

Control Release from Low Acyle Gellan Gum Gels

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ABSTRACT: Salt is a requirement material for human body but should be regulated as its excessive consumption might lead to heart disease and blood pressure. Processed foods due to high salt content might include about three quarter of the daily salt intake therefore many people consume more than their recommended allowances. Processed foods contain added salt for varieties of reasons namely to enhance the taste, develop structure of product and increase microbiological stability by reducing water activity. Methods to reduce salt content are required for consumers that will intake less amount salt while saltiness is not reduced. Therefore salt release from biopolymers is the aim of this research to reduce the amount of salt in processed foods while not changing the saltiness, therefore salt should be trapped in a gel.

Keywords: Control Release, Gellan Gum, Salt.

Introduction

The definition of gel by Ferry (1980) is a substantially diluted system which shows no steady state flow'. This definition includes materials that show solid-like quality while large amount of solvent is attended.

Gel-forming polymers have been used in food industry and particularly processed foods as they can fix elements of formulated foods by trapping them in a three-dimensional network consisting of the polymer molecules which interact at junction zone to provide a solid-like structure. As hydrocolloid gels have some functional properties hence they have been used as gelling, emulsifying, thickening, binding, suspending and coating in food industry (Banerjee & Bhattacharya 2011). Hydrocolloid gels rarely used as a finished product but they usually are used as

additives to improve or control the properties of food products. The main properties of hydrocolloid gels are ability to make aqueous solution with high viscosity at low gel concentration creating required consistency and to make gels with different strengths and stability (Sworn *et al.*, 2009).

Gellan gum is the trade named by Kelco Division and Merck Co to a deacetylated extracellular polysaccharide from the bacteria *Pseudomonas elodea*. Gellan gum was confirmed for food application in 1992 by the FDA. The original form of gellan gum is high acyl gellan (H) and when gellan gum is treated by alkali at high temperature, gellan gum will be deacylated and low acyl gellan gum (L) is obtained (Morris *et al.*, 2012).

Both type of gellan gum (acetylated and deacetylated form) have different mechanical properties. Each type has special properties for instance acetylated form (high

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acyl) and is soft and elastic but fully deacetylated (low acyl) form is hard and brittle, hence a wide range of gel types can be prepared by different degree of deacetylation of polysaccharide.

Gellan gum gelation can occur by cations (monovalent and divalent) but monovalent cations cause gelation at lower temperature than divalent cations (Rodríguez-Hernández *et al.*, 2003).

Foods are materials with different mechanical properties. Texture is depended to numbers of factors hence definition and determination of food texture is difficult. The word texture has more and different means but in this study is meant the complex of mechanical, structural acoustic properties that consumer feel as a food's physical characteristic. For instance, the majority of foods are complex and they are mechanically complicated food properties are changing during chewing in mouth due to variation in temperature, pH and water concentration.

The effect of NaCl, KCl, MgCl₂ and CaCl₂ concentrations on gellan gelation is well documented (Miyoshi *et al.*, 1996; Evageliou *et al.*, 2000; Tang *et al.*, 1996; Huang *et al.*, 2003a). There are critical cation concentration levels and these can modify cation effects on gelatin. For instance, below the critical cation level calcium chloride is apparently a stronger gel promoter than magnesium chloride, whereas above the critical level the larger calcium ion may produce strong repulsive forces that reduce gel strength to a greater degree than the magnesium ion (Lau *et al.* 2000). In equivalent concentrations (<30 mmol/L) divalent cations (MgCl₂ and CaCl₂) have a greater effect on gellan gum gelling properties than do monovalent cations, although the gelation mechanisms differ, and no significant difference exist in gellan gum gelling temperatures between calcium or magnesium, or sodium and potassium (Huang, 2004). The calcium ion is more

effective than magnesium in enhancing gellan gum gelling ability, since the temperature increase of the mechanical transition is less pronounced for CaCl₂ than for MgCl₂ (Tang *et al.*, 2001). Difference in gel strength in gels with maximum levels of calcium or magnesium ions may be associated with differences in cation size (Tang *et al.*, 1994).

Material and Methods

All the chemicals and solutions were obtained from Merck chemical company, Germany.

- Preparation of gel

Low acyl gellan gum was provided by Kelco Company. Weighted low acyl gellan gum powders were dissolved in distilled water then heated to 90 °C using gentle agitation of the gellan gum. This was prepared at the concentrations of 0.6, 0.8 and 1 wt%. Sodium chloride was added to the gellan solution at the concentrations of 0.5-2.6 wt%. The solution was stirred for 1 min and poured into plastic cylindrical tubes (inner diameter 21 mm) covered with parafilm and placed in the fridge at 4 °C for 24 hours.

- Compression Tests

TA.XT2 Texture Analyzer (Stable Micro Systems, Surrey, UK) interfaced by means of a micro-computer was utilized for determining mechanical properties of gellan gum gels.

