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Title: Development of tribology equipment to study dynamic processes

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Abstract

Aiming to obtain an engineering understanding of oral processes, tribology equipment has been modified to allow the study of lubrication during a dynamic process. As a model dynamic process, gel samples have been structured under shear to create fluid gels (concentrated gel particulate systems) by using temperature profiles. These temperature profiles are comparable to the ranges available in a rheometer and are compared herein.

An overall pattern in most cases of increasing polymer or KCl concentration increases onset temperature and extent of viscosity or lubrication change is presented. However lubrication properties of the material cannot be completely predicted by comparison to rheology data in these cases. Investigating viscosity across a range of samples after production in both pieces of equipment, where no differences were found it is assumed similar particles were produced, in the case of small differences for low concentration samples the high shears associated with the narrow gap sizes in tribology are suggested to have created very small particles leading to a viscosity reduction.

Keywords: Tribology, fluid gel, lubrication, oral processing

1. Introduction

The need for better understanding of the way we eat, and to formulate new, functional foods that taste good to the consumer whilst being nutritionally beneficial is important for academics and researchers in the food industry alike. The impact of a physical change in material structure on lubrication properties would have implications for an individual's perception of food products in the mouth. Processes such as melting or agglomeration in the mouth could be studied and correlated with lubrication behaviour. For example work carried out by (Benjamins et al., 2009) has highlighted, for emulsion products, that coalescence in the mouth alters their perception with time. As a model dynamic process, the ordering and gelation of three biopolymers was investigated under shear: κ-carrageenan, gellan and agarose at varying polymer and KCl concentrations. Under these conditions a concentrated dispersion of small gel particles is produced. While this specific process is not likely to occur in the mouth, it does allow us to assess the applicability and sensitivity of tribology as a technique to follow time dependant processes.

1.1. Fluid gels

For a variety of biopolymers the normal gelation process results in a solid quiescent gel. However, this can be altered in some cases with the application of shear during the gelation process. This results in the formation of a number of discrete particles in suspension, giving the final material a mixture of properties as both a solid gel and a liquid system. Two similar systems exist in this form, which are referred to by overlapping terms in literature. The first, which for the purposes of this work is termed a "sheared gel", is formed when a solid gel is broken up into small particles creating a suspension. The second is termed a "fluid gel", where the small individual gel particles are formed during the ordering process by the application of shear, and is of interest in this work. The main advantage of this method is that smaller more uniform particles can be created.

Previous work has shown that a number of materials can be processed in this manner to create fluid gels, such as agar and gellan (Altmann et al., 2004; Norton et al., 1999; Sworn et al., 1995). Final properties of the material is dependent on a number of factors: the concentration of polysaccharide used; the addition of materials to promote gelation; the temperature profile used during gelation and; extent and uniformity of shear experienced (Gabriele et al., 2009). Previous work on agar shows that as the initial gel nuclei form they reach an equilibrium point determined by the shear experienced. With increasing shear smaller particles are formed. The gels can be designed to form a variety of structures and are valuable to fat replacement applications (Jimenez-Colmenero et al., 2012).

It is clear then that fluid gels are interesting structures which are likely to be included in many processed formulations for the future, to give structure to liquid products and replace fats. As such, their behaviour in the mouth will be important to how they are received by the consumer. Further study of this material, with respect to lubrication behaviour, would provide fundamental information to add to the knowledge of the behaviour of these structures, and also give information on how they may perform in the mouth.

1.2. Sensory perception and tribology

Some efforts have been made to compare the friction of a product observed in the tribometer to the sensory perception of lubrication in the mouth, or to infer differences that should exist in the mouth. The common method is to use Stribeck curves to compare friction at different speeds. (Malone et al., 2003) considered emulsions of varying fat content, and found trends in sensory scores for "fattiness" and differences in lubrication behaviour over different speed ranges. Similarly, work by (Chojnicka, 2009) investigated sensory and frictional differences in milk of varying fat contents, and showed correlations for a number of properties such as "creaminess" and "softness". However, the experimental measurements did not consider the

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effect of mixing and transport to the recording surfaces which may be present in the mouth. It has been suggested previously that a reduction in flavour perception on increasing concentration of biopolymers is a result of mixing patterns in the mouth. Thus, this should be considered when drawing comparisons between in-vivo and in-vitro methods (Ferry et al., 2006; Koliandris et al., 2008).

It is clear that tribology does not offer a one-to-one comparison with sensory data since the processes occurring in the mouth are far more complex than represented by tribology equipment. However, sensory correlations can be drawn, and with further refinement and extension of testing conditions better correlations and predictions could be drawn.

The approach taken was to control the temperature profile within the tribometer cell to induce conformational ordering of the structures and to investigate these events input on lubrication. The change was also followed using a standard rheometer at a constant shear rate, in order to compare the two techniques and the materials produced. The structural properties of the final gel were compared with findings described in the literature. The effect of polymer concentration was explored for the three samples. For carrageenan and gellan as salt promotes gelation, additionally the effect of salt concentration was explored. KCl was chosen since this is the preferred ion for promoting gelation in carrageenan, offering clear gelation behaviour compared with other cations.

