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Influence of Fe^{2+}-Cation Concentration and Temperature on the Gelation of Low Methoxyl Pectin

Ajit K. Surabhi[1*], Mohamed I. Elzagheid[2]
[1,2]*Chemical and Process Engineering Technology Department, Jubail Industrial College, Jubail Industrial city, 31961, Kingdom of Saudi Arabia*

Abstract: *Here we have investigated the influence of the Iron (Fe^{2+}) ion concentration, and the temperature on the rheological properties, storage (G') and loss (G'') shear modulus of low methoxyl pectin solutions and gels, in the presence of Fe^{2+} ion. Upon lowering the temperature in the presence of Fe^{2+}, G'and G''increase immediately followed by a further slow logarithmic increase with time. It was observed that, the storage modulus (G')was increasing with increasing cation concentration initially, further increasing in cation concentration lowering the storage modulus. From the frequency sweep curves, Pectin-Fe^{2+} samples exhibiting well structure behaviour at lower Fe^{2+} concentration and showing viscous behaviour at higher Fe^{2+} concentrations.*

Key words: *Pectin, Rheology, Rheometer, Pectin Gelation, Temperature sweep curve, frequency sweep curve,Storage modulus, Loss modulus.*

I. Introduction

Pectin is mainly used in the food industry as a gelling agent in fruit-based preserves such as jams, jellies and marmalade (Christensen, 1986; May, 1990; Rolin, 1993**)** **[1-3]**. It consists of a helical block copolymer of **D**-galacturonic acid and methyl ester in its structure. Pectins are characterized by their degree of methylation (DM) of the carboxyl groups (Thakur et al, 1997) **[4]**, and solutions of pectins with DM less than 50% are called low-methoxyl pectin, and above are called high-methoxyl pectins(Voragen et al, 1982; Visser & Voragen, 1995) **[5, 8]**.Dynamic rheological measurements and analysis of gels could predict product's stability, viscoelasticity and are helpful in monitoring liquid-like and solid-like behavior(May& Stainsby) **[9]**.Dynamic measurements are the most common methods used to get the information on rheological properties and behavior of a sample like, storage (G') and loss (G'') modulus. In general, if G'>G'', the solutions exhibit elastic properties and gel like behavior, when it is opposite G''>G', materials show viscous properties (Jonna et al, 2015)**[6]**.

II. Materials and Methods

Oscillatory shear measurements were carried out using an AR 500 Rheometer with a cone geometry (having dimensions of, 5 cm radius, and 2 degrees cone angle) in conjunction with aPeltier plate to control the temperature. Rheological experiments were carried out in the presence of varying concentrations of Fe^{2+} cation.
A mixture comprising metal ion solution of specific concentrations and 1% pectin solution were used to conduct all the rheology experiments in this study. The principle objective of these experiments was to ascertain the effects on the rheology of pectin including quantifying the extent of metal ion binding with pectin by evaluating the storage modulus (G') and loss modulus (G'') values. A 1% pectin solution was prepared by dissolving 1 g of pectin in 99 ml of water and heating the solution to maintain a temperature of 70°C. Metal cation solution containing Fe^{2+} - equivalent to carboxyl (COOH) concentrations in pectin produced by metal solutions in distilled water were prepared. By utilizing the equivalent carboxyl concentrations in pectin together with the acid equivalent weights, the cation solution concentrations were calculated.

1% pectin solutions and the respective metal cation solutions (of the appropriate concentrations) were maintained at 70°C. An AR 500 Rheometer was employed to carry out all the oscillation experiments. Once the Peltier plate had attained a temperature of 70°c, the pectin-cation sample slowly dispensed onto the plate by means of a syringe, the sample at the edge was covered with oil in order to prevent the evaporation of pectin-cation sample. The frequency sweep was then commenced and various rheological parameters (G', G", tan delta, dynamic viscosity etc) were accrued by the TA Advantage software as the experiment progressed. A graph was plotted illustrating a comparison of the amount (concentration) of bound metal ion (obtained from the binding experiments) with the values of the storage modulus (G') of same amount (concentration) of the same metal ion at an oscillatory frequency of 1 Hz at 25°C.

