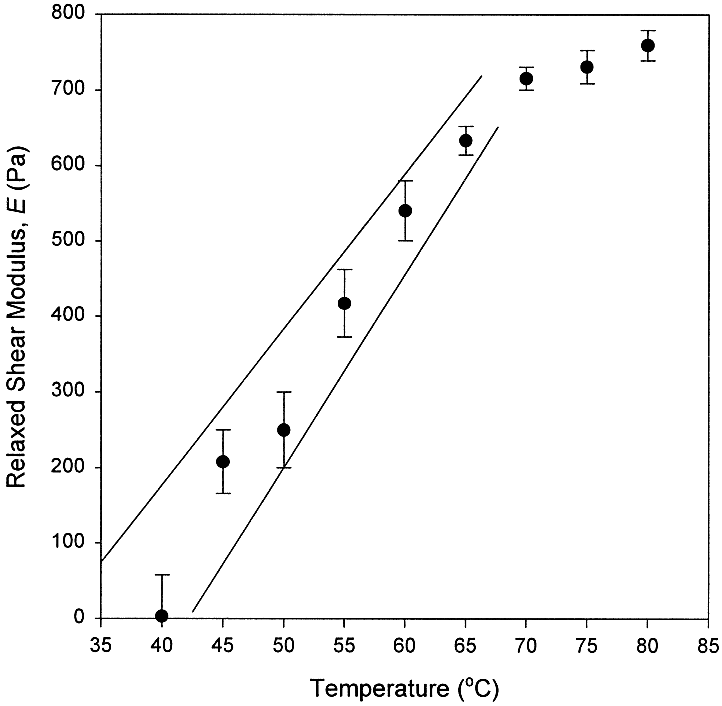

Fig. 4. Relaxed Shear Modulus, E versus Temperature for 0.5 wt% Xanthan and 1400 ppm Al(III). Intercept represents temperature of gelation T_g as defined by Djabourov [2].

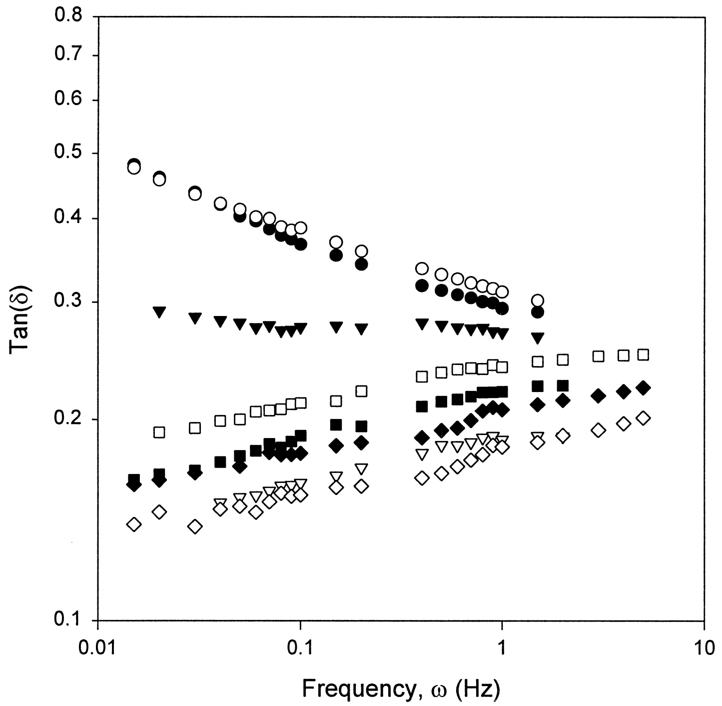

Fig. 5. Tan(δ) versus ω for a range of temperatures for 0.5 wt% Xanthan and 1400 ppm Al(III). (X) 10°C, (W) 20°C, (P) 30°C, (A) 40°C, (B) 50°C, (V) 60°C, (L) 70°C and (S) 80°C.

modulus be directly observed. Fig. 3 illustrates the frequency dependence of G′ for 0.5 wt% xanthan and 1400 ppm Al(III) at a range of temperatures illustrating the ambiguity in observing directly a plateau modulus at low frequencies. The data presented in Fig. 3 was fitted to a three-parameter power law fit:

$$G'(\omega) = E + K\omega^{q} \tag{7}$$

Where K is the coefficient to the power law fit and q represents the slope of the power law fit. Eq. (5) was unable to

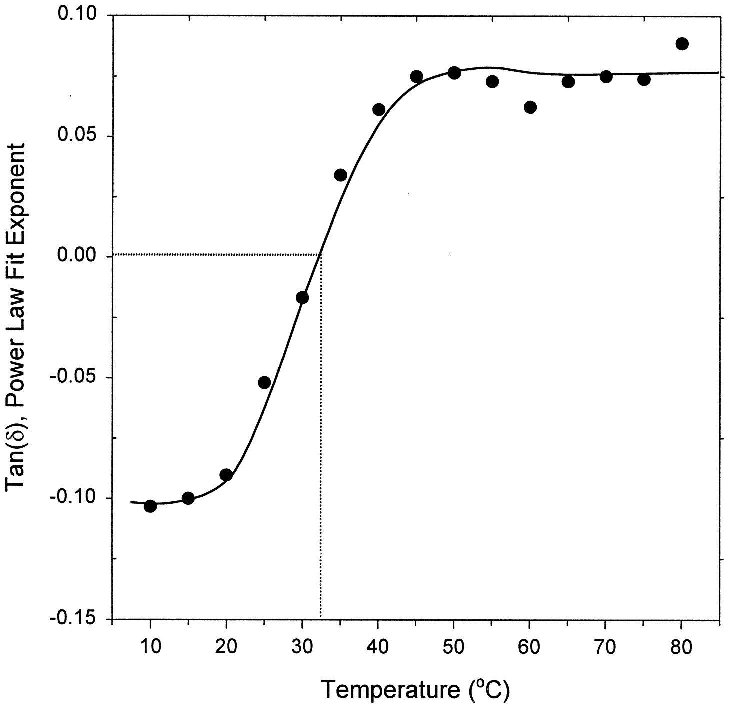

Fig. 6. Tan(δ), power law q versus temperature for 0.5 wt% xanthan and 1400 ppm Al(III). All correlation coefficients for power law fit $R^2 > 0.98$.