2. Experimental

2.1. Materials

Experiments were carried out using three commercially available biopolymers: k-carrageenan (Sigma, UK), agarose (Sigma, UK) and low acyl gellan (CP Kelco, USA). All

were prepared as per manufacturer instructions, outlined below. The different formulations made for comparison are detailed in Table 1.

Table 1.   *Sample formulations (% weight)*

Sample	Concentration (%)	KCl (%)
κ-carrageenan	0.25	0.1,0.2,0.3
κ-carrageenan	0.5,1	0.1
Gellan (Low Acyl)	0.5	0.1,0.2,0.3
Gellan (Low Acyl)	0.25,1	0.1
Agarose	0.5,1,2	0

Samples were produced by heating water to 80°C, to which the powdered polymer was added while stirring and covered. Samples were left for complete hydration and the appropriate quantity of KCl (in the case of gellan and k-carrageenan) was added and allowed to dissolve for 30 minutes before testing.

2.2. Methods

2.2.1. Tribology

The basic tribometer equipment used in this work is the MTM2 manufactured by PCS ltd (London), the principle of operation has been previously discussed (Bongaerts et al., 2007; de Vicente et al., 2005). Further modifications were made to the operation of the equipment shown in Figure 1. The measurement contacts used in this study were a stainless steel ball and elastomer disc. A volume reducing insert was used to reduce the necessary sample size to 20ml. This works by filling the space between the wall and the edge of the disc, creating a sample volume directly above the disc. This insert was used in order to eliminate dead zones around the disc allowing a more homogeneous sample to be produced. A computer controlled water bath was attached to the tribometer pot jacket to implement the temperature profiles, in this case a 1.5°C/min cycle from 40°C to 20°C for carrageenan, 45°C to 20°C for Gellan and 40°C to 10°C for Agarose to sufficiently cover the ordering process.

Timed experiments at 500mm/s over the length required to achieve the desired 1.5°C/min cooling rate for each sample. Ideally a speed in the mixed lubrication regime would be used to allow better comparison with effects in the oral environment. However, preliminary experiments at lower speeds than 500mm/s for some samples were too slow, allowing large solid gel section to form in the tribometer cell, producing inhomogeneous samples. 500mm/s would lie on the very edge of the mixed regime, offering a compromise. Similarly, reverting back to the use of a steel ball and elastomer disc allowed more repeatable results, as at high speed vibrations caused by slightly uneven surfaces of PDMS made recording difficult. Further modification of the tribometer chamber to increase mixing efficiency may offer a solution to this problem, allowing a lower speed assessment, without allowing large sections of the sample to experience low shears. With the use of the volume reducing insert the sample temperature probe is no longer in contact with the sample. Initial experiments show a lag of 3.5°C ± 0.5°C between sample temperature at the ball and the temperature probe. Traction coefficient against temperature data is presented uncorrected for this lag, however subsequent data comparing gelation temperature between tribology and rheology have been altered to include a +3.5°C correction.

Figure 1.   MTM Schematic, left, Side view schematic of MTM configuration right, image of MTM cell with volume reducing insert in place
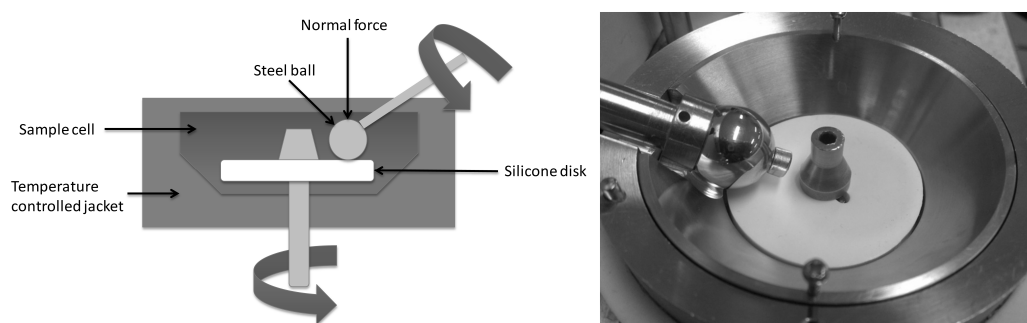
2.2.2. Viscosity measurements during ordering

The rheometer used was a Bohlin Gemini HR Nano Rheometer), with a 60mm acrylic parallel plate system with a 1mm gap. The parallel plate geometry was used as a particulate system; the temperature was varied to offer a reasonable sample size. Testing carried out also used the same geometry because of the particulates formed, to provide a large enough sample to be representative, and to prevent having to excessively move samples to allow different geometries to be fitted between runs. Samples were produced at a rate of 1.5 °C /min at $200s^{-1}$ and tested by measuring viscosity between 0.1-200 s^{-1} at 10°C. This shear rate is taken from (Gabriele et al., 2009) as a shear where homogeneous fluid gel particles are created. All experiments were carried out in triplicate, samples were loaded at 45°C into both tribometer and rheometer where production took place. Immediately after production gels were tested in the rheometer.