III. Results and Discussions

Rheology curves were plotted for G' and G'' (the storage and loss modulus respectively) with varied temperatures and frequencies. Dynamic rheological measurements and analysis of gels could predict a product's stability, viscoelasticity and are helpful in monitoring liquid-like and solid-like behavior (Rao & Cooley, 1993) **[12]**. Hence rheological studies have many applications in food and polymer processing.

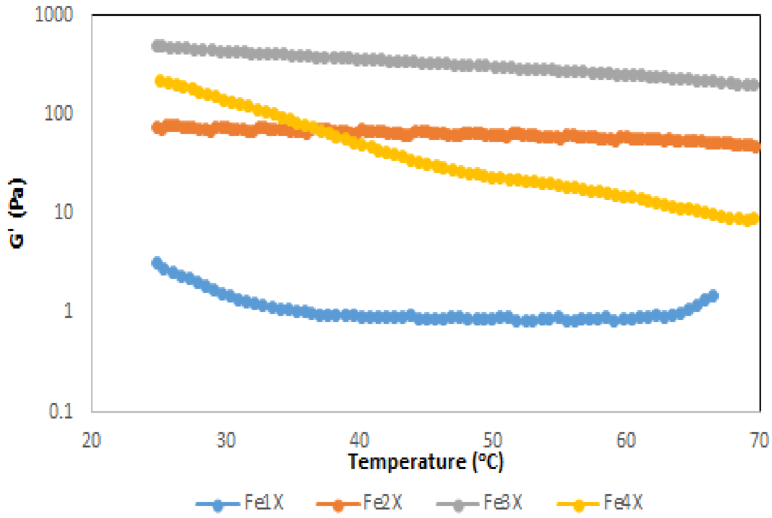

Figure 1: Pectin-Fe^{2+} temperature sweep curves for Storage modulus (G') with LMH pectin.

The temperature and metal ion concentration dependence of, storage (G') and loss modulus (G")of the pectin solutions in the presence of Fe^{2+} ion for a temperature sweep curve on cooling from 70°C-25°C range are shown in figure 1-2. From these results it can be observed that dynamic modulus was increasing with a decrease in temperature for all the samples, and the gel strength increases with ionic strength of the polymer solution (Jiabril at al, Didier Lootens et al)**[7, 11]**.AlsoAt lower ionic concentrations both G' and G'' were almost similar, the difference between storage (G'-elastic) and loss (G''-viscous) modulus was increasing with increasing ionic strength in pectin solution, exhibiting elastic properties, which means a proper gel. Whereas at lower ionic concentrations exhibiting viscous behavior due to the reason there is not much difference between G' and G'', sometimes G'' higher than G'. The gelation process is strongly influenced by initial composition and structural organization of pectin and metal ion concentration in pectin (Jonna et al)**[6]**. At higher temperatures while cooling the cation Fe^{2+} facilitated pectin solution exhibited liquid-like behavior, while lowering the temperature transition from solution state to gel-like behavior was observed.

The gelling mechanism of this system, Pectin-Fe^{2+} was attributed to the formation of (two distinct types) junction jones, mediated by the stoichiometric ratio of cation (M^{2+}/COO^{-}). Short egg-boxtype of co-operative helix junction jones would followed by an aggregation process upon cooling (Siew et al, Jiabril et al)**[10, 7]**.

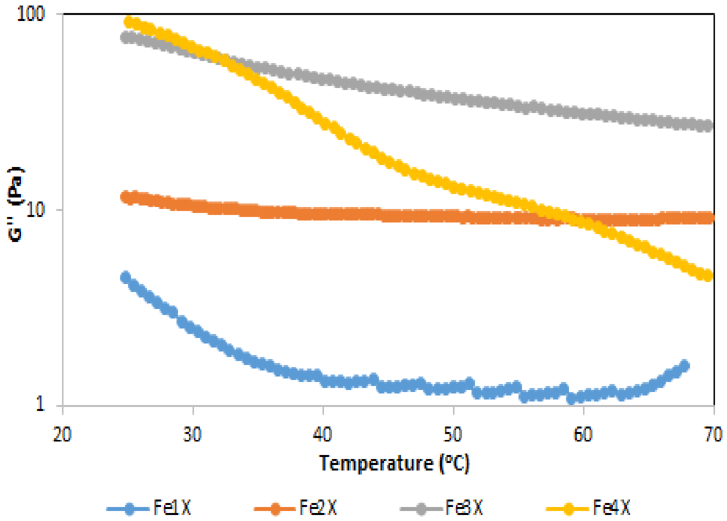

Figure 2: Pectin-Fe^{2+} temperature sweep curves for Loss modulus (G'') with LMH pectin.