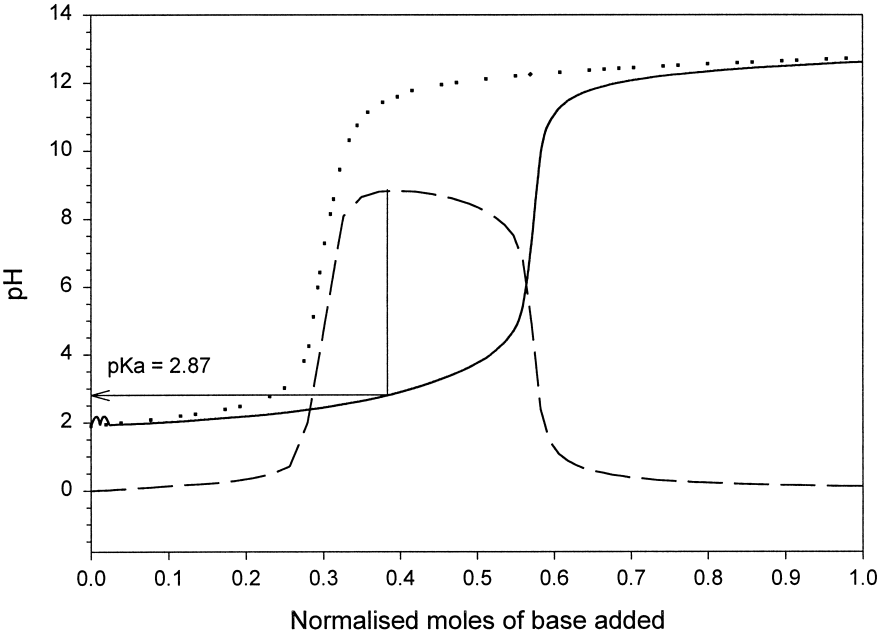

Fig. 7. pK_a for 0.5 wt% xanthan in distilled water. Full curve represents 0.5 wt% Xanthan, dotted curve represents pure distilled water and the dashed curve represents the difference with the maximum illustrating the pK_a due to the contribution of polymer.

describe the data taken at $T < 40°C$, and for $T \geq 40°C$, $E$was determined as being greater than 0. Fig. 4 illustrates the dependence of E on temperature showing a linear relationship up to higher temperatures. Although all correlation coefficients were observed to be greater than 0.995 for the regression with Eq. (5), the limited number of data points at low frequencies suggests the sensitivity to accurate determination of E is questionable, indicated by the broadening error bars in Fig. 4.

Due to such limitations, the point temperature where $E = 0$ can only be determined confidently within a 6°C temperature range. The intercept determined from Fig. 4 is interpreted as the temperature of gelation as defined by Djabourov [2], $T_g = 36.6°C$ for 0.5 wt% xanthan and 1400 ppm Al(III).

Unlike the method proposed by Djabourov [2], the technique of Winter and Chambon [1], fits data over the entire frequency range rather than focusing on the low frequency

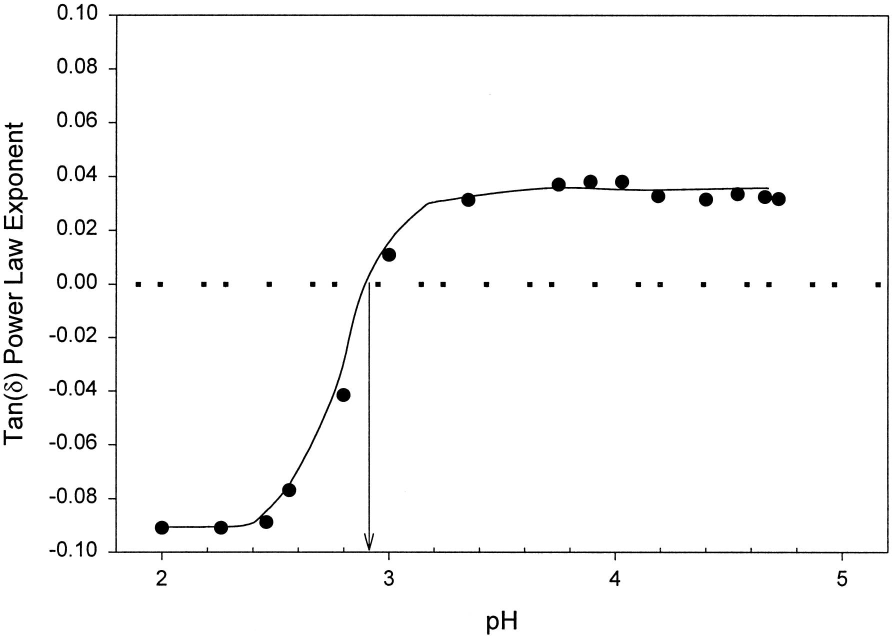

Fig. 8. Tan(δ), power law fit versus pH for 0.5 wt% xanthan and 900 ppm Al(III) at various pH values. All correlation coefficients for power law fit $R^2 > 0.98$.

