

# Temperature Dependence of Electrical Properties of Biopolymer Gel with Increasing Polymer Concentration

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## Abstract

*This study is aimed to investigate the electrical properties of biopolymer gel as functions of polymer concentration and temperature. To perform this study, gellan gum was used as a biopolymer, which is a bacterial polysaccharide. The gellan polymer in solution dissociates into polyelectrolyte and it forms polyelectrolyte gel under a suitable condition. We studied the ionic conductivity variation of this gellan gel electrolytes with varying polymer concentration from 0.5 wt.% to 3.5wt.% which exhibit a slight increase in ionic conductivity at room temperature. In addition to different polymer concentration, we investigated the effect of temperature dependent electrical property from 30°C to 80°C and the Arrhenius plot obtained from this temperature dependence of conductivity revealed a stronger network with increasing polymer concentration.*

**Keywords:** Biopolymer, Bacterial Polysaccharide, Polyelectrolyte Gel, Gellan Gum, Conductivity

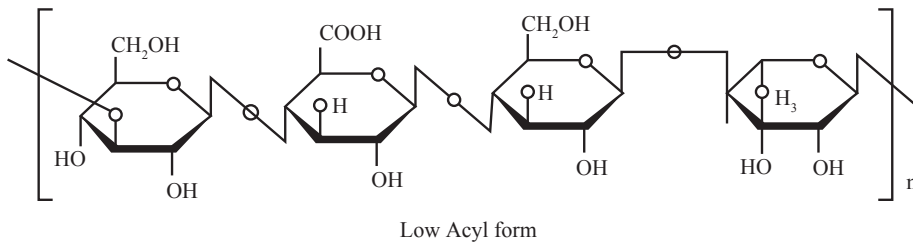
## Introduction

Interest in the study of electrically conductive, renewable and biodegradable, biopolymer system has been continuously growing as a result of its promising application such as electronics, medicine, food packaging, bioplastics and coating. There are two types of biopolymers available: neutral and charged. Gelatin or agarose is the neutral biopolymers and on the other side gellan, carrageenan etc. are the charged biopolymers. The charged biopolymers form polyelectrolytes in solution along with the metallic ions as their counterions. Biopolymer gel formed from these polyelectrolytes can be considered as gel electrolytes. For the interesting properties of biopolymers different polymer electrolytes (SPE) have been obtained from cellulose derivatives, starch, chitosan and pectin among others.

Gellan gum is an anionic microbial polysaccharide derived from *Pseudomonas elodea*. This heteropolysaccharide is basically composed of repetitive units of tetrasaccharide (-D-glucose, -D-glucuronic acid, -D-glucose and -L-rhamnose), and it contains one carboxyl side group per repeating unit.

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*Figure 1: Gellan gum structure*

Gellan gum forms a loose gel by itself because carboxylic side groups in the gellan gum molecule repulse each other by electrostatic interaction which hinders the tight bonding of helices and also a tight aggregation of helices. However, physicochemical properties of gellan gels are influenced strongly by the presence of cations, due to their ability to shield the electrostatic repulsion of the carboxylic groups.

Gellan gum is also a thermo-reversible gel-forming polymer. At temperatures more than 80°C, its chains adopt a random coil, which then undergoes a conformational transition to double-helices upon cooling below 30°C. This conformational transition has been observed and characterised extensively using a variety of experimental techniques including rheology, light scattering, nuclear magnetic resonances, viscometry and circular dichroism spectroscopy. The changes in polymer morphology during the conformational transition and the structure of the gel network formed have even been directly visualised utilising transmission electron microscopy and atomic force microscopy. Due to the compatibility and no danger for the human body, this macromolecule found great application for ascorbic acid carriers in foods, ophthalmic drug delivery and tissue-engineering.

So, considering the intensity of research interest on gellan biopolymer, we think it is an insightful selection of a time to investigate the conductivity property of gellan. At present, there is plenty of research going on increasing of gellan biopolymer conductivity.

N. F. A. Halim, S. R. Majid, A. K. Arof, F. Kajzar, And A. Pawlica studied the electrical properties of pure gellan-based polymer electrolytes, doped with LiI and plasticised with glycerol. Their ionic conductivity measurements showed that the salt concentration influences the ionic conductivity of electrolyte increasing it from  $10^{-8}$  S/cm (pure gellan) to  $3.8 \times 10^{-4}$  S/cm for gellan doped with 40 wt% of LiI. Addition of 10 wt% of glycerol promotes another increase of the ionic conductivity, up to  $1.5 \times 10^{-3}$  S/cm for the sample with 40 wt% of LiI. The repeated ionic conductivity measurements as a function of temperature show that the membranes of the doped sample can be reversibly used between the room temperature and 100°C.

