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# Thermosensitive Nanohydrogels for Food Packaging Fabrication

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**Abstract :** Manufacturing of active packaging with controlled release of biocompounds into food is a challenge for the food industry. The incorporation of thermosensitive nanohydrogels in this type of packaging can modulate the delivery mechanism of bioactive agents. The thermosensitive nanohydrogels phase transition was studied in this work. Nanohydrogels were obtained by covering metal nanoparticles of magnetite ( $\text{Fe}_3\text{O}_4$ ) with a polymeric layer of pNIPAM. Phase transition of nanohydrogels was observed by the change of hydrodynamic diameter in a temperature range below and above the lower critical solution temperature (LCST) of pNIPAM ( $T = 32^\circ\text{C}$ ). Infrared analysis, hydrodynamic diameter, and thermal analysis were performed in this study. The results demonstrated that nanohydrogels have a phase transition at a temperature very close to LCST of pNIPAM. Also, the nanohydrogels can be an option of nanofiller for manufacturing of active packages responding to external stimuli such as a temperature increase.

## Introduction

In food packaging industry, development of active packaging systems has become an important strategy contributing not only to reducing food deterioration, but also ensuring nutritional integrity in marketing process<sup>1</sup>. Active packaging is in contact with food and environment, interacting dynamically to improve safety, sensory properties and preserving food nutritional quality<sup>2</sup>. This packaging type not only allows the reduction of the number of antimicrobial components incorporated within the matrix, but also facilitates a controlled preservatives release system in response to an environmental stimulus<sup>3, 4</sup>. The above is not possible using traditional preservative release systems.

Therefore, the use of thermosensitive polymers such as poly (N-isopropylacrylamide) (PNIPAM) becomes an option for active packages manufacturing responding to changes in the environment temperature during storage<sup>4</sup>. In fact, recent studies have demonstrated the use of this polymer in component release systems in biomedical applications<sup>5</sup>. PNIPAM exhibits a lower critical solution temperature (LCST), above which, its solubility in water decreases, resulting in phase separation<sup>6</sup>.

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Upon reaching this critical temperature, water enthalpy bound to amide groups of PNIPAM chain decreases; resulting in water loss linked to the solution. Hydrophilic amide groups and hydrophobic isopropyl chains allow it to be soluble in water at room temperature and solvents with low polarity. When the PNIPAM reaches its critical temperature (LCST), hydrogen bonds formed with water are broken, and attraction between hydrophobic groups is strengthened, resulting in chains collapse and consequently, the phase transition of the hydrogel.

Nanohydrogels potentiate active packaging thanks to properties such as: size, flexibility, hydrophilicity, water absorption, dispersion capacity in solution, reduction in number of additives to be released, additive protection during loading, increase in surface area / volume, reactivity, improvement of the physicochemical properties of packaging and biocompatibility<sup>7,8</sup>.

Finally, incorporation of nanofillers in polymer films improves the materials mechanical properties, allowing good layers adhesion and dispersion of active substances within the material<sup>9,10</sup>.

## Experimental

N-isopropylacrylamide 97%, oleic acid, acetic acid,  $\alpha$ ,  $\alpha'$ -azobisisobutyronitrile (AIBN), N, N'-methylene bisacrylamide (MBA) were obtained from Sigma Aldrich. Iron salt (III) was brought from Across Organics. 3-methacryloxypropyltrimethoxysilane (MPS) was obtained from the Tokyo Chemical Industry. For nanohydrogels preparation, magnetite nanoparticles covered with oleic acid were synthesized following methodology used by Park and coworkers<sup>11</sup>. After that, nanoparticles were functionalized with 3-(trimethoxysilyl) propyl methacrylate (MPS) to achieve bound exchange with oleic acid<sup>12</sup>. Finally, these nanoparticles were covered with poly-(N-isopropylacrylamide) pNIPAM through a polymerization process of free radicals; using  $\alpha$ ,  $\alpha'$ -azobisisobutyronitrile (AIBN) as initiator and N, N'-methylene bisacrylamide (MBA) as a cross-linking agent<sup>13</sup>.

