

# Thermosensitive Hydrogels with Nanofillers Incorporated to Use in Food Packaging Applications

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## Abstract

Smart packaging systems offer interaction between the packaging environment and the monitoring, quality, and safety of the food. Responsive food packaging belongs to this category and has an informative and corrective function. This work attempts to show the behavior of the hydrogels based chitosan without/with the incorporation of nanofillers when these are exposed to temperature changes. The hydrogels solutions were analyzed by the following techniques: a) FT-IR analysis to identify their functional groups, b) Monitoring of the hydrogels by the mobility and color of the solutions after tilting the test tubes before and after gelation while maintaining the pH of the samples neutral, and c) Rheological characterization of the solutions by the monitoring of the gelation process of the hydrogels by the temperature dependence of the dynamic module of the solution. The gelation temperature was observed by the changes in mobility and appearance of different hydrogels. Rheological measurements showed the solid-like behavior of the samples around 37°C in both solutions. The incorporation of metallic nanoparticles in the solution did not affect the gelation point considerably. Therefore, thermogelling hydrogels based chitosan, beta-glycerophosphate ( $\beta$ -GP), and MNPs can behave as thermoresponsive materials since solutions exhibited gel formation upon heating. Also, these hydrogels could be used as materials to sensing changes of temperature that experiment some food packed.

**Keywords:** nanofillers, chitosan, thermoresponsive hydrogels, nanocomposites, food packaging.

## INTRODUCTION

Nowadays, the traditional packaging materials offer protection and a lower interaction with the food. However, in the food industry, the package must provide protection, containment, communication with the consumer, ergonomics, and marketing[1]. Due to above, the requirements that demand the current market for the quality and safety of food are investigated by the material sciences field. According to this, the innovative packaging systems that not only preserve and distribute the food in a proper manner, but also, act as a sensor

or indicator[2]. Smart packaging systems offer interaction between packaging environment and the food monitoring the quality and safety (i.e., freshness, microorganisms, gas permeability, pH, temperature, etc.) of food from producers to consumers [3][4]. Nowadays, the strategies used to protect and preserve the quality of the food are an object of study in many investigations in food packaging applications.

Responsive food packaging belongs to the group of smart and intelligent packaging[5]. This type of food packaging has an informative and corrective function, which react to external or internal stressors (i.e., food product and external environment). These stimuli-responsive materials exhibit modifications in their chemical and physical structure when are exposed to external stimuli (i.e., pH, temperature, light, etc.). The response of these materials can be evidenced by changes in color or shape[6]. Some hydrogels can experiment shrinking, swelling, or degradation in response to external changes. Thermogelling hydrogels based chitosan and beta-glycerophosphate ( $\beta$ -GP), can behave as thermoresponsive materials since chitosan solutions neutralized using this weak base exhibit gel formation upon heating to 37 °C [7][8]. In addition, this thermoresponsive behavior has already been taken advantage by researchers to design systems that allow bone regeneration in tissue engineering applications.

In food packaging applications, the incorporation of nanofillers in polymer matrices changes the structure of the system and enhance the mechanical, thermal, and barrier properties of the materials[9]. Concerning how the incorporation of nanostructures affect the physical properties in hydrogels, it has found that nanocomposite hydrogels experiment changes in their structure with the increase the filler fraction and, at the same time, the polymer structure evidences the caging effect in the gel state[10]. However, few studies evidence the changes produced by the incorporation of nanofillers in thermoresponsive hydrogels on the gelation temperature. In this study was monitoring the changes in the gelation temperature of hydrogels based chitosan without/with the incorporation of nanofillers.

## METHODOLOGY

Chitosan from shrimp shells,  $\geq 75\%$  (deacetylated),  $\beta$ -glycerophosphate disodium salt, and acetic acid ACS reagent 99.7% were purchased in sigma Aldrich. The metallic nanoparticles used in these experiments were donated by the laboratory of Dr. Magda Latorre-Esteves of the Chemical Engineering Department of the University of Puerto Rico-Mayagüez (United States of America).

