Effect of High Acyl Gellan Addition on Activation Energy Values and Flow Behavior of Film Forming Solutions

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Abstract
Polysaccharides such as gellan gum have been used in the alimentary industry in order to produce functional foods. The estimation of the activation energy of biopolymers materials provides important information for adequate selection and application of these materials, which are utilized in processes such as active film production. This study aims to determine the flow behavior and activation energy of film forming solution (FFS) based on carboxymethylcellulose (CMC) and xanthan gum (XG) formulated with various concentrations (0.1, 0.5 and 0.7 % p/v) of high acyl gellan (HAG). The flow behavior of the dispersions was determined at 25°C with a controlled stress rheometer (HAAKE MARS 60) whereas the activation energy values were established through modeling the relationship between viscosity and temperature employing the Arrhenius equation. All the studied FFS showed non-Newtonian shear-thinning behavior with an adequate
adjustment to the Ostwald de Waele model. With respect to the activation energy values, the highest concentration of HAG yielded, the highest activation energy values (37 to 48 kJ/mol); whereas dispersions without HAG showed the lowest activation energy values (1.27 kJ/mol). These findings indicated that activation energy is proportional to HAG concentration. These results are promising and suggest the possibility of developing heat resistant active films based on HAG.

**Keywords**: gellan gum, rheology, viscosity

## 1 Introduction

Environmental pollution caused by the use of non-biodegradable materials on food packaging has triggered significant interest in natural biodegradable polymers [2]. Various polysaccharides have been employed in the alimentary industry as thickeners, gelling agents and emulsifiers as well as active film production [4]. Carboxymethylcellulose (CMC) is a natural polyelectrolyte derived from cellulose that has attracted considerable interests in a wide range of biomedical applications [3] [9] due to its biodegradability, biocompatibility and good film-forming properties [3] [17]. Xanthan gum (XG) is a heteropolysaccharide produced by bacterium *Xanthomonas spp*, through aerobic fermentation in a non-continuous process [7] [13]. XG was authorized by the Food and Drug Administration (FDA) for applications as stabilizer and emulsifier without any restrictions [5].

Gellan gum is the most recent addition to the class of gelling agents commercially available for food applications. Gellan gum is a linear anionic heteropolysaccharide secreted by the bacterium *Sphingomonas paucimobilis* and consists of repeating units of a tetrasaccharide (1,3-β-D- glucose; 1,4-β-D-glucuronic acid; 1,4 β-D-glucose; and 1,4-α-L-rhamnose)[6]. Native gellan is called as high acyl gellan (HAG) because it presents two acyl groups, an acetate group (C6) and a glycerate group (C2) located in its glucose residue [14]. Various studies have been carried out about film and film forming solution (FFS), for example: Chen at al. [2], stated that incorporation of tea polyphenol on FFS based on gelatins resulted in an increase in tensile strength of films, Ma et al.[10] assessed the rheology of FFS of tara gum film reinforced with polyvinyl alcohol (PVA), Chayad [1] evaluated the electrical conductivity and activation energy of electrospun nylon films; nevertheless, to the knowledge of the authors, flow behavior and activation energy values of FFS based on CMC and xathan gum have not been determined yet. The estimation of the activation energy is a useful parameter at industrial level for selecting materials and using them to produce active films and heat resistant microcapsules. Rheological studies are also important because they provide information about the interactions between different polysaccharides during the film-forming process, which can be hard to understand due to polysaccharides structure [12]. Although there have been few studies on the rheology and activation energy values of different polysaccharides, there is almost no information concerning the effect of HAG on
flow behavior and activation energy of FFS based on CMC and GX. Therefore, this study focuses on determining the flow behavior and activation energy of FFS based on CMC and XG formulated with various concentrations (0.1, 0.5 and 0.7 % p/v) of HAG.

2 Materials and methods

2.1 Dispersions

The FFS were prepared as following: dispersions of CMC at 8 % (p/v) containing GX at 5 % (p/v) and glycerol (10 % p/v) were mixed with increasing amounts of HAG (0.1, 0.5 and 0.7 % p/v) under constant shaking at 90°C during 10 minutes adjusting the pH values at 4.0 by adding glucono-δ-lactone. The mentioned dispersions were then cooled to room temperature and subsequently refrigerated at 4°C for 24 h before flow behavior determination.

2.2 Flow behavior determination of FFS

The flow behavior of FFS was determined at 25°C with a controlled stress rheometer (HAAKE MARS 60). Sensor: P35/Ti-02150467. The rheological parameters were calculated according to the Ostwald-de-Waele model (Eq. 1).

\[ \sigma = K \gamma^n \]  

where, \( \sigma \) is the shear stress (Pa), \( \gamma \) is shear rate (s\(^{-1}\)), \( K \) is the consistency coefficient (Pa.s\(^n\)) and \( n \) is the flow behavior (dimensionless).