Characterization of the nanohydrogels Infrared spectrum analysis of nanohydrogels using an FT-IR (Bruker IF 66 V / S). b) A Zeta Sizer NANO ZS monitored the hydrodynamic diameter of nanohydrogels vs. Temperature. For this study, a solution of these nanohydrogels was prepared in distilled water (1.5% w/v). Then, the sample was heated from a temperature below and above of transition temperature of pNIPAM ( $T \approx 32$  °C). Calorimetric study of nanohydrogels was performed using a Differential Scanning Calorimeter (DSC). Nanohydrogels were suspended in distilled water at a 1.5 % w / v concentration in a temperature range from 17 to 54 ° C with a temperature ramp of 3 ° C / h. At last, Thermogravimetric analysis (TGA) was performed on the sample in the range of temperature (23°C to 600°C).

## Results and Discussion

Figure 1 shows the Infrared spectroscopy analysis of the magnetite nanoparticles covered with oleic acid, MPS, and pNIPAM. Figure 1-a) displays the representative bands at 2923 cm<sup>-1</sup>, 2854 cm<sup>-1</sup>, and 1720 cm<sup>-1</sup> which corresponding to -CH<sub>2</sub> and C=O groups present in oleic acid that cover the magnetite core. The band at 1124 cm<sup>-1</sup> which is representative of siloxane group present onto the magnetic core is illustrated in Figure 1-b). Also, the bands 1637 cm<sup>-1</sup> and 1720 cm<sup>-1</sup> attributed to MPS molecules were observed. Two representative bands at 1546 cm<sup>-1</sup> and 1648 cm<sup>-1</sup> corresponding to the secondary amide and the carbonyl group present in PNIPAM chains covering the magnetite nanoparticles are displayed in Figure 1-c)<sup>14</sup>.

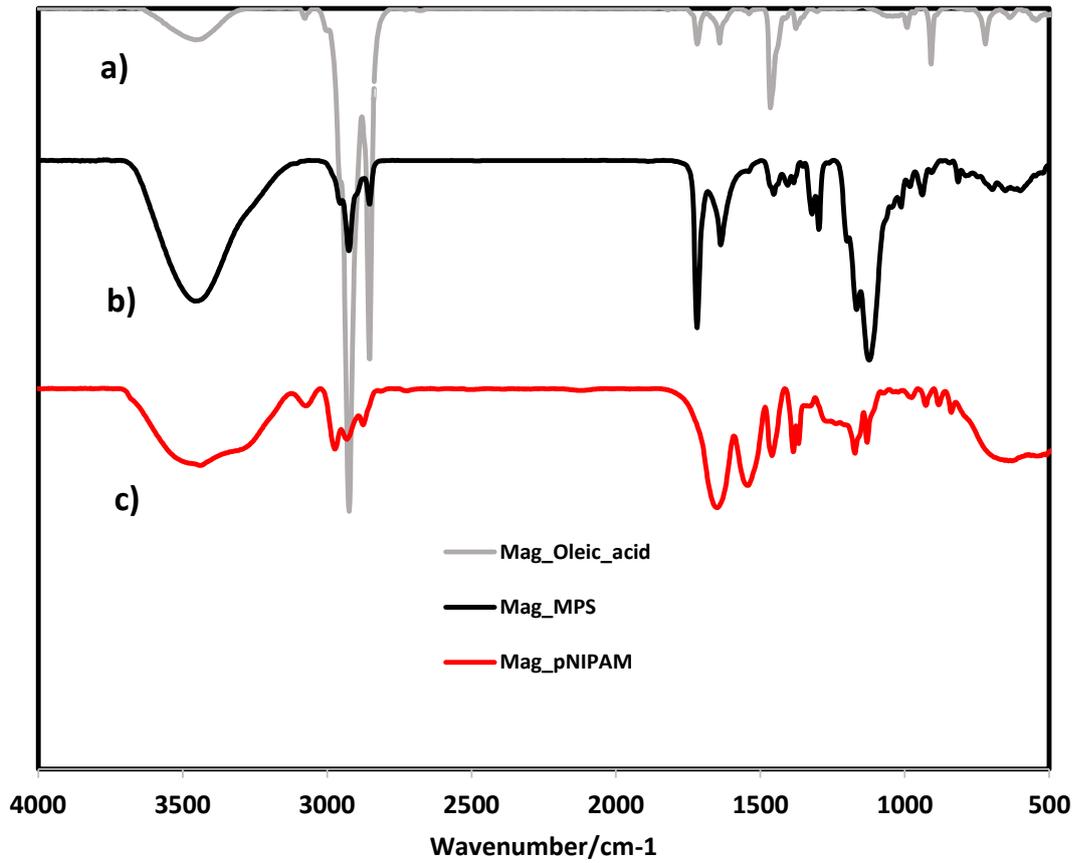


Figure 1. Infrared Spectra of iron oxide nanoparticles covered with oleic acid, MPS, and pNIPAM.