3. Results and Discussion

All the materials tested produced viscosity curves that can be generalised and split into three main sections over the temperature range. A typical curve generated during preliminary experiments is shown in Figure 2. The figure presents three repeat experiments of a 0.25% κ-carrageenan sample cooled at 1.5°C/min. At higher temperatures no ordering occurs. Here a slight viscosity increase can be observed of the order of 0.5 mPas, as expected where cohesive forces between molecules increase with reducing temperature (part 1). This continues until a sharp increase is seen at the onset of conformational ordering; this temperature varies dependant on polymer and KCl concentration for this example. The following part of the curve shows the ordering process of the polymer until it is complete (part 2), this then gives way to third regime where viscosity is purely temperature dependant once again (part 3). In this final section a slight reduction in viscosity is sometimes present. This is a result of the breaking up and smoothing of any aggregates to an equilibrium point that have formed during the ordering process. This effect is often more pronounced in systems

which have a very fast ordering process. This same pattern is evident in tribology measurements. Initial values tend to be stable with slight increases from the change in viscosity observed, although a larger increase in comparison with viscosity measurements was seen over this section. Traction is then seen to increase at the point of ordering, before stabilising once complete at a new level.

Figure 2.   Characteristic viscosity curve for temperature induced ordering of three 0.25% carrageenan samples
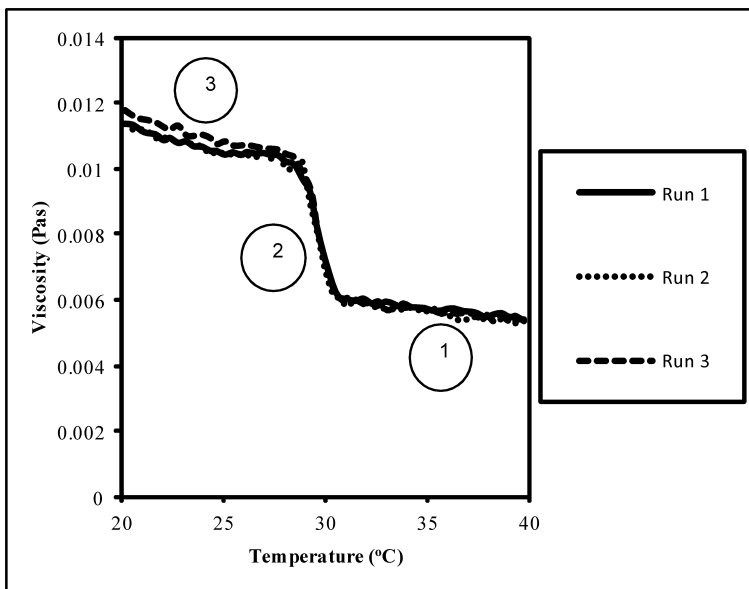

Figure 3 presents rheology and tribology results for temperature induced ordering of κ-carrageenan at three concentrations, 0.25, 0.5 and 1%. The patterns observed for rheology followed those described previously: with increasing concentration of biopolymer an increase in the gelation temperature and the size of the change in viscosity during the ordering process was present. During and after ordering it is expected that bulk viscosity is dependent on the flow of particles in the material moving past one another. As such, an increase in polymer concentration should decrease the deformability of gel particles which hinders movement, leading to an increased viscosity, which is observed. In the tribology results the initial pattern is not the same as in rheology. The lowest concentration results in

the highest value of traction. It is expected that here because of the low concentration of carrageenan, insufficient material is present to properly lubricate, making the lubrication behaviour similar to that of water. When sufficient concentration is reached the carrageenan is able to lubricate efficiently to where the two higher concentration samples sit.

It is possible that the viscosity change with concentration, including the contribution of the increased change in viscosity brought about by the coil overlap (detailed later), produces the pattern of differences seen in the initial traction measurements. The shear rate experienced is not uniform since the flow patterns of material being entrained into the gap is not well defined and cannot be measured with the current equipment. The viscosity of the material in the gap is therefore unknown so its contribution is difficult to confirm. Previous work has also suggested that it is not just viscosity which affects the extent of lubrication but also the structure of the material even at similar viscosities (de Vicente et al., 2005).