The relation between storage and loss modulus Vs oscillatory frequency are called as "mechanical spectrum" of materials. The frequency dependence and metal ion concentration dependence of, storage (G') and loss modulus (G") of the pectin solutions in the presence of Fe^{2+} ion for a frequency sweep curve are shown in figure 3-4.

In the frequency domain it was observed that, by oscillatory experiments that G' and G'' were frequency dependent, and decreases with decrease in frequency. As the frequency increases that dependence on the Fe concentration a rapid rise of the storage (G') and loss (G'') modulus followed by a much weaker frequency dependence at higher frequencies. The dynamic modulus exhibits cation concentration. Even at higher frequencies for higher cation concentrations, the storage modulus is higher than loss modulus (G'>G''), which means that the solutions behaving elastic and solid-like behavior. Dynamic modulus (G' & G'') and gel strength are also cation concentration dependent in pectin solution. The storage modulus and gel strength are alike properties and, proportional to each other, G' and gel strength increase with increasing ionic strength of polymer solution for both the ions investigated. This increase was observed until $3XCOO^-$equivalent concentration for Fe^{2+}-Pectin solution, later a drop less dependent was observed. Even though G' and G'' were both increasing with increasing ion concentration, since G' was higher than the G'', the samples predominantly exhibits elastic behaviour gel like properties, and increasing gel strength with ionic concentration.

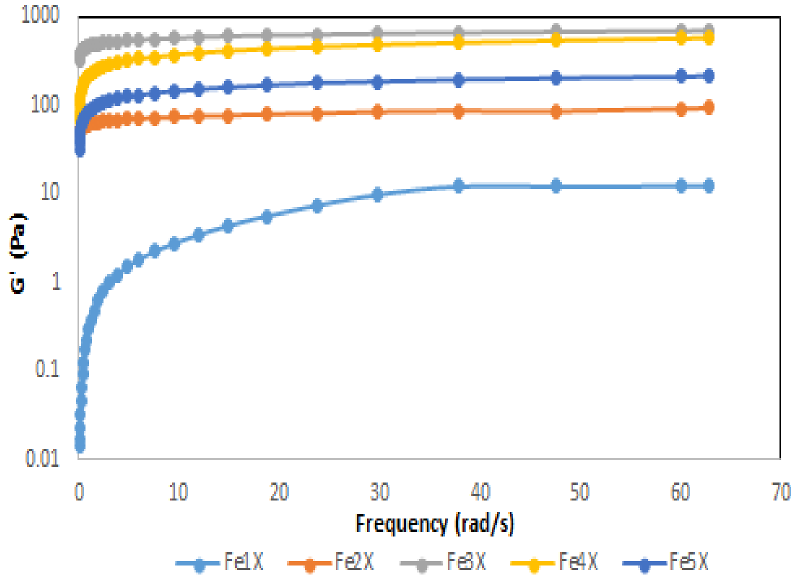

Figure 3: Pectin-Fe^{2+} frequency sweep curves for Storage modulus (G') with LMH pectin.