data. To consider the applicability of the gel point determination method proposed by Winter and Chambon [1], it is necessary to take a power law fit of tan(δ) over a range of frequencies. Fig. 5 illustrates the frequency dependence of tan(δ) for each temperature of the system described in Fig. 2. A transition of tan(δ) behaviour from a negative to positive slope is observed as temperature is increased. A power law fit to the data in Fig. 5 was obtained over at least two decades of frequency with a correlation coefficient, $R^2 \geq 0.97$. The technique of Winter and Chambon [1] has been applied to a number of systems where two or less decades of frequency have been considered [20,24,31]. Fitting tan(δ) to a power law relationship yields a power law coefficient at each temperature, the relationship of which is described in Fig. 6. The temperature at which the power law index of tan(δ) passes through 0 represents a frequency independent measure of tan(δ) and thus congruency in the behaviour of G' and G'' fulfilling the requirements of the gel point as outlined in Eq. (4). From the value of tan(δ) at the gel point a relaxation exponent is calculated. Fig. 6 suggests a T_g of 32°C, which is on the low end of that observed in Fig. 4 however still within the error range. The linearity of log [tan(δ)] with log[ω] over a number of decades of frequency suggests physical associations are masked by the association of xanthan with Al(III). An increase of tan(δ) at lower ω, characteristic of physically associating systems [24], is not observed. It is postulated that a power law relationship holds over an even greater frequency range, however it was impractical to access lower frequencies as discussed and inertia effects were observed at higher frequencies.

Application of the Winter and Chambon [1] criterion for gelation suggests that small amplitude oscillatory rheometry may be used to characterise the sol–gel transition in terms of a temperature of gelation T_g, relaxation exponent n, and storage modulus G' at the gel point.

4. Stoichiometric dependence of the gel point

Defining a stoichiometric ratio between polymer (xanthan) and crosslinking species Al(III) is complicated by the nature of both the crosslinker and the polymer components. Xanthan exists in aqueous solutions in an ordered conformation at room temperature and the conformation transition from a semi-flexible ordered molecule to a random coil occurs over the temperature range 30–80°C depending on ionic strength [32,33]. Additionally, the hydration of Al(III) with water provides a range of hydrated species, the concentration of each being dependent on pH.

The xanthan used in this study was determined as having a weight average molecular weight of $M_w = 3.4 \times 10^6$ and a polydispersity of $M_w/M_n = 1.26$ as measured by Gas Permeation Chromatography-Static Light Scattering (GPC-SLS). The degree of pyruvate substitution on the terminal manose residue of the trisaccharide side-chain is reported to vary between 0.31 and 0.56 [34,35]. For preliminary estimates it is hypothesised that each monomer unit is a potential crosslinking site. The average molecular weight of a repeat unit is calculated at 1042 suggesting 3450 repeat units per molecule and subsequently 3450 potential crosslinking sites. This model is based on the assumption that the carboxylic acid group on the side-chain is critical in the association of xanthan with trivalent metal ions [29,36].

Evidence for the carboxylic acid being active in the crosslinking process is observed when considering the pK_a of xanthan solutions and the subsequent pH dependence of the Xanthan-Al(III) gelation process. Fig. 7 illustrates the determination of the pK_a of 0.5 wt% xanthan by comparison with titration curves for pure water. This results in a pK_a of 2.87, which is in reasonable agreement with 2.6 in 0.1 M NaCl previously reported [9]. Fig. 8 illustrates the pH dependence of the slope of tan(δ) for 0.5 wt% xanthan and 900 ppm Al(III) equilibrated at 85°C. For pH <2.9 no gelation is observed suggesting that increasing the number of protonated carboxylic acid sites reduces the ability of the system to crosslink. For pH > 3.6 the slope of tan(δ) is seen to be constant suggesting control of the pH between 3.6 and 4.0 is reasonable to ensure the state of protonation of the xanthan molecule does not affect the gelation mechanism and hence the rheological properties. Any changes to the rate of gelation or final properties of the gel are then due only the concentration of Al(III) species present, or to the number of carboxylic acid residues available, postulated to be a function of the conformation transition. The affect of the conformation transition and its relation to the gelation process will be addressed later in the discussion.

In addition to the effect of pH on xanthan, the dependence on the disassociation of Al(III) has been considered. Aluminum is known to dissociate into a number of hydrated species [37,38]. If the total concentration of aluminum is kept below a critical amount, no precipitation of solid $Al(OH)_{3(s)}$ will occur and the hydrated species will follow the general dissociation equation [38]:

$$x\mathrm{Al}^{3+} + y\mathrm{H_2O} \leftrightarrow \mathrm{Al}_x(\mathrm{OH})_y^{(3x-y)+} + \mathrm{yH}^+ \quad (8)$$

The formation constant (Q_{xy}) from which the relative concentrations of each species may be calculated follows:

$$Q_{xy} = \frac{[\mathrm{Al}_x(\mathrm{OH})_y^{(3x-y)+}] \times [\mathrm{H}^+]^y}{[\mathrm{Al}^{3+}]^x} \quad (9)$$

For all concentrations of Al(III) applied in this work, a pH < 5 is sufficient to ensure no precipitation of solid $Al(OH)_{3(s)}$. It shall be assumed that the crosslink forms through an ionic bridge consisting of a hydrated aluminium ion and two polymers. The pH dependence of the gel point presented in Fig. 8 suggests that at pH > 2.9 there are sufficient concentrations present of the hydrated aluminium ions required for crosslinking species. Solving Eq. (7) with the activity coefficients (Q_{xy}) for 1400 ppm Al(III) [38], it was