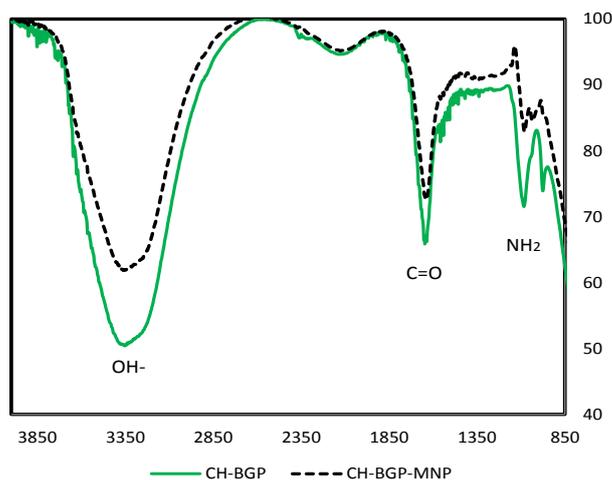
Chitosan (CH) was dissolved in acetic acid at 2.0 wt%; then it was prepared polymer solutions with incorporated magnetic nanoparticles (MNPs). To chitosan solution was added magnetic nanoparticles until reaching a concentration of 1% wt. The hydrogels were obtained adding an appropriate amount of pre-cooled 58% wt  $\beta$ -glycerophosphate ( $\beta$ -GP) solution until solving 15% wt [7]. The nanoparticles are magnetic ( $\text{Fe}_3\text{O}_4$ ) in nature covered with carboxymethyl dextran and were prepared following the procedure described by Herrera et al., 2008[11]. The polymer solutions remain in solution at neutral pH and room temperature, while gelation of these systems was triggered at 37°C.

## CHARACTERIZATION

The functional groups that are part of the structure of the hydrogels were obtained by an Infrared Spectrum Analysis using a FT-IR (Bruker IF 66 V/S). The gelation of the hydrogels was observed by the mobility and color of the solutions after tilting the test tubes before and after gelation while maintaining the pH of the samples neutral. The sample before gelation was kept at a temperature of 18°C; then it was placed in a bath at a constant temperature of 37 °C. Rheological characterization of the solutions was performed in an Anton Paar Physica MCR 301 Rheometer using a cylindrical configuration with Peltier temperature control. The monitoring of the gelation process of the hydrogels was obtained by the temperature dependence of the dynamic module of the solution of these hydrogels. The evolution of this process was monitored by the behavior of the curves of the modulus of elasticity ( $G'$ ) and the modulus of viscosity ( $G''$ ) at 1 Hz and a temperature increase of 1°C / s in a temperature range from 23 to 60 ° C. The gelation temperature was defined from the intersection of  $G'$  and  $G''$  (i.e., the temperature at which both  $G'$  and  $G''$  follow a frequency power law with the same exponent  $n$  (i.e.,  $G'$  and  $G'' \propto \omega^n$ )[12].

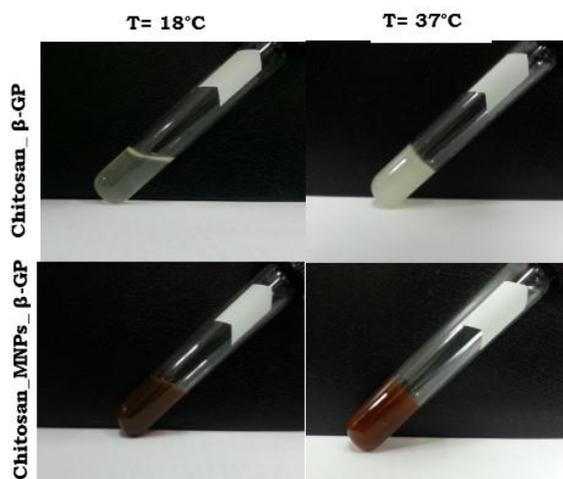
## RESULTS AND DISCUSSION

The analysis of the functional groups present in the sample with and without incorporated nanoparticles showed a broad absorption peak between 3383  $\text{cm}^{-1}$  and 3224  $\text{cm}^{-1}$  which corresponds to the O-H band. The visible peak that appears at 1635  $\text{cm}^{-1}$  is assigned to the carbonyl group of the secondary amine band of the chitosan. The band of the C-N bond at 1200  $\text{cm}^{-1}$  was also observed, which is typical of secondary amines present in the chitosan chain (See Figure 1).