Cameron J. Ferris and Marc investigated the gelation and conductivity behaviour of gellan gum-carbon nanotube composite materials. It has been shown that the addition of carbon nanotubes allowed more efficient cooling and heating of composite dispersions compared to

gellan gum solutions. In their study, it was suggested that the current contains an electrical contribution from electron transport through the nanotubes and an ionic contribution due to cations. They showed that increasing the nanotube mass fraction increases the relative contribution to the current of the electron transport over ion mobility & the ionic contribution was found to scale exponentially with increasing nanotube mass fraction.

Our main objective of this research will be to investigate the DC electrical behaviour of gellan in solution and gel state and the variation of conductivity as a function of polymer concentration and temperature which may reveal the application of this biopolymer in electronic devices.

## **Experiment**

### **Materials**

In this study, we used gellan powder as the main raw material. This commercial powder sample was obtained from Saneigen F.F.I Inc. Japan and used in this study without further purification. To get the best result nano-pure water (conductivity 0.055 micro-siemens/cm) was used for preparing the solution.

### **Sample Preparation**

To prepare the sample solution of certain polymer concentration required amount of powdered gellan was mixed with nano pure water. To ensure homogeneity and complete dissolution of powdered gellan magnetic stirrer and a water bath maintained at temperature 70°-80°C was used. For example, to make polymer concentration,  $C_p=2\text{wt.}\%$ , 0.2gm of gellan powder was mixed with 9.8gm. of water in a 50ml bottle. After the mixing, a magnet was inserted inside the bottle and the entrance was sealed with Teflon, so the concentration of the prepared solution remains the same during the entire preparation process. Then the solution bottle was put inside a water bath on a magnetic stirrer for 1 hour at a temperature between 70- 80°C. After 1 hour the hot gellan solution was poured into a sample holder. The solution turned into gel just after reaching the room temperature. By this method, we prepared 5 samples of different polymer concentration from 0.5 wt% to 3.5 wt%.

### **Measurement Technique**

Simultaneous measurement of different samples electrical characteristics was carried out using an experimental system consisting of a sample holder placed within a controlled temperature chamber and electrical characterisation equipment. The sample holder consisted of two electrodes separated by an insulator and they were connected with electrical characterisation equipment (Keithley 2401 source meter) by two copper wire. The equipment itself was operated through Lab tracer 2.9 software. For Current (I) – voltage (V) characteristics we choose to apply the voltage range from -5V to +5V from the source menu and current data were recorded with sweep delay 10 (ms). The temperature dependence of electrical transport through the sample was determined by measuring the I–V characteristics inside the controlled temperature chamber as the temperature was slowly increased from 30–70°C.

## Results and Discussion

The electrical conductivity of any material is the ability of a material to carry the flow of an electric current (a flow of electrons). In this study, we have observed the variation of conductivity as a function of temperature and polymer concentration. The electrical conductivity ( $\sigma$ ) of the sample was found using the equation,

$$\sigma = d/RA \quad (\text{i})$$

Where R is the resistance, d is the thickness of the sample and A is the area of the sample in contact with the electrode. The temperature dependence electrical conductivity of a polymer is known to be given by

$$\sigma = \sigma_0 \exp(-E_a/RT) \quad (\text{ii})$$

Where,  $E_a$  is the activation energy. We found the activation energy required from plot  $\ln \sigma$  vs  $1000/T$ . The slope found from this linear plot was then used in the following equation (iii) to give the activation energy,  $E_a$ ,

$$E_a = -(\text{slope})R \times 1000 \quad (\text{iii})$$

The electrical properties were measured for 5 samples of concentration 0.5 wt. %, 2.0 wt%, 2.5 wt. %, 3.0 wt. %, 3.5 wt. % from temperature 30°C to 70°C.

### Temperature Dependent Conductivity Variation

Figure: 2 (a) clearly demonstrates the resistivity of gellan polyelectrolyte decreases with increasing temperature which is analogous to a semiconductor behaviour. In fig (b) and (c) we see the change of conductivity at different temperature for polymer concentration,  $C_p=0.5\text{wt}\%$  and  $C_p=2.0\text{wt}\%$ . We find that the conductivity rises non-linearly for  $C_p=0.5\text{wt}\%$  from  $6.56 \times 10^{-4}$  S/cm at 30°C to  $4.74 \times 10^{-2}$  S/cm at 70°C. The reason for this drastic increment suggests as with increasing temperature the gellan forms a complete viscous liquid and the counterion present in the viscous liquid becomes highly mobile. Whereas in Fig (c), the conductivity for  $C_p=2.0\text{wt}\%$  is found to increase linearly with temperature from  $7.95 \times 10^{-4}$  S/cm at 30°C to  $1.52 \times 10^{-3}$  S/cm at 70°C. It can be explained by suggesting that, as the gellan polymer changes in conformation from double helices to a random coil with increasing temperatures, the counter ions in gellan achieves high mobility which therefore increases conductivity.