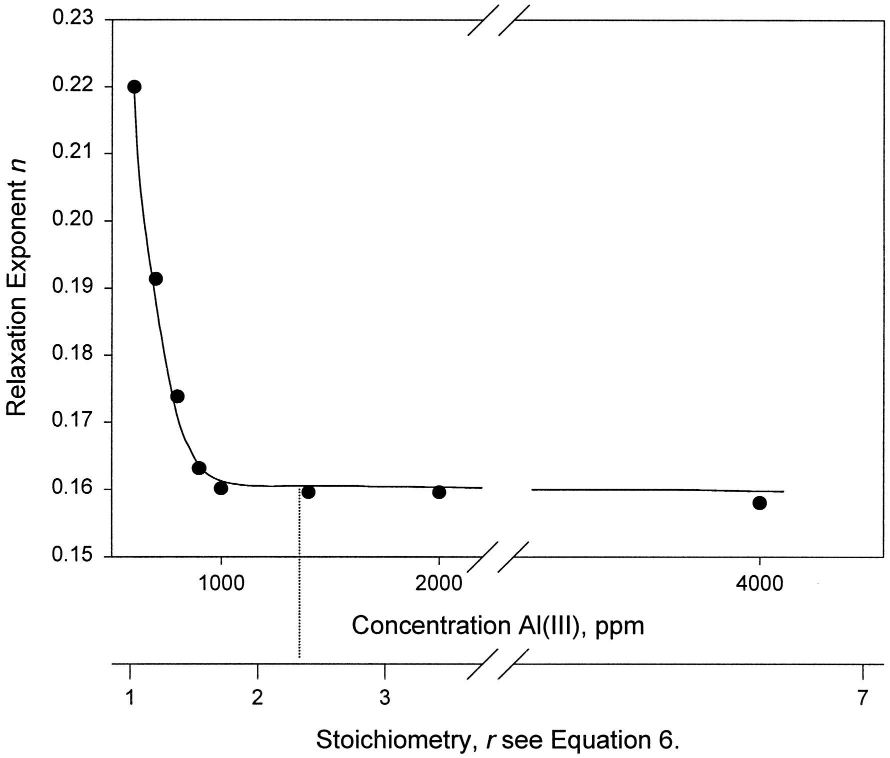

Fig. 9. Relaxation Exponent *n* versus Stoichiometry for 0.5 wt% Xanthan. Stoichiometry *r*, based on Eq. (14) and all values of *n* determined by Winter and Chambon [1] technique.

found that Al^{3+}, $Al(OH)_2^+$ and $Al(OH)^{2+}$ are the only species present in any significant quantities. The dependence of the gel point on pH illustrated in Fig. 8 combined with solutions to Eq. (7) suggests that monomeric species are responsible for the formation of crosslinks.

To consider the effect of the ratio of crosslinker to polymer concentration on the gelation process, it is convenient to define a stoichiometric ratio, *r*. In order to define a stoichiometry for xanthan-Al(III), the arguments presented by Flory [12] for the crosslinking of polymer chains are used. Application of Flory's [12] model necessitates a defined crosslink structure. It is proposed that the crosslinks in this system consist of a hydrated aluminum species combined with two repeat units, each on different xanthan molecules. If we consider each xanthan molecule to consist of exactly *y* repeat units, with a number of crosslinks *v*/2 introduced to the system, then the probability of any repeat unit in the system containing a crosslink is given by

$$p = (v/2) \times 2 \times (1/N_o) = v/N_o \qquad (10)$$

where N_o is the total number of repeat units in the entire system. Flory [12] then defines the primary degree of polymerisation as *y* as it represents the initial number of repeat units joined before any crosslinking occurs. It follows that if the crosslinking is random, the expectancy of crosslinks on any molecules may be expressed as

$$\varepsilon = p \times (y - 1) \qquad (11)$$

For $\varepsilon < 1$, an infinite expanding network is not expected. If $\varepsilon > 1$ then statistically, an infinite expanding network is expected and gelation is seen to occur. Therefore $\varepsilon = 1$ is the critical value required for gelation. In terms of xanthan and Al(III), it follows that:

$$N_o = [\text{xanthan}] \times \left(\frac{M_w}{M_l}\right) \qquad (12)$$

where [xanthan] is the molar concentration of xanthan and M_w and M_l are the molecular weights of xanthan and a xanthan repeat unit, respectively. Similarly the primary degree of polymerisation may be expressed as:

$$y = \left(\frac{M_w}{M_l}\right) \qquad (13)$$

If *v*/2 is the potential number of crosslinks that may be introduced into the system, as each crosslink contains one $Al_x(OH)_y^{(3x-y)+}$, then $v = [Al_x(OH)_y^{(3x-y)+}] \times 2$. Combination of Eqs. (11)–(14) yields:

$$\varepsilon = \left(\frac{[Al_x(OH)_y^{(3x-y)+}] \times 2}{[\text{xanthan}] \times M_w/M_l}\right) \times \left(\frac{M_w}{M_l} - 1\right) \qquad (14)$$

If we assume that M_w/M_l q 1 then the expectancy of crosslinks simplifies to the stoichiometric ratio *r*:

$$r = \varepsilon \approx \left(\frac{[Al_x(OH)_y^{(3x-y)+}] \times 2}{[\text{xanthan}]}\right). \qquad (15)$$