The gels were removed from the plastic cylinders and the cut into cylinders of 20 mm length and 21 mm diameter and then subjected to an instrumental texture profile analysis. The samples were uniaxially compressed in a texture analyser machine. Sand paper was placed between sample surface and container in order to prevent the slippage of the gel. The gels were compressed at 0.5, 1 and 1.5 mm/Sec crosshead speed up to failure point.

Mechanical parameters of low acyl gellan gum gels such as true stress, true strain, and energy per unit volume can be obtained from the texture profile analysis curves. At least three duplications were employed for every gel (Tang et al. 1997).

- Measurement of salt release

The measurement of salt release into the water is carried out by measuring the conductivity of the proximate volume of water and a normal curve and presented as:

$$\text{Salt release (\%)} = \frac{\text{released Salt}}{\text{total Salt}} \times 100$$

Where, the released salt was calculated from the salt concentration measured in the total solution volume and total salt was the amount loaded in each specimen or hydrogel. All experiments were carried out in triplicate order.

The salt release was measured in online. To adjust the calculation of the conductivity to the concentration, the established concentration of liquid was used. This is presented in Fig. 1.

- Measurement of Riboflavin release

Riboflavin released into the water was determined from the measurement of absorbance at 445 nm and a standard curve was expressed by the below formula:

$$\text{Riboflavin release (\%)} = \frac{\text{released Riboflavin}}{\text{total Riboflavin}} \times 100$$

where released riboflavin was calculated from the riboflavin concentration (mol/L) measured in the total solution volume and total riboflavin was the amount loaded in each specimen or hydrogel. To avoid photodecomposition of riboflavin, all the experiments were performed in the Amber vessel.

This was carried out side by side or parallel with salt release to understand the mechanism involved.

A 1.5 ml of sample was positioned in a cuvette for calculating the riboflavin concentration and its intensity was calculated by using the fluorimeters.

Fig. 2 shows the standard curve between the intensity and the concentrations used. This graph will help in calculating the utilizing identified liquid concentration.

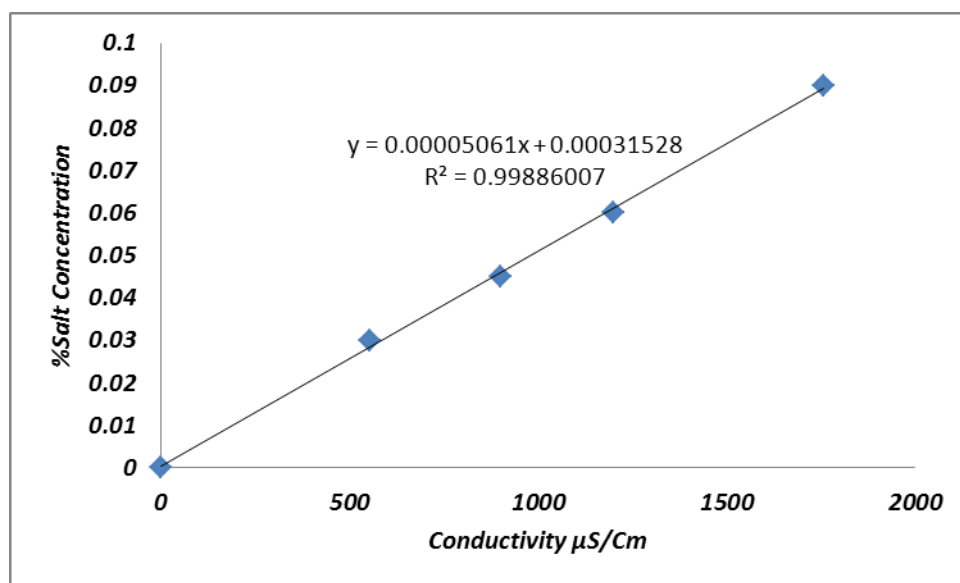


Fig. 1. Calibration line of the known salt concentration versus the conductivity of the solution.

