Changes of the Dynamic Properties of Films Based on Carrageenan by Microcapsules Incorporation

Rafael González-Cuello, Fidel Guardo-Palomino, Andrés Sánchez-Castilla, Maira Alvear-Picón and Ronald Marsiglia-Fuentes

University of Cartagena, Department of Food Engineering, Food Engineering Program, Research Group of Complex Fluid and Food Rheology, Cartagena-Bolivar 130015, Colombia

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Abstract

The use of edible films for covering food matrices has been of great importance due to they protect and extend the shelf life of different foods. The aim of this paper was to determine the rheological changes caused by microcapsules incorporation on edible films made from carrageenan. All rheological measurements were carried out in the viscoelastic zone, which was determined using the Kelvin–Voigt model. Both films (with and without microcapsules) presented predominantly elastic characteristics ($G' > G''$). The microcapsules addition decreased the recovery values as a result of a film-degradation structure. The relaxation time ranged between $9.245 \times 10^{-3}$ to $9.427 \times 10^{-3}$ s and the instantaneous compliance ($J_0$) values were 88.51 times higher than the retarded compliance ($J_1$) values in the studied films indicating the loss of elasticity of the films due to microcapsules incorporation.

Keywords: Rheological behavior, Viscoelasticity, microencapsulation

1 Introduction

Hydrocolloids (alginites, starch, gelatin and gellans) are high molecular weight macromolecules that can easily be dispersed and dissolved in water [12]. Besides, they can produce a three-dimensional network which under suitable conditions can be used for the preparation of edible films and coatings [2]. Nowadays, the development of edible films and coatings has been focus mainly on how to replace the use of synthetic materials employed for food products packaging [5].
On edible films have been carried out different studies, where the shelf life of coated foods [15], mechanical and barrier properties [14] have been evaluated. There is almost no information concerning to the rheological changes on edible films attributable to the microcapsules addition. Microcapsules are structures that allow a material to be packaged and protected from environmental and deleterious conditions. Besides a microencapsulated material can be gradually released into a target place [10].

Rheological studies are essential considering that provide information on gelling mechanisms of polymeric materials [6]. An edible film is a gel, which is a system of two phases constituted by a solid three-dimensional network that retains a liquid phase in its interior. It means that gels have a viscoelastic behavior due to their solid-liquid nature [4]. Different methods for evaluating the viscoelasticity employing the relationship between stresses, relative strain and time. For example, the creep recovery curves are obtained in terms of compliance (Jt), which is the quantitative relation between the stresses applied to the sample and the resulting deformation [13, 3]. A mathematical representation of these creep curves employs various models that include springs and dashpot. Spring is an element that describes the behavior of Newtonian liquid, while dashpot describes the behavior of elastic solid of Hooke [13]. When these elements are line up in series or parallel, it is possible to determine viscoelastic properties of solids and fluids through the mathematical equations. The Maxwell, Kelvin–Voigt, and Burgers are the main models employed for viscoelastic characterization [11]. Analysis of dynamic rheological parameters and creep curves allow the characterization of a complex system made from polymeric materials. Besides, the modifications on these parameters can be determined as a function as the microcapsules incorporation. The present study employed the Kelvin–Voigt model, which describes the behavior of a viscoelastic solid. The aim of this research was to determinate the rheological changes originated by microcapsules incorporation on films made from carrageenan.

2 Materials y Methods

Microencapsulation

Microcapsules were prepared using polymeric dispersions of low acyl gellan (0.75 %w/v) containing calcium (30 mM) under constant stirring (hot-stirring plate, Thermolyne nuova II) at 90°C. Then, the polymeric dispersion was added into vegetable oil (canola oil) in a ratio (1:2 v/v) dispersion:oil under constant agitation. Finally, the gelation process was carried out through δ-gluconolactone added until a pH of 4.2. Microcapsules were harvested by centrifugation at 5000 rpm / 10 min and stored at 4 °C until its use.
Edible film formation

The film forming solutions (FFS) of carrageenan (0.35 % w/v) were obtained by dispersing in distilled water containing glycerol (8 % w/v) as plasticizer under constant stirring at 80°C during 10 minutes. Then, the FFS were cooled at 37°C and microcapsules previously prepared were incorporated. Afterward, 25 mL of FFS containing microcapsules were poured into sterile Petri dishes controlling the film thickness. The films dried was carried out for 48 h in an incubator at 34 °C. Finally, the films were peeled off and placed in Petri plates covered using parafilm for air-tight storage. It must be highlight that films control were prepared without microcapsules addition.