Eq. (16) suggests that for $r < 1$, insufficient combination of

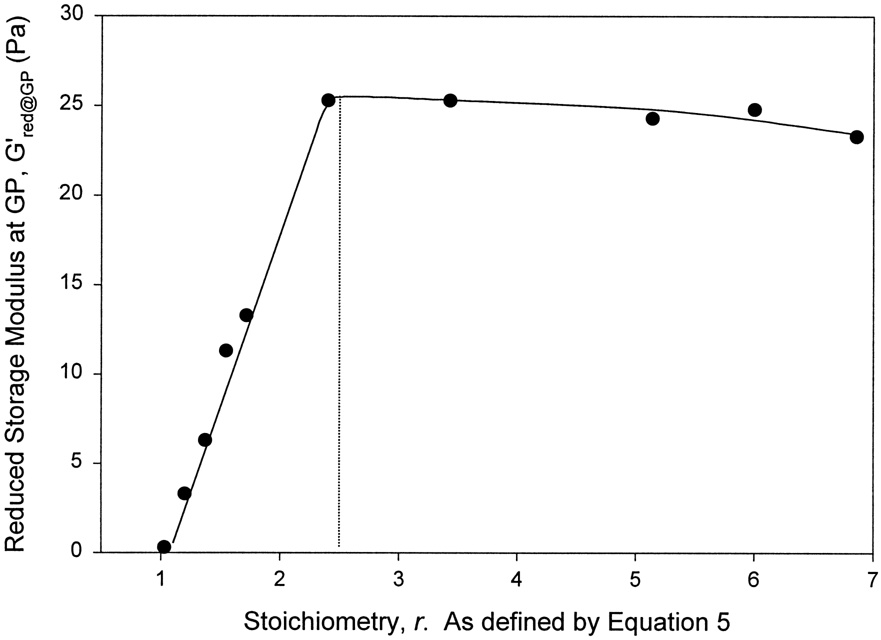

Fig. 10. G'_{red} as measured at the gel point (G'_{red} at the gel point) as a function of Stoichiometry, r for 0.5 wt% Xanthan. Dotted line indicating r_e and full line is a guide to the eye. All values taken at $\omega = 1$ Hz.

polymer and crosslinker is present for gelation to occur, whereas at $r = 1$ the system is balanced stoichiometrically while for $r > 1$ excess crosslinker is present. It is proposed to analyse the dependence of the gelation of solutions of xanthan-Al(III) for a range of stoichiometries to test the definition of r as defined by Eq. (16).

The thermal gelation has been investigated for Al(III) concentrations ranging between 400 ppm (1.27 mmol Al(III)) and 4000 ppm (12.7 mmol Al(III) and for 0.5 wt% (5 mg/ml) xanthan to establish a lower limit of crosslinker required for gelation as defined by Winter and Chambon [1]. Bench tests showed 0.5 wt% xanthan with less than 600 ppm Al(III) would not gel under any thermal conditions. Therefore a concentration of 600 ppm Al(III) has been allocated $r = 1$ as defined by Eq. (16). The concentration of $Al_x(OH)_y^{(3x-y)+}$ required in Eq. (16) for $r = 1$ is within 10% of the total concentration $Al(OH)_2^+$ and $Al(OH)^{2+}$ species present for 600 ppm Al(III) at a pH of

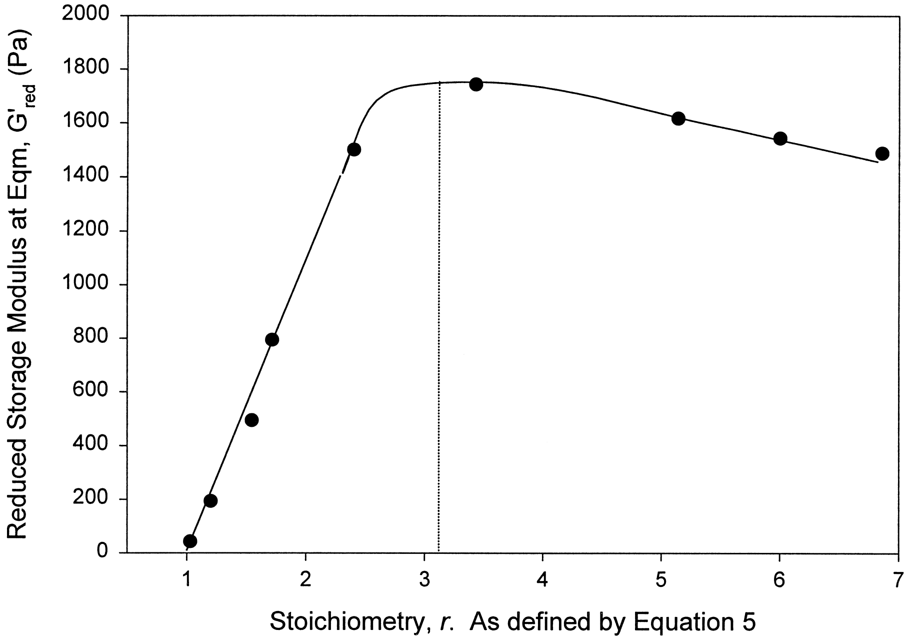

Fig. 11. G'_{red} versus Stoichiometry r for 0.5 wt% Xanthan. All values of G'_{red} estimated from development of mechanical properties with Temperature. Dotted line indicating r_e and full line is to guide the eye. All values taken at $\omega = 1$ Hz.