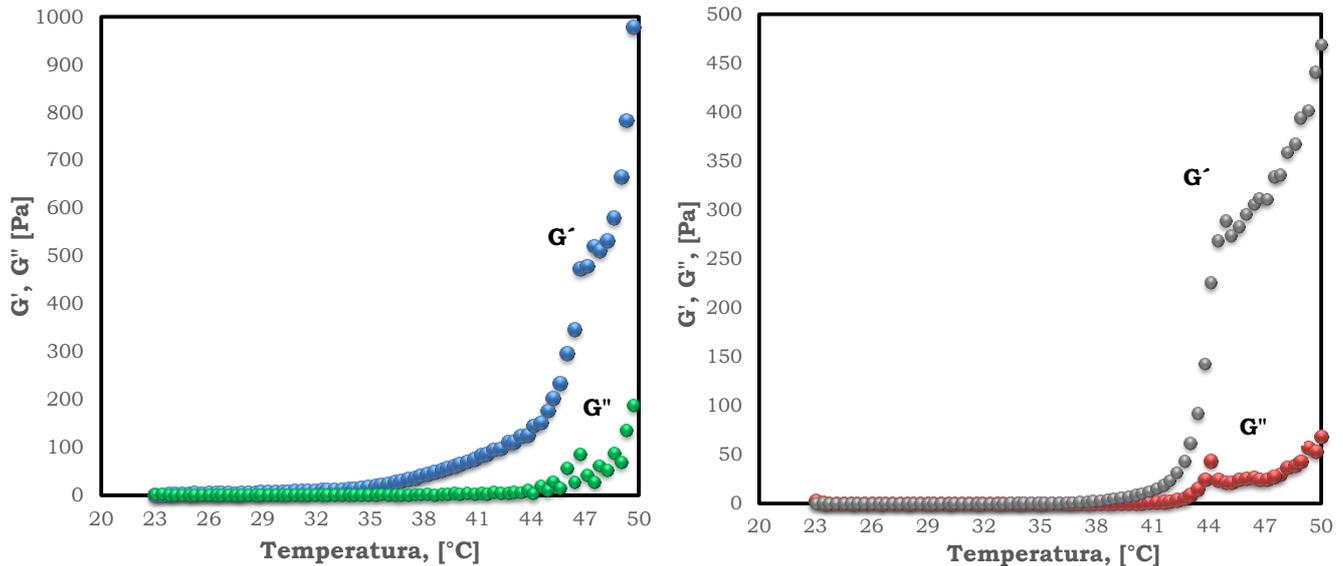
**Figure 1.** FTIR analysis of the different films synthesized.

The hydrogels at the gelation temperature had changes in mobility and appearance as is shown in Figure 2. At the temperature of 18° C, the samples without and with metallic nanofillers showed a liquid appearance, translucent, and with mobility when inclined. After being exposed to a temperature of 37° C, all samples reached the gelation temperature with changes in their mobility and change in the color of the samples.



**Figure 2.** Mobility and color of the solutions of CH- $\beta$ GP hydrogel and CH- $\beta$ GP-MNPs at 18°C and 37°C.

The Figure 3 shows that the dynamic moduli of the solution of these hydrogels presented a temperature dependence with a nonlinear variation. The behavior of  $G'$  and  $G''$  curves indicates the evolution of the gelling process. First,  $G'$  and  $G''$  remained stable and with low values. Then, with a temperature increase,  $G'$  increased fast while  $G''$  remained constant. The gelation temperature was reached around 37°C in both solutions. After the gel point,  $G'$  showed high values compared to  $G''$  which evidenced the solid-like behavior of the samples. [12]. The presence of metallic nanofillers in the samples did not affect the gelation point considerably. The mobility and appearance of the solutions during the experiment were supported by these results obtained.



**Figure 3.** Temperature-Dependence of elastic ( $G'$ ) and viscous ( $G''$ ) modulus of CH-BGP solution and CH-BGP-MNPs solution, upon heating from 23 to 50°C.

## CONCLUSION

By this study, it was possible to observe the physical changes of thermoresponsive hydrogels when experiment temperature changes. The gelation temperature was determined by the changes in mobility and appearance of both solutions. At the same time, rheological measurements evidenced the solid-like behavior of the samples around 37°C in both solutions. The incorporation of metallic nanoparticles in the solution did not affect the gelation point considerably. However, the effects caused by the incorporation of nanofillers into thermogelling hydrogels should be studied.

According to this, thermogelling hydrogels based chitosan, beta-glycerophosphate ( $\beta$ -GP), and MNPs can behave as thermoresponsive materials since solutions exhibited gel formation upon heating. The behavior of these hydrogels can serve to monitor the changes of temperature of the food when they are packed.

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