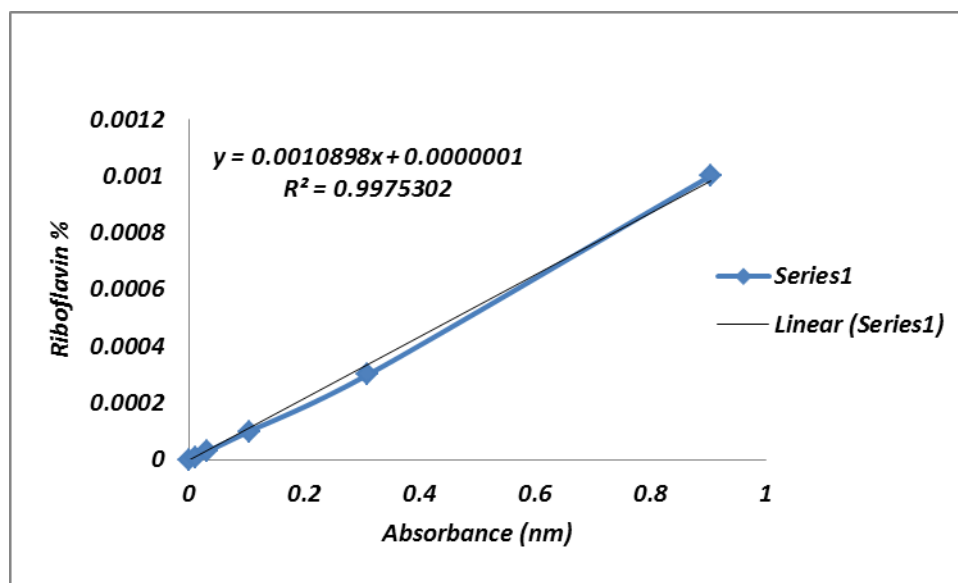


Fig. 2. Calibration line of the known riboflavin concentration versus the intensity (absorbance) for riboflavin at 445 nm.

Results and Discussion

In order to investigate the effect of the crosshead speed of compression test on the mechanical properties of the low acyl gellan gels like true stress, true strain, Young's modulus and energy per unit volume, compression tests were performed. By examining the force displacement curve acquired at different crosshead speed, the mechanical properties at failure point were collected. Fig. 4 shows the true stress at failure point of gellan gels taken at different crosshead speeds. As it can be seen there is not much of difference between the true stress of the gels while subjected to different compression crosshead speeds; therefore, it can be concluded that crosshead speed in this range does not have any effect on the mechanical properties of the low acyl gellan gels. Hence, 1 mm/sec is selected as the compression crosshead speed for further compression tests.

An effort was made to compare the mechanical properties of immersed and dry gels. To achieve this goal true stress of the immerse and dry gels were compared (Fig. 4). As it can be seen there are not any significant differences between the

mechanical properties of immersed and dry gels; therefore, it can be concluded that immersing of the gels in the water doesn't have any effects on the gellan gels mechanical properties.

In order to examine the effect of low acyl gellan gum concentration and salt concentration on the mechanical properties of the gellan gels, the uniaxial compression test was performed. At failure point, the limits of gellan gum concentration were employed to examine the effect of the gellan gum concentration on the mechanical properties of the gels. The variance of gellan gum was from 0.6 to 1% (w/w); in addition, sodium chloride concentration as a cation (cross linking agent) ranged from 0.5 to 2.6% (w/w), at a fix crosshead speed of 1 mm/sec and the gels were compressed up to the failure point.

Stress at the failure point reflects the strength of the gel. It also represents the maximum external force that can be tolerated by the gel without fracturing, and the corresponding strain is an indication of gel deformability. The strength of the gellan gels increases with gellan concentration at all levels of salt (Fig. 5). This happens due to

the higher concentration of the gellan that results in higher cross link densities, in the gel network; therefore, it forms stronger gels. If the salt concentration is more than 0.6%, or 0.7% weight (critical salt concentration), then the strength of the

gellan gels sharply decreases with the increase of salt concentrations. Also, gellan gels are weakened by additional added salt. This is in agreement with the findings of Huang *et al.* (2003b).