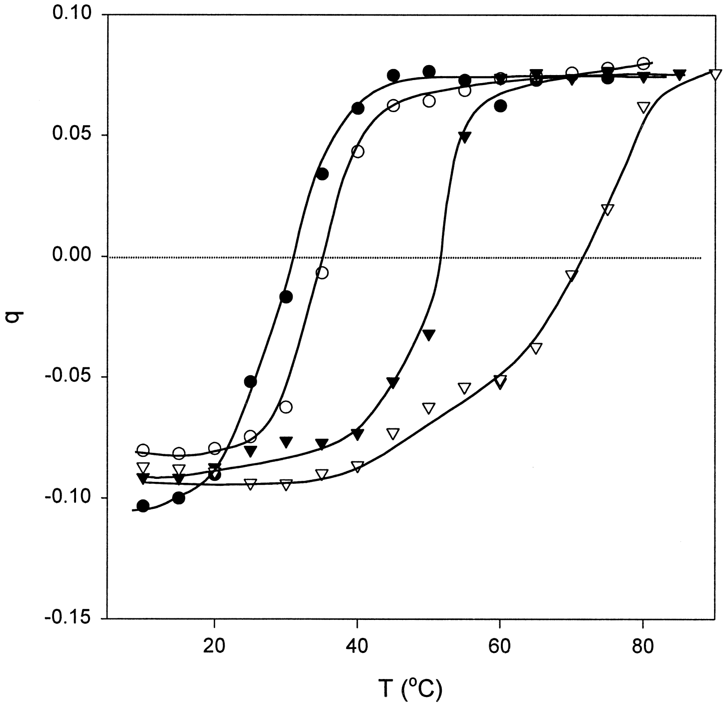

Fig. 12. Tan(δ) power law coefficient versus temperature for a range of stoichiometries for 0.5 wt% Xanthan. (L) 600 ppm Al(III), $r = 1.0$, (P) 700 ppm Al(III), $r = 1.20$, (W) 1000 ppm Al(III), $r = 1.71$ and (X)1400 ppm Al(III), $r = 2.40$. All correlation coefficients for power law fit $R^2 > 0.98$.

3.8, providing further evidence for the monomeric species being critical in the formation of elastically effective cross-links.

For each stoichiometry meeting the gel point criteria of Winter and Chambon [1], a relaxation exponent, *n* was calculated and is presented in Fig. 9. The maximum determined value of $n = 0.22$ at 600 ppm ($r = 1.0$) is low compared to previous findings of $n = 0.5$ for balanced stoichiometric systems [17]. A low value of *n* is suggested to be due to the high value of the initial polymer molecular weight which is consistent with previous observations [21]. The relaxation exponent appears to plateau to a constant value

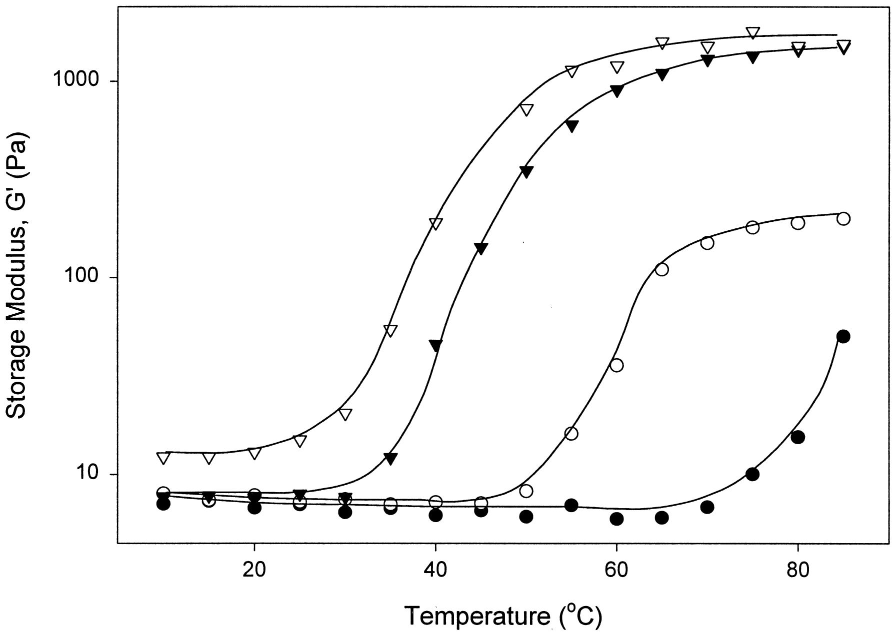

Fig. 13. Development of storage modulus with temperature for a range of stoichiometries for 0.5 wt% xanthan. (X) 600 ppm Al(III), (W) 700 ppm Al(III), (P) 1000 ppm Al(III) and (L) 1400 ppm Al(III). All measurements taken at $\omega = 1$ Hz and lines provide a guide to the eye.