Increasing biopolymer concentration increases onset temperature and the overall traction coefficient change in tribology studies. Because of the initial pattern of tractions recorded for the different concentrations, the final traction values of each of the samples once again do not follow the same pattern as in the rheology studies. After ordering, competing characteristics mean that a pattern across materials is not apparent. For carrageenan the final traction for 0.25 and 1% samples show the same value, despite having a different increase in traction upon ordering and final viscosities, while the 0.5% sample shows a reduced friction compared with the others. The higher concentration samples have more material to lubricate and so are expected to produce lower traction coefficients. However they are also expected to have harder particles. This could mean that while there is more material to lubricate and separate the contacts, there could also be an increased difficulty in deforming particles allowing them into the contact thus creating less lubrication.

Figure 3.   Concentration effects of κ-Carrageenan gels, Top: Viscosity curves during temperature induced ordering. Bottom, Traction curves during temperature induced ordering.
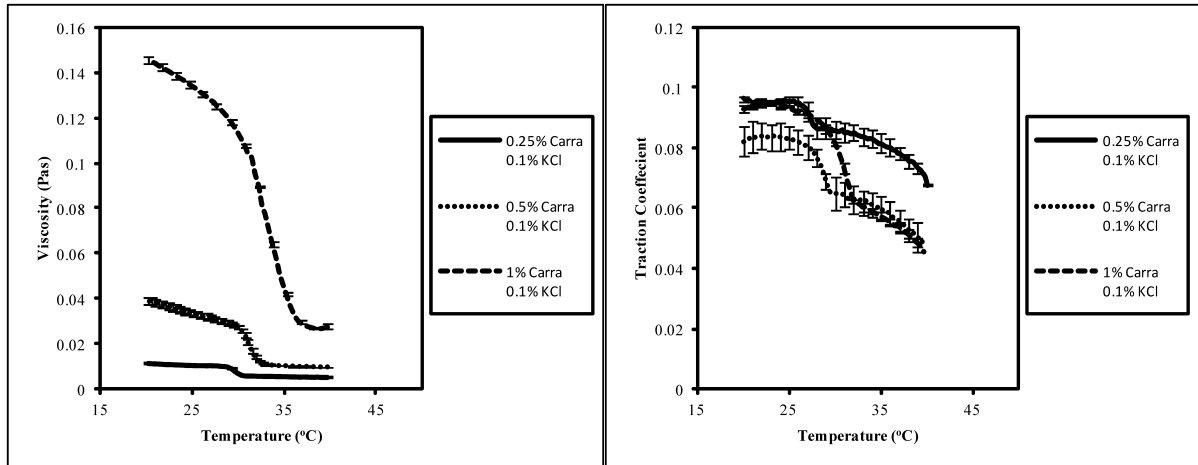
Further testing was carried out on carrageenan samples by repeating experiments using different KCl concentrations of 0.1, 0.2 and 0.3%. Once again onset of gelation temperature increased with increasing content, as did the extent of change in viscosity, although over a shorter range of temperatures and viscosities than for sample concentration. Salt concentration promotes gelation by altering charge and enhancing conformational ordering of chains (Rochas and Rinaudo, 1984). For carrageenan the increase in gelation temperature with KCl is much greater than for sample concentration. For 0.3% KCl gelation begins at approximately 47.5°C and completes in less than 1°C because of this the viscosity at the end of ordering reaches a peak which then reduces unlike the other samples. This is suggested to be due to the particles forming large linked chains over a very short timescale, which are then subsequently broken up into an equilibrium particle size (Gabriele et al., 2009).

Samples of gellan were also prepared in the same manner, considering gellan concentration and KCl concentration. Rheology and tribology data for most samples followed the same trends as for carrageenan. With increasing concentration an increase in onset of ordering temperature and extent of viscosity or traction change was observed. One exception is present at 0.5% gellan with 0.2% KCl, where less of an increase in viscosity during ordering

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is seen compared to 0.1% KCl. However, no such pattern is seen in tribology measurements. It is unclear why, especially given that independent repeats were carried out. However, it could be as a result of the small differences between the final values for these samples (0.03-0.05 Pas) compared with the differences seen with increasing gellan concentration (0.015-0.15 Pas). Another explanation is the nature of the measurements carried out: for rheology bulk properties are measured whereas for tribology the thin film behaviour is assessed. For this sample a difference in bulk structure may have been present, which did not affect tribology measurements.

Finally, agarose samples were prepared using both methods. Only polymer concentration effects were studied as even a small addition of salts created very quick forming and hard gels, which prevented accurate measurement and created large visible gel chunks, rather than a fluid gel sample. Patterns observed showed once again the same key features with increasing concentration. However, at the lower concentrations an extended ordering temperature range when compared with gellan and carrageenan is present.

