NATAMYCIN-LOADED POLY(N-ISOPROPYLACRYLAMIDE) NANOHYDROGELS FOR SMART EDIBLE PACKAGING: DEVELOPMENT AND CHARACTERIZATION

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The development of new formulations for antimicrobial agents release has attracted great attention due to the possibility of using such formulations in several applications (e.g. food packaging and surface treatments in biomedical devices). Smart packaging appears in the last years as one of the most promissory application to food packaging in order to enhance the capacity to maintain food quality and safety. Moreover, edible packaging, using edible and biodegradable biopolymers, has been stated as one of the promises in packaging science (e.g. fresh-cut products, cheese, fruits, fish). Based on this and in the fact that no work has been reported with the incorporation of smart nanohydrogels in edible packaging, a smart delivery device consisting in poly(N-isopropylacrylamide) nanohydrogels and polysaccharide-based films was developed. Polysaccharide-based films with and without the incorporation of natamycin-loaded poly(N-isopropylacrylamide) nanohydrogels were charactherized in terms of: transport (water vapour, oxygen and carbon dioxide permeabilities) and mechanical properties (tensile strength and elongation-at-break), opacity, water sensitivity (moisture content and contact angle) and thermal properties (differential scanning calorimetry - DSC and thermogravimetric analyses - TGA). Chemical interactions were studied by means of Fourier Transform Infrared Spectroscopy (FTIR) and scanning electron microscopy was used to verify the presence of nanohydrogel in the film matrix.

Results showed that natamycin-loaded poly(N-isopropylacrylamide) nanohydrogels can be successfully added to edible films as confirmed by the SEM images, with the presence of nanohydrogels in film surface. The incorporation of PNIPA nanohydrogels can be done without changing the main properties of the films, however some of the physical properties of the edible films are diminished with the presence of nanohydrogels. Tensile strength values decrease ($p<0.01$) from 24.44 to 16.63 MPa, while elongation-at-break values decrease ($p<0.01$) from 15.58 to 11.91%. With the incorporation of nanohydrogels films became more opaque from 8.34 to 11.08% and showed to be more sensitive to water (i.e. higher values of moisture content and decrease of contact angle) (Table 1). From thermal analyses it can be seen that all the melting temperature values are close for all the samples, around 150 ºC, however the presence of natamycin-loaded PNIPA nanohydrogel (GA-PNIPA) lead to the increase of enthalphy of melting explained by the increase of the crystallinity of the films [1]. Thermogravimetric analyses showed similar behaviours for all samples, with the presence of four thermal events, attributed to water evaporation (from 65 to 70 ºC), chemisorbed water through hydrogen bonds (from 215 to 225 °C), dehydration, depolymerization and pyrolytic decomposition of the polysaccharide backbone (from 260 to 270 ºC) and the last thermal event related with the decomposition of the samples.

Overall, results show that the presence of natamycin-loaded PNIPA nanohydrogels led to an increase of water affinity of edible films that can be related with the capacity to bond water of the PNIPA due the presence of high numbers of hydroxyl groups at the surface of the film. In fact, the hydrophilic/hydrophobic balance of PNIPA structure is known and the hydrogen bonds formed between water molecules and hydrophilic groups possibly form a stable shell around the hydrophobic groups [2]. In conclusion, it can be stated that natamycin-loaded poly(N-isopropylacrylamide) nanohydrogels can be successfully added to polysaccharide based films and can be used as smart packaging for food applications.

Table 1. Values of moisture content, contact angle, water vapour, oxygen and carbon dioxide permeabilities (WVP, O_2P and CO_2P, respectively) of the films without (GA) and with natamycin-loaded PNIPA nanohydrogels

Film samples	**Moisture content (%)**	**Contact angle (θ)**	**WVP × 10^{-11} (g (m s Pa)$^{-1}$)**	**O_2P × 10^{-13} (g (m s Pa)$^{-1}$)**	**CO_2P × 10^{-13} (g (m s Pa)$^{-1}$)**
GA	17.72±0.07^{a}	112.36±6.40^{a}	5.940.82^{a}	5.84±0.87^{a}	1.970.48^{ab}
GA-PNIPA	19.16±0.27^{b}	74.48±2.09^{b}	6.480.91^{ab}	6.98±2.29^{ab}	1.820.18^{b}

Values reported are the means ± standard deviations. $^{a-b}$Different letters in the same column indicate a statistically significant difference ($p<0.01$).

References

1. Cerqueira, M.A., et al., *Food Hydrocolloids,* 27, 175-184, 2012
2. Fuciños, C., et al., *Journal of Food Science*, 77 (7), N21-8, 2012