2.3 Activation energy determination

This parameter was established through Eyring' premise which stated the possibility of modeling the relationship between viscosity and temperature employing the Arrhenius equation:

\[ \eta = A e^{\left(\frac{E_f}{RT}\right)} \]  

where \( \eta \) is material's viscosity (Pa s), \( T \) is temperature (K), \( A \) is the pre-exponential factor, \( E_f \) is the flow activation energy, and \( R \) is the universal gas constant (8.3149 \( 10^3 \) kJ/mol K) [6] [8] by plotting \( \ln(\eta) \) versus \( 1/T \), a straight line is obtained with the slope \( E_f/R \). Viscosity values were determined at different temperatures (35, 45, 55, and 65 °C).

2.4 Statistical analysis

The data were analyzed by means of ANOVA (one way) in order to statistically determine significant differences (p < 0.05) among the samples. The software SPSS (version 17.0 for Windows) was used. Three samples were run per test.
3 Results

3.1 Flow behavior

Figure 1 shows that HAG addition on FFS has no effect on the flow behavior. All these solutions exhibited a non-Newtonian shear thinning flow behavior in which viscosity decreased in value when the shear rate was increased. This can be attributed to the conformational changes of gellan, which can transform from a spiral to a helix and it is easily oriented by the shear flow [11].

Figure 1: Viscosity behavior of FFS based on CMC and XG containing various concentrations (0.1, 0.5 and 0.7 % p/v) of HAG.

The experimental data were adjusted to the Ostwald-de-Waele model in order to establish the rheological parameters such as consistency coefficient (K) and flow behavior index (n), both parameters are important considering that flow behavior is a measure of the pseudoplasticity of different solutions, while the consistency coefficient yields the magnitude to the viscosity. This means, that both parameters are useful for process design at industrial levels [16]. It is interesting to mention that the adjustments were appropriate because correlation coefficients between 0.96 and 1.00 were obtained (data not shown). The viscosity values obtained from FFS containing HAG ranged from 11.3 to 32.1 Pa.s (Table 1), whereas the solution without HAG resulted on a viscosity of 3.57 Pa.s. These values were significantly different (p<0.05) among them. Higher HAG content produced greater viscosities which indicate that the viscosity is mainly determined by the HAG concentration rather than that of CMC and GX. This behavior may be originated because of gelification mechanisms of HAG. With regards to the consistency coefficient (K), it was observed that K values were directly proportional to the viscosity results showing that the highest coefficients for the FFS containing 0.7 % (p/v) of HAG.
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(30.4 Pa.s^n), while K values for the solution without gellan was lower (1.54 Pa.s^n). The flow behavior index (n) means how close or far is the liquid behavior with respect to the Newtonian fluid; considering this premise, all FFS had n values minor that one unit confirming that dispersion behavior was non-Newtonian type shear-thinning [16].

Table 1: Activation energy values and rheological parameters of the Ostwald-de-Waele model of FFS

<table>
<thead>
<tr>
<th>CMC/GX/HAG</th>
<th>η (Pa s)</th>
<th>K (Pa^n)</th>
<th>n (-)</th>
<th>Ea (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/5/0.0</td>
<td>3.57^a</td>
<td>1.54^a</td>
<td>0.75^a</td>
<td>1.27^a</td>
</tr>
<tr>
<td>8/5/0.1</td>
<td>11.3^b</td>
<td>8.43^b</td>
<td>0.22^b</td>
<td>37.23^b</td>
</tr>
<tr>
<td>8/5/0.5</td>
<td>22.6^c</td>
<td>20.3^c</td>
<td>0.18^b</td>
<td>41.02^c</td>
</tr>
<tr>
<td>8/5/0.7</td>
<td>32.1^d</td>
<td>30.4^d</td>
<td>0.31^c</td>
<td>48.07^d</td>
</tr>
</tbody>
</table>

Rows with no common letter showed statistically significant difference (significance level p<0.05) η = viscosity; K = consistency coefficient; n = flow behavior index; (-) = dimensionless.

3.2 Activation energy

The activation energy provides valuable information for adequate selection and application of different materials for example, hydrocolloids and proteins, which are utilized in processes such as active film design and microencapsulation of active compounds [15]. The activation energy values are also shown in Table 1. Where it can be observed that the highest Ea value (48.07 kJ/mol) was obtained for the FFS containing 0.7 % (p/v); while the lowest Ea value (1.27 kJ/mol) was obtained on dispersions without HAG followed by dispersions containing 0.1 and 0.5 % (p/v) of HAG with 37.23 and 41.02 kJ/mol respectively. This behavior could be caused mainly due to the fact that HAG gelifies as a result of hydrogen bonds formation between the gellan helix. It was observed that an increase in HAG concentration leads to an increase in the Ea value. Hence, One-way ANOVA of Ea values revealed significant differences (p<0.05) among the studied FFSs due to the different HAG contents.

3 Conclusions

Film forming solutions based on CMC, GX and increasing amounts of HAG showed non-Newtonian shear-thinning behavior with the adequate adjustment to the Ostwald-de-Waele model. Regarding the activation energy, high concentrations of HAG are recommended for obtaining heat-resistant active film due to the increase of the mean activation energy value, which was proportional to the rise in HAG concentration. It should be noted that these results could likely contribute to the development of new products or applications containing functional biopolymers such as gellan.
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Conflict of interests. The authors declare that there is no conflict of interests regarding the publication of this paper.

References


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