During the viscosity studies each material shows that as biopolymer concentration increases, an increase in initial viscosity is observed. This relationship for each material should be linear on a double log plot to the coil overlap concentration, above which the gradient of the relationship increases (Morris et al., 1981). Below the concentration the chains within the sample exist without fully interacting with each other, and viscosity is determined by the number of chains present. When their concentration increases to a point where they start to interact, their movement is restricted by tangling with other chains. This concentration is dependent on material and shear rate applied (Clegg, 1995). For the range of concentrations in this work, the relationship between initial viscosity and sample concentration is not linear. This suggests the coil overlap concentration could be present within the range studied for a shear rate of $200s^{-1}$. Figure 4 shows a double log plot of the

correlation, with the viscosity of ordering taken from the point just before ordering changes the viscosity gradient on viscosity/temperature curves for each material. However, since only three concentration points are available for each biopolymer the relationship is not conclusive. Previous work by (Cook et al., 2011) has isolated this coil overlap concentration for guar gum, λ-carrageenan and HPMC to be between 0.2 and 0.6% w/w at zero shear, depending on material used. Similarly values were obtained for guar gum, λ-carrageenan, locust bean gum and scleroglucan which are in agreement with the range of values used here (Garrec and Norton 2011).

Figure 4.   Viscosity dependence on polymer concentration, double log plot of initial viscosity against concentration (w/w %) for each biopolymer. Values are taken from the initial section of viscosity measurements.
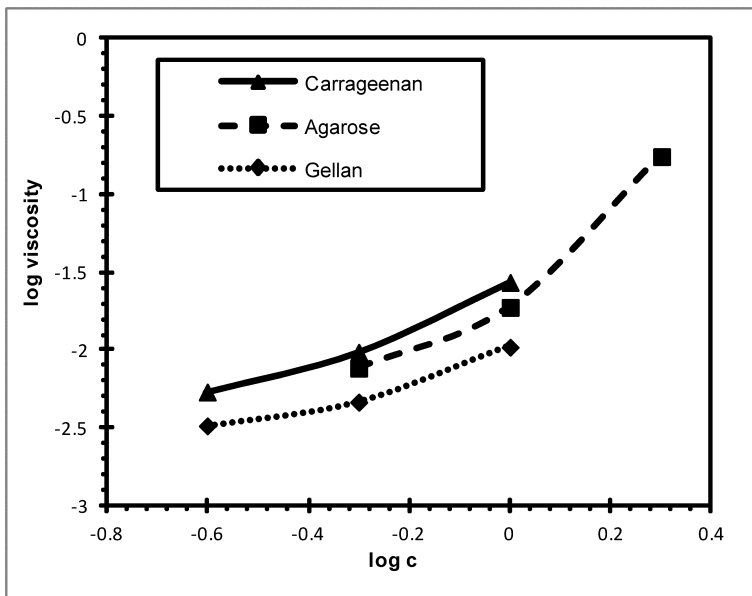

Figure 5 shows a comparison curve between ordering of 1% κ-carrageenan, 0.1% KCl in the rheometer and tribometer. Data was normalised to show the rates involved with the ordering process recorded by each technique. The tribology curve has been shifted 3.5°C to compensate for the recorded temperature lag. The curves in general have similar rates during ordering for all samples, and some key features are present across experiments. The initial temperature region before ordering in tribology experiments shows a much steeper

increase in traction compared with rheology. Some increase in this region is expected since with decreasing temperature an increase in viscosity will be observed. It is also possible at this point that the solution present has some interaction and deposition on the recording surface influencing the initial traction data.

Figure 5.   Normalised κ-carrageenan ordering curve, data for 1% κ-carrageenan 0.1% KCl following the ordering process by tribology and rheology.
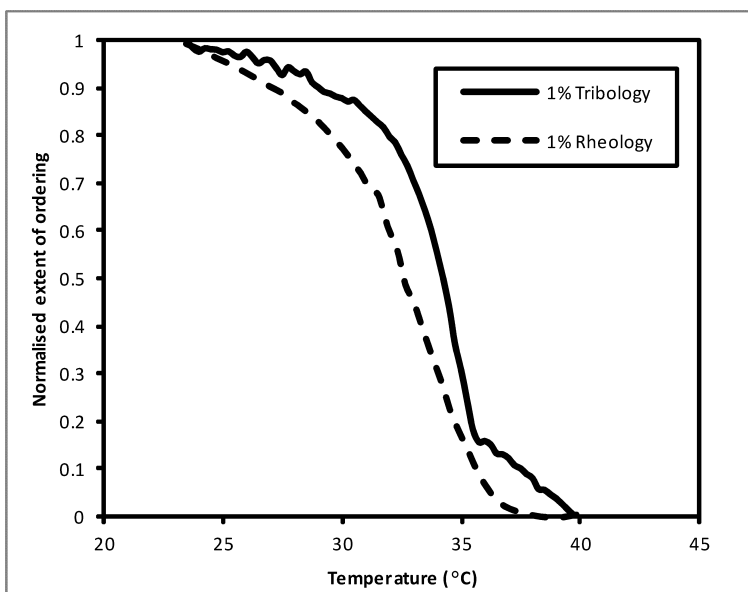
Work in (Gabriele et al., 2009) characterises particle sizes created in shear rates greater than $1s^{-1}$ in the rheometer. Under a uniform shear particles are around 5 microns reducing with increasing shear rate. Above this value for any given sample, shear thinning behaviour over a range of shear rates is similar. Below this value, large irregular particles were found, leading to a slightly higher viscosity over the range as well as an increased error between measurements. Below the $1s^{-1}$ shear rate the material is allowed to form large links between chains that are not broken by the applied shear. The formation of these large particles creates an irregular distribution of particles that affects bulk rheology measurements resulting in more variation. Comparisons of material produced in the rheometer and tribometer were made by measuring viscosity from 0.1 to a maximum of $200s^{-1}$. This maximum matches the