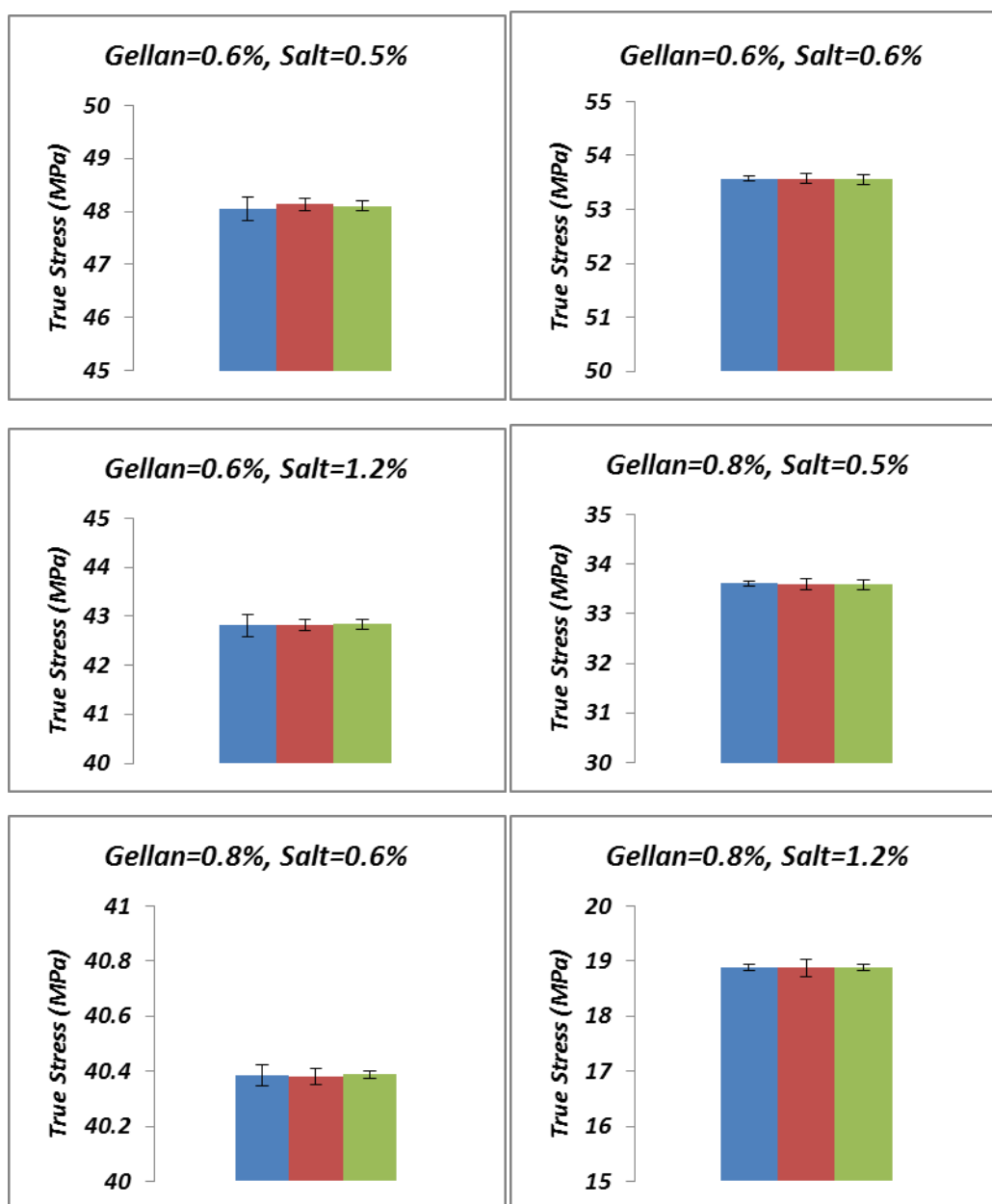
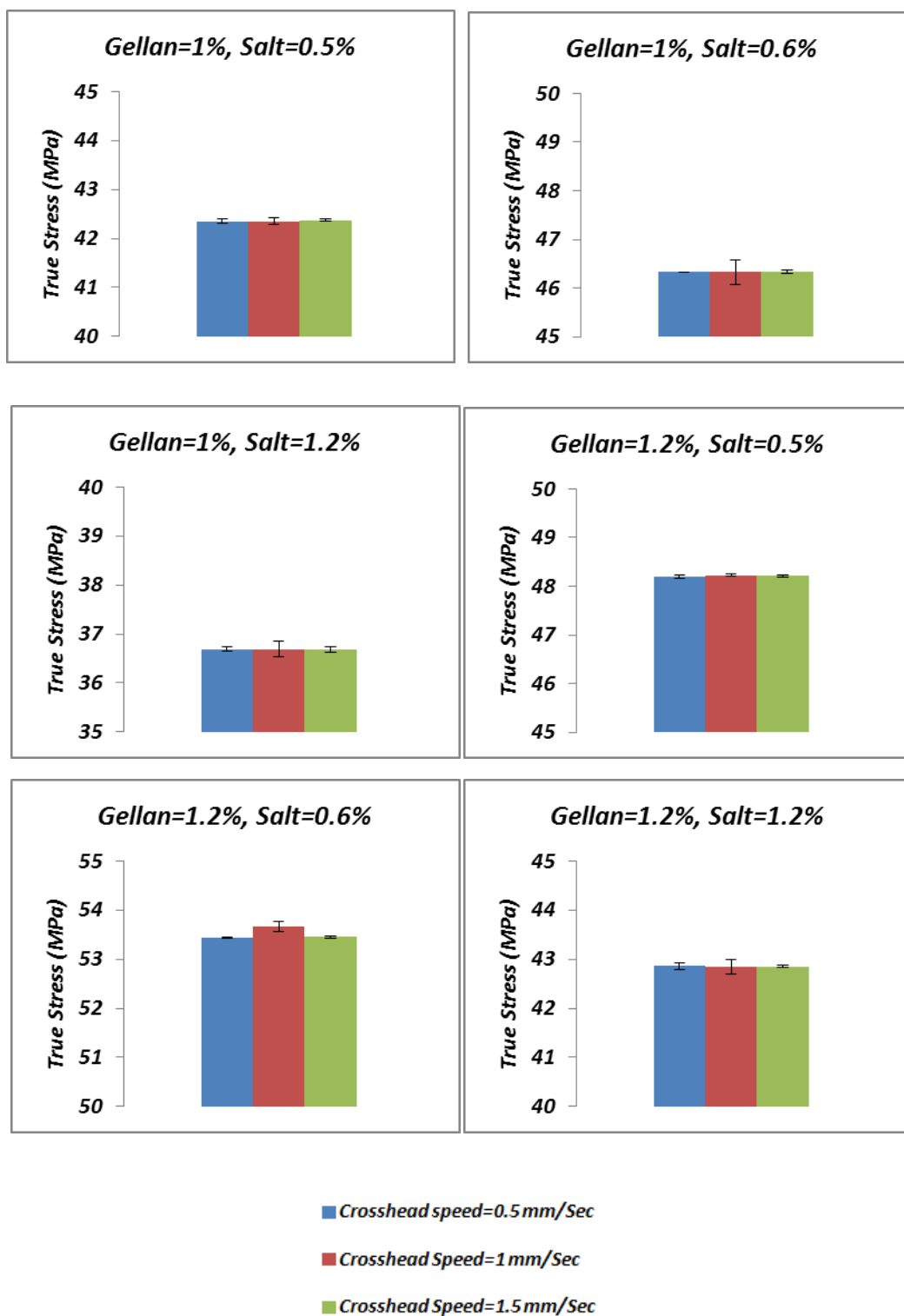