Dynamic rheology characterization

The determinations were performed in a Modular Advanced Rheometer System MARS 60, HAAKE (Thermo Scientific, Germany), equipped with a coaxial cylinder (inner radius 12.54 mm, outer radius 11.60 mm, cylinder length 37.6 mm). Samples were placed in the bottom plate and the gap was set (2.8 mm). The linear viscoelastic region was obtained through an amplitude sweep and G’ and G” moduli are independent of the amplitude. Subsequently, a frequency sweep was performed between 0.010 and 20 Hz in order to define the behavior of viscous and elastic modulus versus the frequency.

Creep recovery curves

This test is about applying stress to a sample and evaluating the strain material in function of the time [11]. The shear stress value is calculated within the lineal viscoelastic region. The results are expressed in term of compliance adjusted to the Kelvin Voigt model (equation 1).

\[ J(t) = J_0 + \sum_{i=1}^{n} J_i \left(1 - e^{-t/\lambda_{rel}}\right) + \frac{t}{\eta_0} \]

Where, \(J_0\) is the instantaneous elastic compliance (Pa \(^{-1}\)), \(J_i\) is the retarded compliance (Pa \(^{-1}\)), \(\lambda_{rel}\) is the relaxation time (s) and \(\eta_0\) is zero-shear viscosity. The recovery percentage was calculated according to the equation:

\[ \% \text{ Recovery} = \left(\frac{J_{max} - J_\infty}{J_{max}}\right) \times 100 \]

Where, \(J_{max}\) is compliance when the stress is suspended and \(J_\infty\) is the last recovery value [3].
Statistical analysis

The data were analyzed through ANOVA (one way) employing the software SPSS (version 17.0 for Windows) in order to determine statistically significant differences (p<0.05) among the samples. All the test were done in triplicate.

3 Results and Discussion

Dynamic rheology

Changes in the study of the dynamic rheology of edible films made from carrageenan can be seen in table 1, where significant differences (p<0.05) in storage modulus (G’) and loss modulus (G’”) were appreciated when microcapsules were incorporated into the films. G’ is a measure of the energy temporarily stored in a material, while G’” is a measure of the energy employed to activate a flow, its mean, that energy is dissipated and transformed into heat. Regarding tan δ, this parameter indicates the relationship between the viscous and the elastic moduli of a viscoelastic system.

Table 1. Material functions of edible films based on carrageenan

<table>
<thead>
<tr>
<th>Edible film</th>
<th>G’(Pa)</th>
<th>G’” (Pa)</th>
<th>Tan δ (·)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With microcapsules</td>
<td>19893a</td>
<td>2685a</td>
<td>0.13a</td>
</tr>
<tr>
<td>Without microcapsules</td>
<td>16585b</td>
<td>1890b</td>
<td>0.11a</td>
</tr>
</tbody>
</table>

Rows with no common letter showed a statistically significant difference (significance level < 0.05).

The increase in G’ has been associated with a denser and more interwoven structure, although may also be related to moisture loss. When elastic modulus is higher than viscous (G’>G’”) indicated a dominant influence of the storage modulus in the viscoelasticity of both edible films in the frequency range studied (0.01 to 16 Hz). This behavior is characteristic of a strong gel according with the classification of Clark y Ross-Murphy [1]; which consist in determining the behavior of a strong or weak gel and macromolecular solution according to the dependence of G’ and G’” as a function of frequency. In other words, when G’ is greater than G’”, the energy is stored and recovered in each oscillatory cycle and only a piece amount of energy is lost in heat form [4]. One-way ANOVA of moduli revealed significant differences (p<0.05) among the studied films due to the presence of microcapsules.
Changes of the dynamic properties of films ...