production shear rate, ensuring that further structure breakdown does not occur, affecting results and producing hysteresis in the viscosity curves. It is expected that under these conditions uniform mixing occurs in the tribometer cell, and that sufficiently high shear is created through the sample to prevent large particles forming. Preliminary experiments at lower speeds produced inhomogeneous samples containing large gel particles, and suggest that these conditions would be required to produce a homogeneous sample.

In the case of carrageenan samples, at 0.5% seen in Figure 6(b) repeatability was good and no difference is seen between samples, indicating that reasonably uniform particles of comparable order are being produced. The same is true for 1% samples, however differences are seen for the 0.25% carrageenan sample (Figure 6 (a)): viscosity over most of the range tested is lower for the material from tribology than from rheology. This is unexpected since tribology would be likely to produce less uniform samples, given that the sample size is larger and the shear across the sample is not uniform. However, it is also expected that the shear experienced would be higher as material entrained would be exposed to large forces in the recording gap, so any material forming while being entrained would be exposed to this. It is also unexpected as increasing KCl concentrations this effect is no longer present past the 0.1% KCl sample. However, results produced were repeatable and so it is possible that as this is the weakest gel tested the high shears present in the tribometer created much smaller particles than in other cases. This is reinforced by data from gellan, where small differences are seen between samples of 0.25% and 0.5% created in the different equipment. The differences between samples are much smaller than seen previously, however the same reasoning could be applied (Figure 7(a)). For agarose samples in each concentration no differences are seen, again suggesting that similar particles are produced in both environments. However, higher variability between repeats was seen indicating the possible presence of some larger, more irregular particles. Both these occurrences can be explained given the much higher viscosities created across the

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concentrations used compared with carrageenan and gellan giving rise to a greater number of less flexible particles (Figure 7(b)).

Further examination of the viscosity curves show in some cases for carrageenan and agarose samples a small change in the shape of the curve was observed at approximately $20s^{-1}$. A levelling out of the viscosity occurs until around $90s^{-1}$ where a sharp decrease then takes place. This behaviour could be explained as a change in the material structure during shearing: at the low shears very little movement occurs in the sample meaning some inter-particle connections may still be present, which hinder movement. When the plateau is reached a sufficiently high shear is applied to stretch these connections, which then break and allow the particles to move more freely and align giving a sharper decrease in viscosity. This bridging between particles is shown in previous work such as (Gabriele et al., 2009) and is shown to depend on the sample and processing environment. This bridging behaviour could also offer an explanation for some differences seen between tribology and rheology samples. For tribology samples a spoonful of material is transferred from the tribometer cell to the rheometer for viscosity testing whereas the rheology sample is already in place. This could allow the rheology sample to form more structure, which would be broken in the tribology sample when moving. However, a difference is not always present despite the repeated method and so this cannot be solely responsible for differences observed.