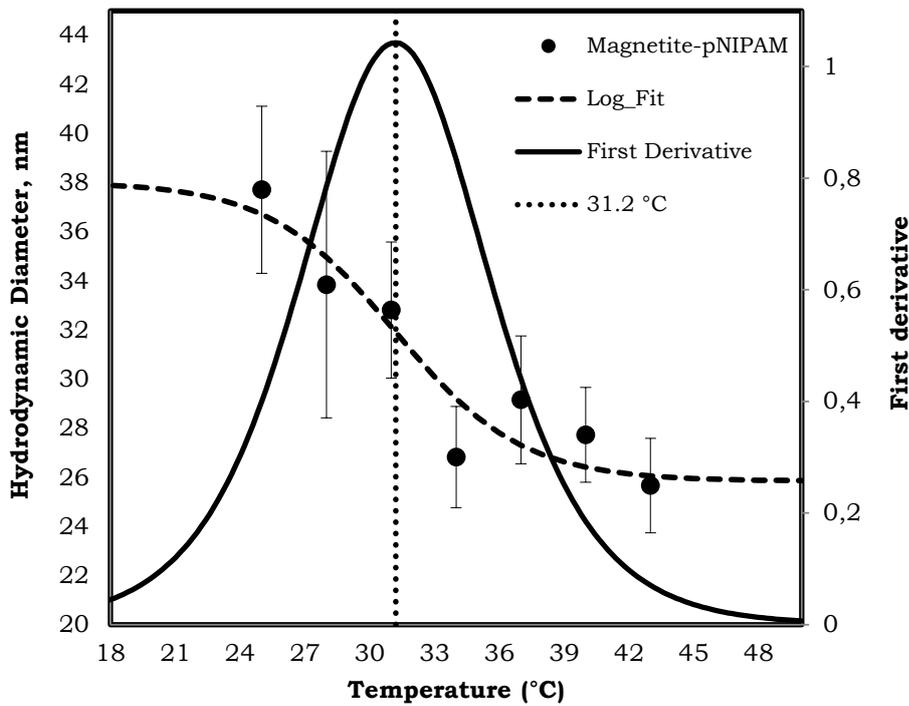


Figure 2. Hydrodynamic diameter of nanohydrogels in distilled water (1.5 % w/v) vs. Temperature.

The nanohydrogels hydrodynamic diameter behavior regarding temperature is presented in Figure 2. The figure shows a transition temperature around 31.2°C which corresponding to LCST of pNIPAM ( $T \approx 32^\circ\text{C}$ ). The change of hydrodynamic diameter evidence the hydrophilicity and hydrophobicity that experiment the pNIPAM chains when are below and above of this transition temperature.