Fig. 3. True stress at failure point of the low acyl gellan gels at various crosshead speeds. The error bars show standard deviation from compression of three replicates.



Continued Fig. 3. True stress at failure point of the low acyl gellan gels at various crosshead speeds. The error bars show standard deviation from compression of three replicates.

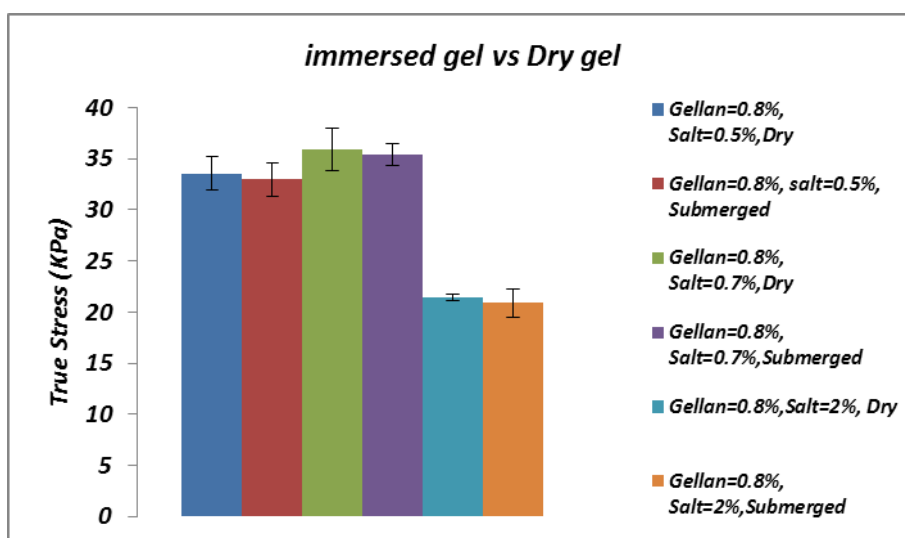
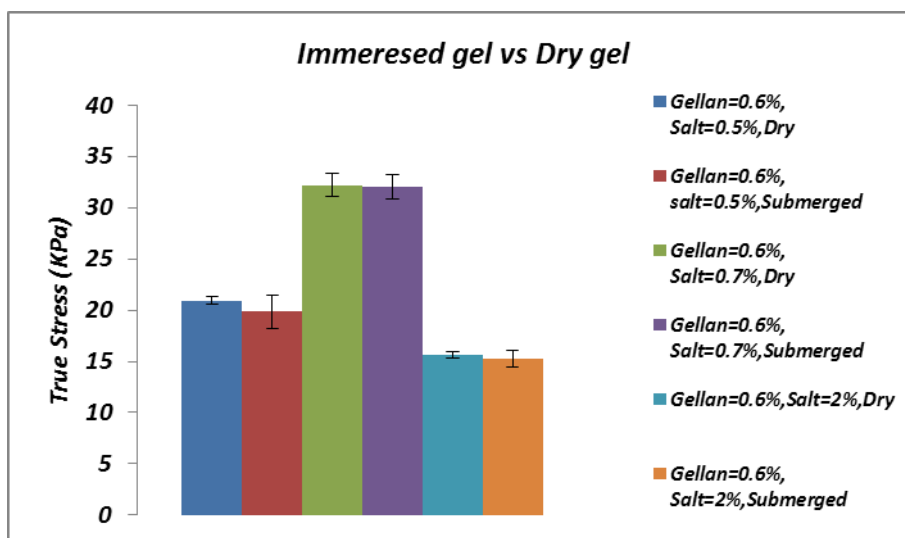


Fig. 4. True stress versus true strain of submerged gels and dry gels. The error bars show standard deviation from compression of 3 replicates.