Figure 6.   Viscometry post production of κ-carrageenan samples, comparison of material formed in the tribometer and rheometer for samples of two concentrations.
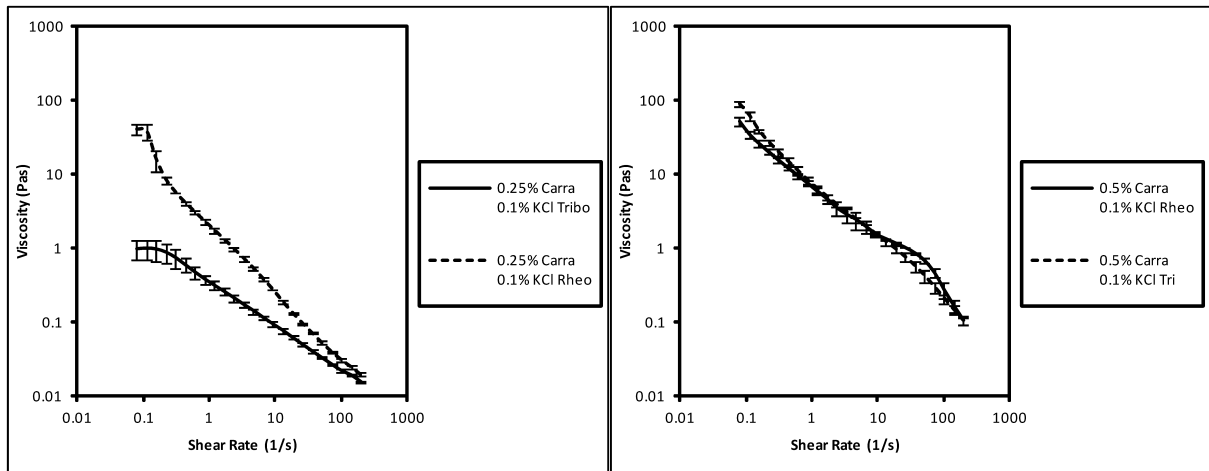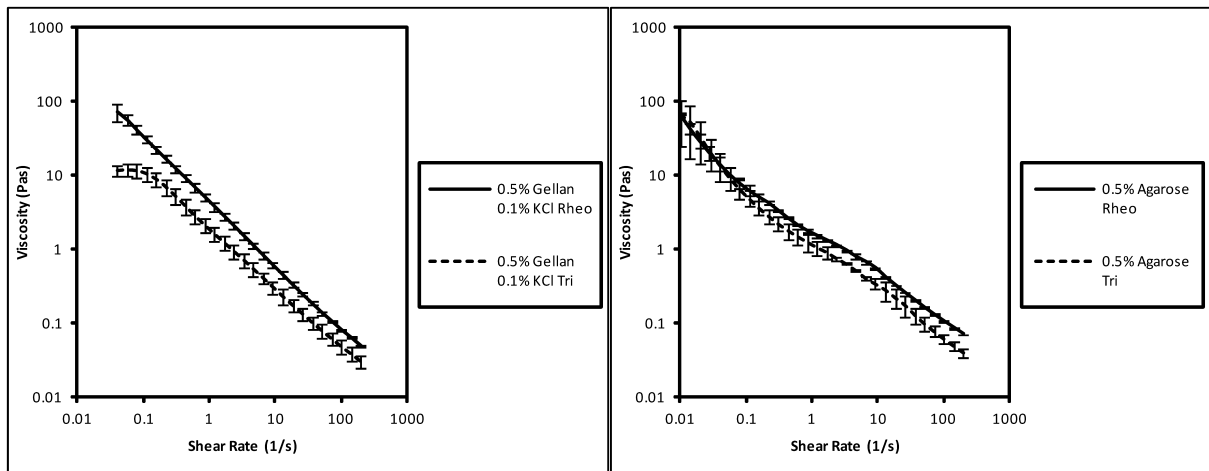

Figure 7.   Viscometry post production of gellan and agarose, comparison of material formed in the tribometer and rheometer.

Analysis of the patterns recorded during ordering of the samples was carried out to try to ascertain how each technique shows the ordering process taking place and what similarities are present between them. Initially, a comparison of the onset of ordering temperature is made for all samples. Values for temperature were taken at the point where a gradient change is present. Temperature values for tribology data have been increased by 3.5°C to account for the lag caused by the location of the temperature probe. Data for κ-Carrageenan is presented in Figure 8; a linear dependence on both polymer and KCl concentration is

apparent. Some difference between the two techniques is seen at the higher concentrations but values are still within experimental errors. It is possible that at the higher concentrations, the increased viscosity of the sample hinders mixing and therefore heat transfer within the tribometer cell creating a larger temperature profile across the sample, increasing the lag experienced. A similar correlation is seen for gellan samples and for agarose. Linear relationships for both experimental conditions hold. For rheology this change in viscosity has previously been identified to be a result of the ordering process as discussed earlier by (Gabriele et al., 2009). This indicates the traction changes recorded during tribology are a result of the ordering process taking place.

Figure 8.   Onset of ordering temperatures for κ-carrageenan, temperature at the point of ordering is taken where a gradient change on viscosity or traction curves is present. KCl effects are studied at 0.25% κ-Carrageenan concentration.
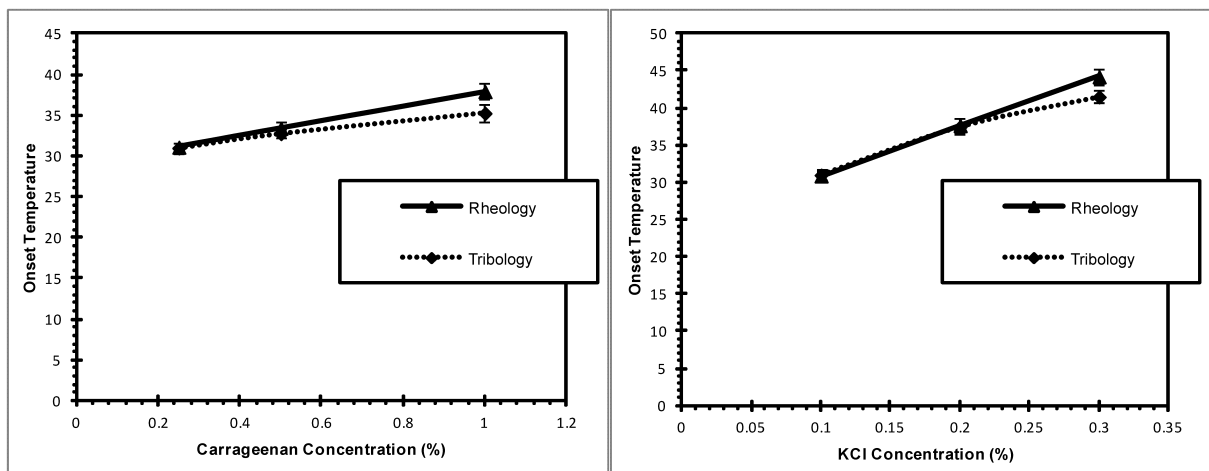
Differences are present between the two measurement techniques, an example of this is seen with 0.5% agarose, where the change in traction during ordering is not apparent from the graph however a change of approximately 0.05 Pas is observed in viscosity. Some effect could be attributed to shear experienced in the tribometer. Previous rheology work has shown a dependency on shear rate on the extent of ordering. The shear used in this study is taken from the range in (Gabriele et al., 2009), $200s^{-1}$ is at a point where shear is high