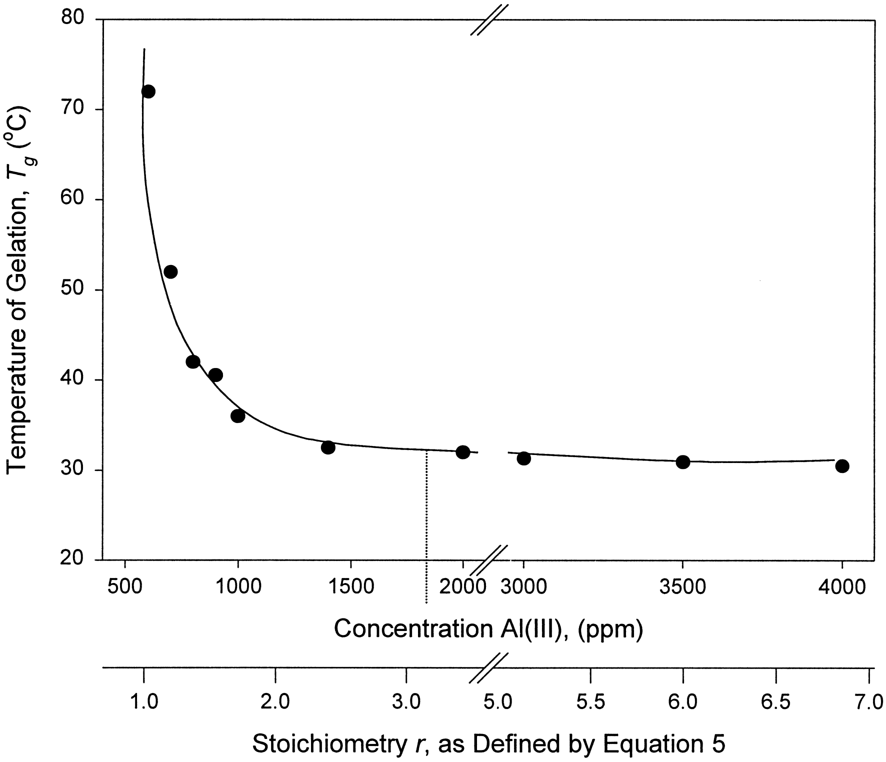

Fig. 14. Dependence of T_g on r for 0.5 wt% Xanthan. Closed circles represent T_g as defined by Winter and Chambon [1] for a range of stoichiometries. Above the curve may be regarded as a gel whereas below the curve gelation has not occurred and may be regarded as a viscoelastic solid.

of $n = 0.16$ for stoichiometries above $r \approx 2.2$ suggesting the structure at the gel point does not increase in elasticity for higher stoichiometries ($r > 2.2$).

To consider the trend in relaxation exponent with stoichiometry it is important to determine the elastic strength at the gel point by analysing the dependence of G′ at the gel point, on stoichiometry. To evaluate the effect of elastically effective crosslinks only, it is necessary to convert G′ to a reduced form:

$$G'_{red}(T) = G'_{gel}(T) - G'_{sol}(T). \qquad (16)$$

$G'_{sol}(T)$ represents the storage modulus of xanthan in the absence of crosslinker at temperature T, and G'_{gel} is the storage modulus of the gelled system. Eq. (15) suggests that below a limiting concentration of Al(III) where it is not possible for a gel to form, $G'_{red} \rightarrow 0$. It is recognised that in addition to elastically effective crosslinks resulting from chemical crosslinking, there will exist a contribution from "trapped entanglements" [39]. It is proposed that before the percolation threshold (gel point), the contribution of "trapped entanglements" to the overall modulus shall be minimal. Following percolation, if quantitative analysis of the storage modulus is to be conducted, it is necessary to account for the existence of "trapped entanglement" [40].

Fig. 10 illustrates G'_{red} at the gel point as a function of stoichiometry for 0.5 wt% xanthan. G'_{red} appears to approaches 0 at a stoichiometric ratio of $r = 1$. In addition, a maximum in G'_{red} occurs at $r = 2.4$. This is the effective stoichiometry, r_e [17]. Beyond r_e, any further increase in r results in a limited contribution to the density of elastically effective crosslinks at the gel point. The correlation of $r_e = 2.4$ at the gel point observed in Fig. 10 with the plateau in the relaxation exponent at $r = 2.2$ observed in Fig. 9 supports this hypothesis. If no increase in G'_{red} at the gel point is observed for $r > r_e$, it is reasonable to assume that the relaxation exponent will become constant as it represents the elasticity of the gel structure at the gel point. An r_e of 1.3 was observed in an ideal PDMS system [17] compared to the theoretically expected value of 1, the difference suggested to be due to side-branching [17]. The xanthan-Al(III) system reported here has a high initial degree of polymersiation, $y \approx 3000$, suggesting the occurrence of side-branching to be statistically significant and the high value of r_e to be reasonable.

A similar trend is observed for G'_{red} at $T = 85$°C as shown in Fig. 11. G'_{red} at $T = 85$°C also approaches 0 at a stoichiometric ratio of $r = 1$. However, a maximum in G'_{red} $T = 85$°C occurs at $r = 3.2$, which is significantly higher than is observed when considering the elasticity at the gel point (r_e at the gel point $= 2.4$). To further investigate the observations of G'_{red} at 85°C and the high value of r_e ($r_e \approx 3.2$) it is appropriate to consider the trend in temperature on gelation with stoichiometry.

At both the gel point and at $T = 85$°C, the observations of

$G'_{red} \rightarrow 0$ at $r = 1$, suggests that the proposed definition of stoichiometry derived from Flory [12] to be valid. For $r < 1$, the gel point criteria of Winter and Chambon was not fulfilled. The decrease of G'_{red} at $r > r_e$ is hypothesised to be due to an increased probability of the occurrence of a closed loop system of molecules which will not contribute to the overall elasticity of the gel.

5. Thermal dependence of the gel point

The xanthan-Al(III) system undergoes a gel transition through the addition of heat. The dissociation of Al(III) and the equilibrium relationships described in Eqs. (8) and (9) are known to have limited thermal dependence [37] and no solid precipitate was observed in all experiments reported. We hypothesise the conformation transition of xanthan is responsible for the development of the gel state with a similar mechanism to that proposed for methylcellulose [41,42]. That is, as the xanthan molecule attains its random conformation, opposed to the ordered semi-flexible form at room temperature, statistically, more sites are available for crosslinking between the carboxylic acid on the xanthan sidebranches and the available hydrated Al(III) species. If this is the case, at a constant xanthan concentration, we would expect that as less Al(III) is available, i.e. higher *r*, the gel transition would occur at higher temperatures and the gel strength would decrease. These trends are well exemplified in Figs. 12 and 13 for 0.5 wt% xanthan and varying concentrations of Al(III). Fig. 12 illustrates the power law coefficients from $\tan(\delta)$ versus ω as a function of temperature. Both a shift in the intercept to higher temperatures and a broadening of the inflection can be observed with a decrease in *r* to a limiting value of 600 ppm Al(III), $r = 1.0$. Below $r = 1.0$ gelation was not observed within the temperature range investigated. The broadening of the inflection of power law coefficients at lower stoichiometries suggests that gelation occurs gradually over a wider temperature range. Fig. 13 illustrates the dependence of the development of G' for a range of *r*, showing although the gel point criterion is observed for 600 ppm no plateau in the storage modulus is seen. Additionally, a shift of the inflection to higher temperatures with decreasing *r* is observed as is the reduction in the final plateau value of G' at 85°C suggesting a decrease in gel strength and number of effective crosslinks.