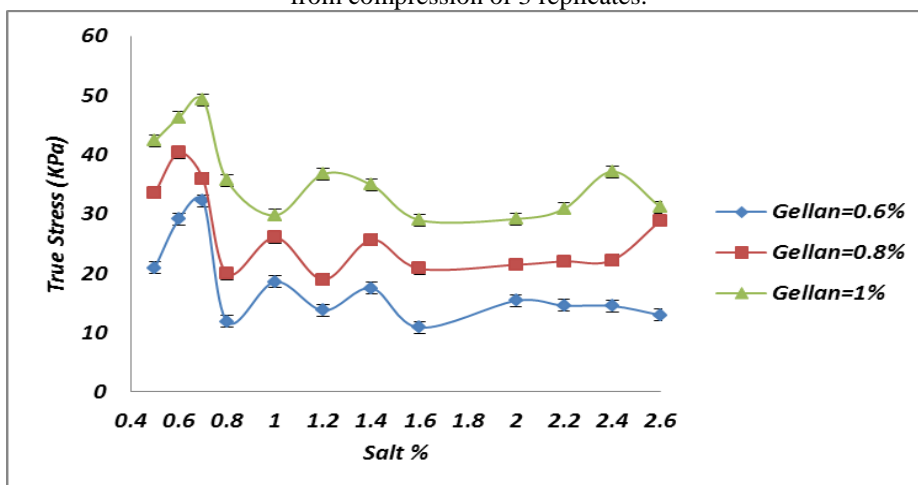


Fig. 5. True Stress as a function of salt concentration at different gellan concentrations. The error bars show standard deviation from compression of 5 replicates.

Gellan gels are deformed at a relatively large extent in low salt concentrations. When the salt concentrations were more than 0.7%, true strain at the failure point increased sharply by increasing salt concentrations (Fig. 6) and the true strain at the failure point attained to a maximum value. It is crucial to notify that the points where the strains approaches the maximum value as shown in Fig. 6, this will match closely to the salt concentration at the minimum strength of each gel as presented in Fig. 5. This finding is in line with the earlier study when the concentration of cation is increased the gel tends to be more brittle. Thus the cation concentration plays a major role in making a gel brittle (Lau *et al.*, 2001).

The area under force-displacement curve during compression up to failure point can be transformed into the real amount of work which is needed to rupture the gel. The force applied during the compression can be used

for indicating the rupture force or rupture strength of a gel. The areas under the force-displacement curve, which can be obtained from compression test, represents the amount of energy needed to breakdown and rupture the sample (energy per unit volume). The failure or breakdown of a gel is not only related to the strength, but it is also related to the energy that is required to rupture. A gel with extensive strength and less required energy per unit volume is destroyed or fractured more easily than a gel with lesser strength and high energy required per unit volume. Thus, by increasing gellan concentrations, energy per unit volume also follows an ascending order, that causes the gel not to rupture easily. By increasing salt concentration above 0.6 %, the energy per unit volume has been sharply decreased; thus, the gels were ruptured more easily. As it can be seen in Fig. 7 the energy per unit volume was comparable to the trend observed in failure stress.

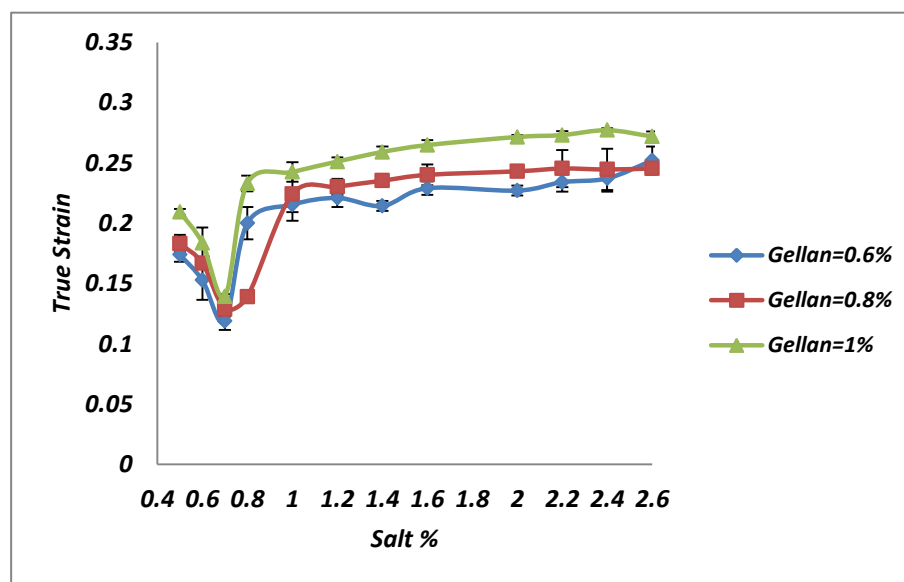


Fig. 6. True Strain as a function of salt concentration at different gellan concentrations. The error bars show standard deviation from compression of 5 replicates.