enough to give uniform particles, but at higher shears particles become so small that their effect on the viscosity is reduced, making it difficult to distinguish between samples. For carrageenan a difference of 0.005 Pas between the onset and end of ordering is observed at 700s^{-1}, compared with 0.03 Pas at 200s^{-1}. Shear in the tribometer is difficult to quantify because of the recording cell volume and the free changing nature of the shearing gap, so it is possible that it is higher than in the rheometer, resulting in samples with less distinguishable ordering changes. A final explanation for the difference is that while the rheometer generates data from the whole of the sample, tribology data is gathered from a small section between the contacts of the two surfaces. As this gap is often very small the material that passes through may not be an accurate representative of the bulk of the fluid. This could be an effect of bulk mixing which prevents all of the material being entrained. When working with materials that have a high low shear viscosity there is little mixing within the measurement cell and so the material in the contact is not regularly replaced. This effect could also be a result of particles being excluded from the gap between surfaces. Previous work in emulsion tribology by (Malone et al., 2003) has suggested that in the boundary and mixed regime the gap size is often smaller than that of the oil droplets and so the gap is mostly filled with the continuous water phase. A similar situation may exist in the fluid gel system with most particles being excluded except the smallest or weakest which can be broken down and entrained. A recent study by (Gabriele et al., 2010) has looked at lubrication of agarose fluid gels to identify their mechanism of lubrication. Here, traction data for a pre-made fluid gel is presented over a range of different speeds to a maximum of 100mm/s. Three distinct regions over the speed range were identified, at low speeds up to about 20mm/s speed is not high enough to entrain the particles, so only the fluid medium can enter and lubricate. This causes a reduction in traction coefficient. When speed reaches a point that is fast enough to entrain particles an increase in traction coefficient occurs where the gap is of a similar size to the particles and so a single layer provides lubrication. Traction is then determined by the rolling and sliding of those particles through the gap that begins to

increases the traction coefficient. In addition to this as the surfaces become more separated an increasing number of particles are able to fill the gap creating a film which is comparably larger than the entrained particles, allowing less restrictive motion between the contacts and lowering traction coefficient. The speed ranges at which each of these situations are present is dependent on a number of factors. The material used and particle size and hardness associated, the surface properties, normal force and SRR will all affect the type of lubrication at each speed. In this study a value of 500mm/s is much higher than the literature value and so it is expected that full multilayer particle lubrication should be present. However, previous work by (de Vicente et al., 2005) looked at lubrication by carbopol microgel suspensions and a similar shape lubrication curve is present in neutralised carbopol samples. In this case, the multilayer lubrication stage occurs around 100-200mm/s compared with 35mm/s.   This indicates that it is not clear the type of lubrication present in this study at 500mm/s, and so further investigation should clarify this.

4. Conclusions

This work demonstrates that time dependent tribological measurements are possible, and that the equipment can be set up to produce data over temperature profiles. Gel samples can be structured under shear to create fluid gels containing gel particles.   These temperature profiles are comparable to the ranges available during viscosity measurements. This approach could be useful to look at temperature effects on foods such as melting, viscosity changes or structure breakdown, which would occur during an acclimatisation period in the mouth.   In this case, as a model dynamic process, temperature induced ordering of different biopolymers was studied showing that this can be followed using tribology, this approach could be used for a number of other dynamic processes.

An overall pattern in most cases of increasing polymer or KCl concentration increases onset temperature and extent of viscosity or lubrication change has been presented.   However

lubrication properties of the material cannot be completely predicted by comparison to rheology data in these cases. Investigating viscosity across a range of samples after production in both pieces of equipment, where no differences were found it is assumed similar particles were produced, in the case of small differences for low concentration samples the high shears associated with the narrow gap sizes in tribology are suggested to have created very small particles leading to a viscosity reduction.

5. Acknowledgements

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