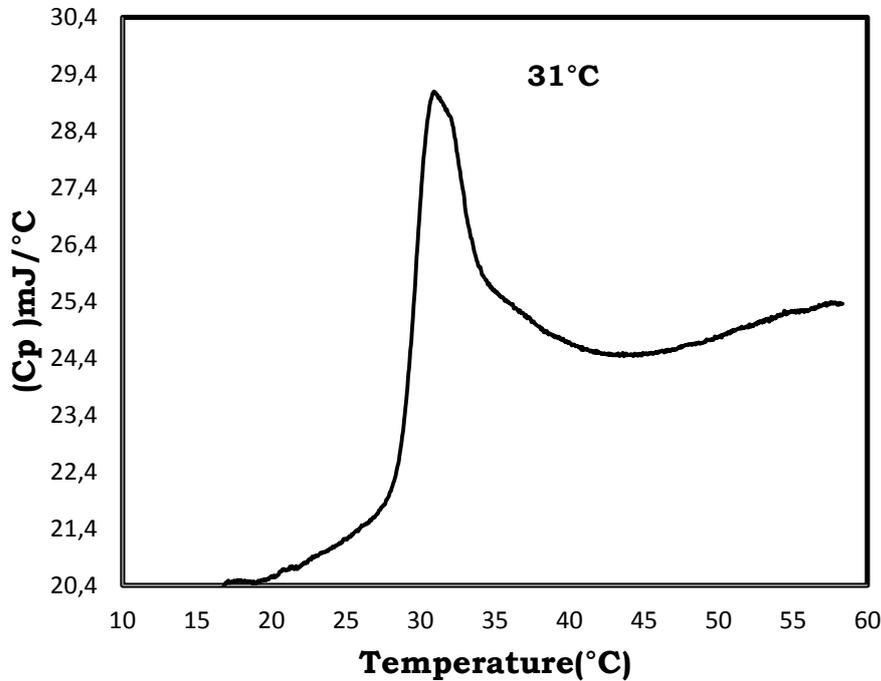


Figure 3. Specific Heat Capacity ( $C_p$ ) of the nanohydrogels.

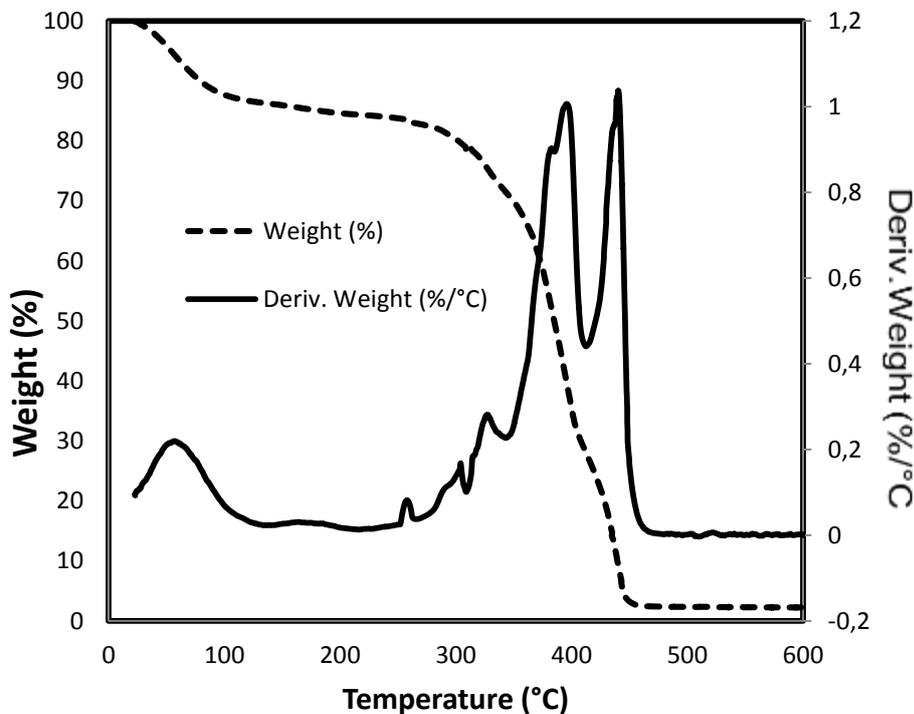


Figure 4. Thermogravimetric Analysis of nanohydrogels.

The thermal response of nanohydrogels in solution is illustrated in Figure 3 and 4. The dissociation of the thermosensitive polymer chains in an endothermic process, so that a transition temperature of about 31 °C was evident in the sample. These results agree with those obtained from the study of size change with temperature, where a transition temperature of the sample was obtained at 31°C too. (See Figure 3). Finally in Figure 4 is evidenced a weight loss below 200°C due to loss of water present in the sample. In the range of 200°C to 300°C has not observed anything change in weight. A weight loss is observed between 300° to 450°C which is attributed to the degradation of the polymer chain<sup>15</sup>.