The relationship between T_g and *r* is presented in Fig. 14. The solid line represents the limiting temperature for gelation as a function of *r*, according to the gel point criteria of Winter and Chambon [1]. The direct observation of the thermal dependence of the gel point adds important insight into the mode of gelation of xanthan gum to the previous studies of xanthan with trivalent metal ions [8,9,29]. Nolte et al. (1995) observed an increase in both final gel strength and gelation rate with temperature however, no report on the variation of T_g with *r* is made. Fig. 14 illustrates at high values of *r*, T_g can be seen to approach a limiting value of 28°C. This asymptotic behaviour indicates that only a limited proportion of xanthan in the random coil conformation is required for gelation at this specific polymer concentration. No further reduction in T_g is observed for $r > 3.2$, which is similar to the r_e determined for G'_{red} at 85°C in Fig. 11. To correlate the gelation with the conformational transition and to further test the proposed mechanism of gelation, investigation of the kinetics of gelation and optical activity of xanthan in the presence of Al(III) will be undertaken in a range of Al(III) concentrations.

In addition to the plateau of T_g at high *r*, Fig. 14 shows asymptotic behaviour at low stoichiometries towards $r = 1$. This behaviour suggests that further increase in temperature would not induce gelation at lower stoichiometries. This supports the stoichiometric definition that suggests at $r < 1$ gelation will not occur as well as the importance of the conformation transition to the gelation process which is reported to be complete at between 70 and 80°C [43,44].

Unlike many other naturally occurring systems studied, solutions of xanthan-Al(III) gel on the addition of heat as opposed to setting on the removal of thermal energy of the system as is observed for carrageenan, pectin, gellan, gelatin and other naturally occurring polymers [45–47]. The proposed gelation mechanisms of many biological systems are based on the formation of ordered domains through the association of molecules. For the gelation of xanthan-Al(III) it appears necessary to remove the ordered conformation of xanthan so that a critical number of repeat units are available for association with monomeric hydrated aluminum species. The gelation of methylcellulose is similar to the proposed mechanism of xanthan-Al(III) as it too gels with the addition of heat [41]. However, for the gelation of methylcellulose, as the solution is heated the ends of the bundles come apart, exposing methyl groups to the aqueous environment and the ends then associate with other molecules. The strength of these gels depends upon the degree of methyl substitution [41]. With the xanthan-Al(III) system, once enough repeat units are available at temperatures above the initiation of the conformation transition, crosslinking begins. The number of repeat units available is not effected by *r*, however as *r* is increased the extent of gelation at that specific temperature also increases. This supports the proposed mechanism, as more Al(III) is available for crosslinking at a specific temperature (or stage of the conformation transition), the greater the potential for association between xanthan and Al^{3+}(aq) and hence the greater the density of crosslinks. Further insight into the validity of the proposed mechanism will be obtained through a detailed analysis of the thermal reversibility of xanthan-Al(III) gels.

6. Conclusions

The stoichiometric and thermal dependence of the gelation of xanthan solutions in the presence of Al(III) has been studied. The criteria for gelation presented by Djabourov [2] suggesting $E \rightarrow 0$ as $r \rightarrow 1$ holds, however evaluation and interpretation of E is difficult due to experimental constraints associated with accessing low frequency data. The power law relaxation of G' and G'' holds over at least two decades of frequency at the gel point suggesting the applicability of Winter and Chambon [1] as a criteria for gelation. The xanthan-Al(III) gels fulfil the gel point criteria of Winter and Chambon [1] and Chambon and Winter [17], for a range of stoichiometries, however no crossover in G' and G'' or maximum in G'' was observed in any of the systems investigated. The relaxation varies between 0.22 and 0.16 indicating an elastic gel even at balanced stoichiometries. The stoichiometry was derived from arguments presented by Flory [12] and agreed with a limiting stoichiometric ratio required for gelation, determined as $r = 1$. Xanthan-Al(III) gelled through the addition of heat with T_g being raised as r was lowered to an asymptotic limit of $r = 1$. Beyond $r = 3.2$, T_g appears to asymptote to a limiting lower value of $T_g = 28$°C. Maxima in equilibrium network strength at 85°C and at the gel point are reported as $r_e = 3.2$ and 2.4, respectively. The correlation of $r_e = 2.4$ at the gel point, with the onset of a plateau in the relaxation exponent $n = 0.16$, is consistent with additional crosslinker not contributing to the gel elasticity at the gel point, whereas r_e determined 85°C ($r_e = 3.2$) correlates with the asymptotic lower limit of T_g. The rheological behaviour observed here has been interpreted in terms of a preliminary model similar to that proposed for the thermogelation of methylcellulose. To investigate further the relationship of the gelation process, and particularly the resultant T_g with the conformation transition, it is proposed to conduct kinetic, polarimetry and thermal calorimetric studies.

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