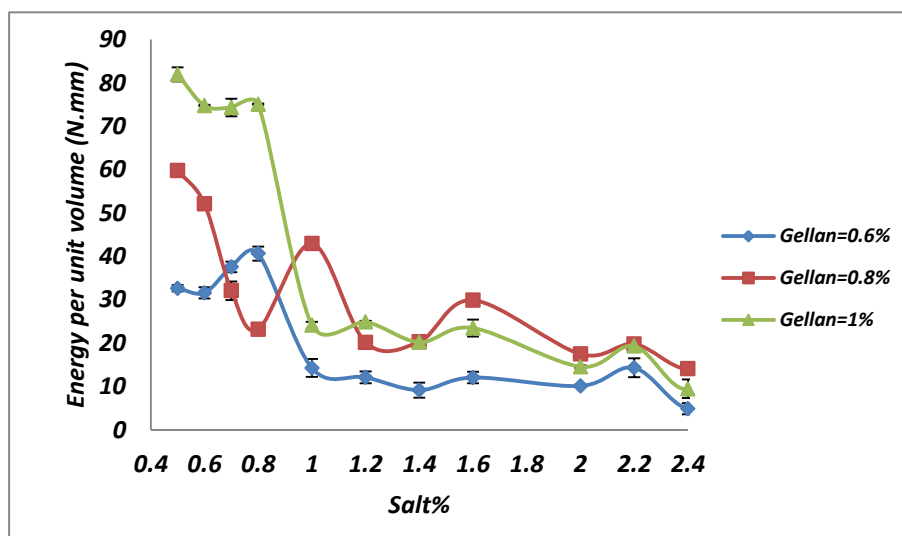


Fig. 7. Energy per unit volume as a function of salt concentration at different gellan concentrations. The error bars show standard deviation from compression of 5 replicates.

- Salt release from gellan gum gels

Conductivity method was applied to measure the amount of salt released from the gels. The gels were submerged in distilled water then were compressed by texture profile analyzer in order to release the salt from the gels then released salt was measured by conductivity meter instrument. Conductivity was measured by Seven Multi Mettler-Toledo instrument.

Represents the results of the salt release. It can be observed that the gellan gels having 0.6% gellan concentration demonstrated the maximum release of salt. Yet, the gel having 1% gellan concentration shows minimum amount of salt release. It can be seen that with the increase of gel concentration, the salt release decreases. When the gellan concentration is increased, the true stress and energy per unit volume increases, whereas Young' modulus decreases at failure point. Regarding the microstructure of the gels, when gellan concentration increases, the gel becomes stronger. For higher gellan concentrations, the higher true stress at failure point might be because of greater concentrated gellan network as gels having higher gellan concentrations are stronger because of lower porosity and,

hence, it can be deduced that the gellan concentration influences the salt release. Therefore, the experimental work shows that an increase in gellan gum concentration will cause a decrease in the release of salt from the gels. As already discussed above, the mechanical properties of the gellan gels is influenced by the concentration of the gellan. When the gellan concentration is increased, the gel tends to be stronger and harder because of the elevated level of stress at failure point. Hence, when the gellan concentration is increased, the salt release is decreased. Already it was mentioned that hard gels need more energy per unit volume at failure point; hence, any increase in gellan gum concentration will cause an increase in the energy per unit volume at failure point. Therefore, the gels need additional energy to rupture, therefore, the serum is released. The derived conclusions are in accordance with previous studies. Other studies indicated that firm gels release flavour with lower maximum intensity as compared to soft or medium gels (Boland, 2004; Guinard & Marty, 1995). Brittle gels were observed to release more salt during a two-bite compression as compared to soft and elastic ones (Koliandris, 2008). Koliandris and co-

workers demonstrated that fracture strain was inversely correlated with salt release.