Lastly, the activation energy,  $E_a$ , found from conductivity vs temperature for samples from 2.0wt% to 3.5wt% in Table 1 suggests with increasing temperature gellan solution is of Arrhenius type, and therefore can be used as sensor materials.

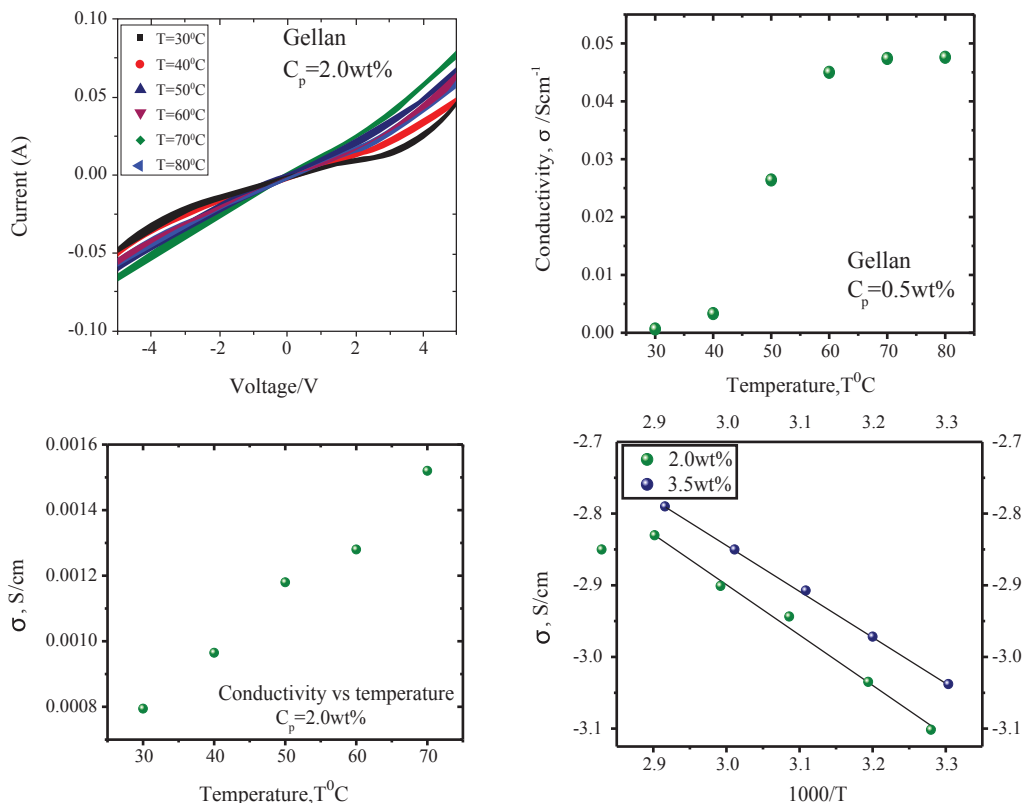


Figure: 2 Conductivity variation of gellan gum as a function of temperature a) Plot of I-V characteristic curve for polymer concentration,  $C_p=2.0$  wt.%. b) Plot of Conductivity Vs Temperature at 0.5wt% c) Plot of Conductivity vs Temperature at 2.0wt% d)  $\log \sigma$  vs  $1000/T$  ( $K^{-1}$ ) with increasing polymer concentration.

Table 1: Activation energy with increasing polymer concentration

Polymer Concentration, $C_p$	Activation Energy, $E_a$ KJ/mol
$C_p=2.0$ wt. %	4.74 KJ/mol
$C_p=3.5$ wt. %	5.20 KJ/mol

From Table 1, we find that the activation energy increases with increasing polymer concentration which confirms the formation of stronger and concentrated network.

### Concentration-dependent Conductivity Variation

The conductivity as a function of concentration has been studied in figure 3 which demonstrates with increasing concentration from 2.0wt% to 3.5wt% the conductivity increases slightly from  $7.95 \times 10^{-4}$  S/cm to  $9.26 \times 10^{-4}$  S/cm. Since the temperature was kept constant at  $30^\circ\text{C}$  this increase suggests that it is entirely determined by the polymer concentration.

As we increase our concentration 1.8 times the counterion concentration also increases with decreasing water content. So, we suggest with increasing concentration the transport properties are governed by counter ion concentration.

## Conclusion

DC electrical properties of gellan biopolymer gel have been intensively studied as a function of temperature with varying polymer concentration. The I-V characteristic curve was analysed and the increase of conductivity with temperature confirms that gellan conductivity is temperature depended and increasing polymer concentration also increases in conductivity confirms counterion concentration plays an important role in increasing its conductivity. The variation of conductivity as a function of temperature and concentration confirms that gellan conductivity can be controlled. From the results, we would like to emphasise that cation mobility and polymer conformation plays an important role in gellan conductivity and the control over conductivity can find its application as a bio-sensor in many electronic devices.

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