Values of tan δ are key due to they allow classify various materials, for example, δ values < 1 indicate a gel-like behavior [4]. The value of film containing microcapsules was 0.13; while film without microcapsules had a value of 0.11. These findings confirm that although both edible films are strong, those without microcapsules are stronger than others.

Creep recovery curves

Figure 2 shows the creep and recovery curves of edible films, where can be seen that both films had a recovery when the applied stress was suspended. The recovery percentage of films containing microcapsules was 94.7 %; while films without microcapsules had 94.1 %. These findings confirm the solid elastic behavior for both films; although, it must be mentioned that a decrease of 0.6 % on the film’s recovery was appreciated, which likely is caused by the material degradation as a result of the applied stress. Rha [9] stated that if a material is deformed under force, the recovery will be less than the initial and the level recovery will depend on the time intervals under which the material was deformed [11]. In figure 2 it is clear that microcapsules addition does not affect significantly (p>0.05) the recoveries of the films studied.

Table 2 shows the rheological parameters of the Kelvin -Voigt's model for edible films evaluated, the instantaneous compliance ($J_0$), retarded compliance ($J_1$), viscosity (η) and recovery percentage. As can be seen (table 2), the viscosity increased significantly (p<0.05) by the microcapsules incorporation, while $J_1$ values remained constant. Both films (with and without microcapsules) showed a higher $J_0$ than $J_1$ ($J_1<J_0$), because films firstly need to deform before established the flow and deform again by the stress application. Likewise, it must be noted that compliance is the opposite of applied stress [7].
Regarding the relaxation compliance time ($\lambda_{rel}$), it was $9.427 \times 10^{-3}$ s for the edible film containing microcapsules and $9.245 \times 10^{-3}$ s for the film without microcapsules. This behavior shows a little loss of elasticity by microcapsules incorporation because of compliance indicates the ability of one material to recovery from one deformation [11].

Table 2. Rheological parameters of the Kelvin–Voigt model of edible films based on carrageenan mixtures

<table>
<thead>
<tr>
<th>Edible film</th>
<th>Viscosity (Pa.s)</th>
<th>J_1 (Pa⁻¹)</th>
<th>J_0 (Pa⁻¹)</th>
<th>$\lambda_{rel}$ (s)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With microcapsules</td>
<td>$3.19 \times 10^6$</td>
<td>$1.031 \times 10^{-6}$</td>
<td>$9.32 \times 10^{-5}$</td>
<td>$9.427 \times 10^{-3}$</td>
<td>94.7</td>
</tr>
<tr>
<td>Without microcapsules</td>
<td>$2.08 \times 10^6$</td>
<td>$1.033 \times 10^{-6}$</td>
<td>$8.95 \times 10^{-5}$</td>
<td>$9.245 \times 10^{-3}$</td>
<td>94.1</td>
</tr>
</tbody>
</table>

4 Conclusions

The addition of microcapsules produced rheological changes on the studied films. Although, both edible films presented a solid elastic behavior, where G' was higher than G'', statistical differences were appreciated for both moduli when microcapsules were added. It seems that microcapsules improve the association of polymeric chains increasing the storage modulus of edible films. Among the rheological parameters studied, the viscosity and instantaneous compliance were dependent on the microcapsules addition. Although the relaxation time did not present significant differences between both films evaluated, it was observed an increase caused by microcapsules. This implies the elasticity loss of edible film as a result of microcapsules presence. In future studies, it is important to evaluate the
effect of active compounds loaded into microcapsules on the rheological behavior as well as the mechanical and barrier behavior of these films.

Acknowledgements. The authors acknowledge to University of Cartagena for the financial support

References


Received: March 10, 2018; Published: April 4, 2018