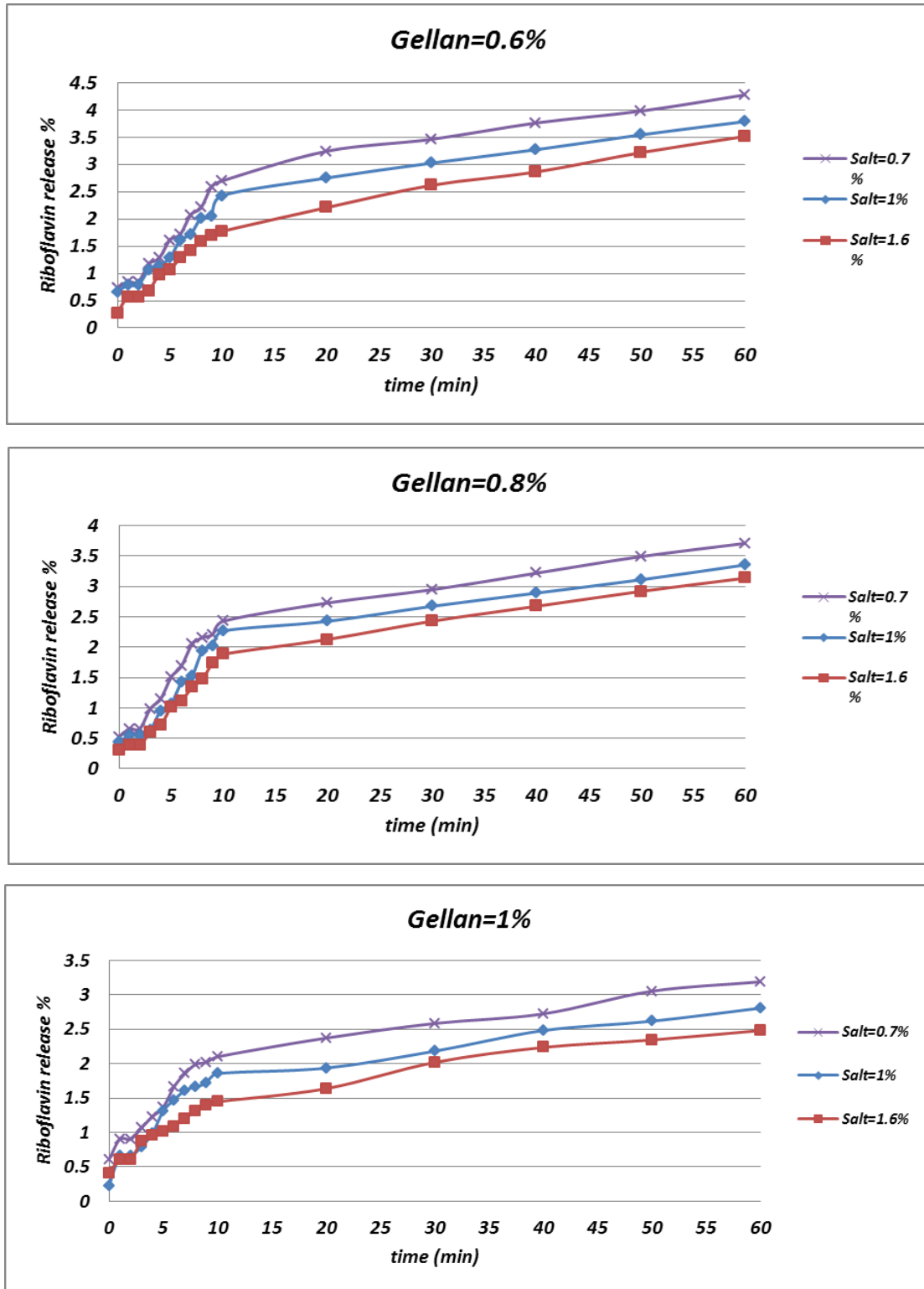


Fig. 8. The effect of the salt and gellan gum concentration on riboflavin release from gellan gels with different gellan concentrations.

The gathered results indicated that the absolute riboflavin release is greater in comparison to the salt release as there is no interaction between the riboflavin and gellan gum structure. Hence, the riboflavin can be released much easily as compared to the salt from the gel structure. Comparing riboflavin with the salt, a higher overall release was noted for the former. The deduced results are in accordance with previous studies. Researcher (Çakır et al., 2011) examined that as the rigidity of the gels is increased, the flavor release is reduced. Meanwhile, Boland (2004) and Guinard and Marty (1995) explained that solid and strong gels release flavor with lower maximum intensity as compared to soft or medium gels. Prior studies indicated that the physical entrapment of flavor molecules inside the food matrix is important for the release of flavor from hydrocolloid gels (Boland, 2004). In addition, (Baines & Morris, 1987) observed that the presence of an entangled polymer network restricts the transmission of small molecules, like flavor from inside the gel system to the surface. The interaction between the flavor molecules and the components of the gel will influence the flavor release from inside the gels (Boland 2004; Mälkki et al., 1993). Since there is no interacting or joining capacity of riboflavin to low acyl gellan gel, it can be deduced that it is much easy to release riboflavin than the salt from the low acyl gellan gum gels.

It is imperative to mention here that riboflavin's nature is rather amphoteric due to which it has a small net charge and has no interaction with ionic areas in the gellan gel structure (Abd El-Ghaffar et al., 2012). Furthermore, the active groups in low acyl gellan gum chains are basically involved with Na in the formation of cross links. Consequently, it is seen that the weak riboflavin-gellan interactions causes faster and greater amount of riboflavin to be released as compared to salt through the gellan gels.

Conclusion

The subject of this experiment has highlighted on the significant role of gellan and salt concentrations on the mechanical properties of the gellan gels. The mechanical properties like true stress, true strain and energy per unit volume of the gellan gels can be affected by the primary essentials like salt and gellan concentration. For all levels of salt, an increase in the gellan concentration leads to an increase in the strength of the gellan gels. This is due to the greater concentration of biopolymer which causes greater cross link densities within the gel network and hence it creates firm gels. It can be deduced from the release of salt and riboflavin that both of these releases are influenced by gellan gum concentration. As per the acquired results, a reduction in the release from the gellan gels is observed due to an increase in gellan concentration. This is because of diminished brittleness of gellan gels. Greatest salt and riboflavin release through the gels is observed for gellan gels which were most brittle. The findings indicated similarity in the release of salt and riboflavin from the gellan gels. This can be attributed to the absence of any interaction or binding ability of riboflavin to low acyl gellan gum. It is much easier to release riboflavin from the gellan gels as compared to the salt. It is also probable that the weak riboflavin-gellan interactions cause quicker and greater release of riboflavin from the gellan gels as compared to salt.

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