Nanohydrogels thermosensitive behavior was demonstrated by the transition temperature around 31 °C obtained by the calorimetric study and the hydrodynamic size change of nanohydrogels. This nanohydrogels property is attractive for manufacturing of active packages in food industry applications since they can potentiate controlled release system of bioactive components in response to an increase in temperature. At the same time, reduced size and biocompatibility of these materials allow an increase in the surface/volume ratio, increasing reactivity and improving mechanical, electrical and optical properties<sup>7</sup> and having a low immune response in the human body<sup>8</sup> respectively.

## Conclusion

Thermosensitive nanohydrogels are a very advantageous alternative for manufacturing of active food packaging. These materials potentiate process of controlled release of additives and preservatives in foods when they are exposed to external stimuli such as temperature increase. At the same time, these materials can be incorporated into polymer matrices used as food packaging systems contributing to their mechanical, barrier properties and antimicrobial activity.

## References

1. Marsh K and Bugusu B. Food packaging - Roles, materials, and environmental issues: Scientific status summary. *Journal of Food Science.*,2017, 72(3); 39-55.
2. Vermeiren L, Devlieghere F, Van Beest M, De Kruijf N, and Debevere J. Developments in the active packaging of foods. *Trends in Food Science and Technology.*, 1999 10(3); 77–86.
3. Fuciños C, Fuciños P, Pastrana LM and Rua M.L. Functional Characterization of Poly (N-isopropylacrylamide) Nanohydrogels for the Controlled Release of Food Preservatives, *Food Bioprocess Technol.*, 2014 7(12);3429–3441.
4. Fuciños C, Fuciños P, Fajardo P, Amado IR, Pastrana LM and RúaM.L (2015) Evaluation of Antimicrobial Effectiveness of Pimaricin-Loaded ThermosensitiveNanohydrogels in Grape Juice, *Food Bioprocess Technol.*, 2015, 8(7); 1583–1592.
5. Gandhi A, Paul A, Sen, SO y Sen KK. Studies on thermoresponsive polymers: Phase behavior, drug delivery and biomedical applications, *Asian Journal of pharmaceutical Sciences.*, 2015, 10 (2); 99-107
6. Kumara A, Srivastava A, Galaev IY, Mattiasson B. Smart polymers: physical forms and bioengineering applications, *ProgPolym Sci.*,2007 32(10); 1205–1237.
7. Neethirajan S, and Jayas DS. Nanotechnology for the food and bioprocessing industries, *Food and Bioprocess Technology.*, 2011, 4(1); 39–47.
8. Weiss J, Takhistov P, and McClements DJ. Functional materials in food nanotechnology, *Journal of Food Science.*, 2006, 71(9); 107-116
9. Rešček A, Ščetar M, Hrnjak-Murgić Z, Dimitrov N, andGalić K. Polyethylene/Polycaprolactone Nanocomposite Films for Food Packaging Modified with Magnetite and Casein: Oxygen Barrier, Mechanical, and Thermal Properties, *Polymer-Plastics Technology and Engineering.*, 2016, 55 (14); 1450-1459.
10. Polo-Corrales L, Feria-Díaz JJ, Hernández-Ramos EJ. Recent advances in the fabrication of Chitosan-based films for food packaging applications. *International Journal of ChemTech Research.*, 2016, 9(11); 466-483.
11. Park K, Hwang Y, Park J, Noh H, Kim J, Hwang N, andHyeon T. Ultra large-scale synthesis of monodispersenanocrystals, *Nature Materials.*, 2004 3 (12); 891-895.
12. De Palma R, Peeters S, Van Bael M, Van den Run H, Bonroy K, Laureyn W, Mullens J, Borghs G, and Maes G.Silane ligand exchange to make hydrophobic superparamagnetic nanoparticles water-dispersible”, *Chemistry of Materials.*, 2007, 19 (7); 1821–1831.

13. Herrera AP, Rodriguez M, Torres-Lugo M, and Rinaldi C. Multifunctional magnetite nanoparticles coated with fluorescent thermo-responsive polymeric shells, *Journal of Materials Chemistry.*, 2008 18(8); 855-858.
14. Lin-Vien D, Colthup N, Fateley W, Graselli J. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, San Diego, 1991.
15. Shekhar S, Mukherjee M and Akhil Kumar Sen. Studies on thermal and swelling properties of Poly (NIPAM-co-2-HEA) based hydrogels, *Advances in Materials Research.*, 2012, 1 (4);269-284.

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