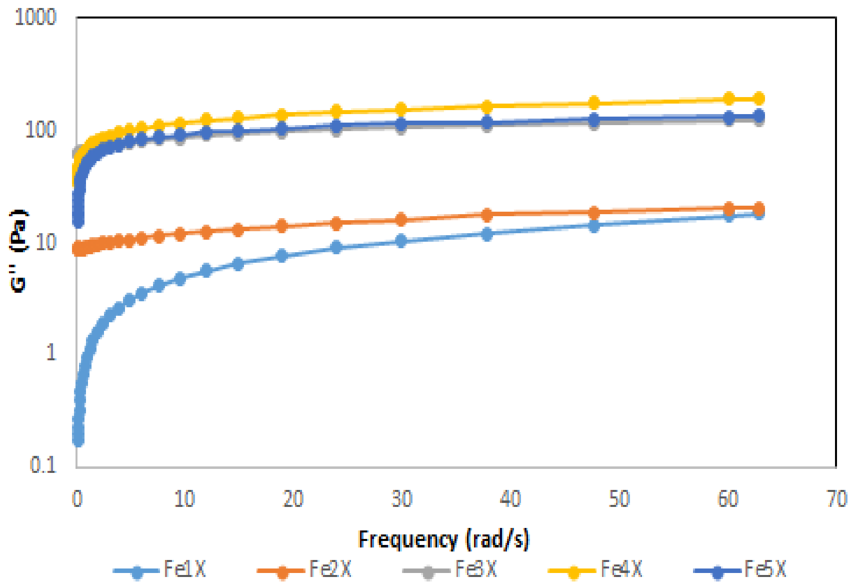

Figure 4: Pectin-Fe^{2+} frequency sweep curves for Loss modulus (G'') with LMH pectin.

Figure 5 illustrate the change in G' with a change in the ratio of Fe^{2+} concentrations, equivalent to carboxylic (COO^-)ion concentrations. The G' values are taken from the individual frequency sweep curves where G' corresponds to frequency of 1rad/s. The G' values are seen to increase and reached the maximum up to 3X Fe^{2+} ionequivalent concentration and then decreased. It can be observed that the gel strength increases when ionic strength of solvent increases up to a certain extent concentrations of the ions. Most of the pectin-Fe^{2+} samples are exhibiting elastic properties rather than viscous behaviour, because the storage modulus is higher than the loss modulus. At higher concentration of cation, G' decreases this could be because of pectin-cation forming a complex molecules instead of forming a gel, evidence comes from the work of Siewet al 2005**[10]**.

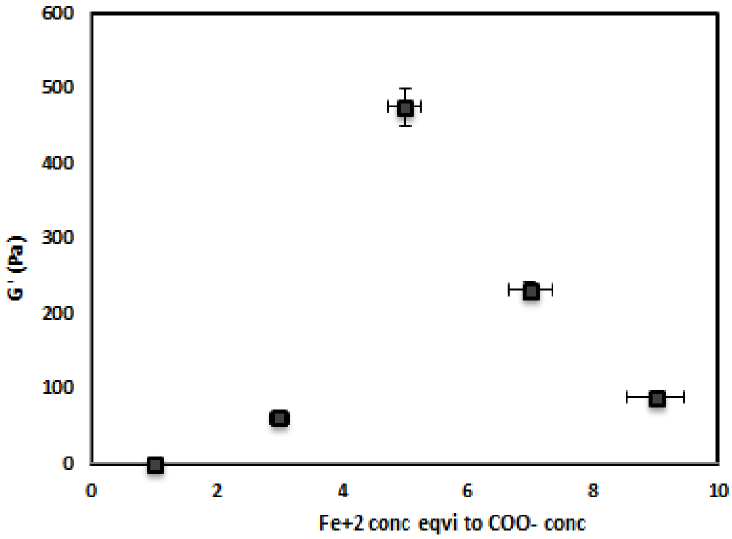

Figure 5: Storage modulus (G' corresponds to frequency of 1rad/s in frequency sweep curves) curve for Fe^{2+} with using LMH pectin.

IV. Conclusions

Rheology studies have shown that storage modulus increased as the concentration of metal ion rose to a certain level. A further increase of the cation concentration caused the storage modulus to fall off sharply. G' was also high at lower temperatures owing to the fact that at reduced temperatures, gelation was favorable and the sample showing good elastic behaviour. In contrast, at higher temperatures, the storage modulus recorded were low, asa consequence of the fact that temperature greatly affects gel formation. Frequency sweep results indicated that the storage modulus were higher than the loss modulus. Thus the system can be described as being a well-structured one (at higher concentrations of metal ion) when the particles are strongly associated. It can be concluded that the gel formation is very sensitive to the ionic strength of the solution and viscoelastic properties of the gel greatly affected by cation concentrations and finally the gel strength increasing with decreasing temperature and increasing cation concentration up to maximum level than decreasing.

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