Abstract

Nowadays, the development of plant-based systems to replace or reduce the utilization of synthetic materials has been receiving significant attention, in view to fulfil consumers demand natural products in all the industrial areas.

Hydrogels represent a group of polymeric materials, composed of three-dimensional crosslinked polymeric networks, capable to absorb and retain a significant amount of water. They have been listed as “smart structures” whose tailor-made design confers them different functional attributes allowing their use in biomedical, cosmeceutical, pharmaceutical and food applications. Hydrogels can be produced either from natural or synthetic sources. However, those produced from natural sources have gained a great interest in research for the development of novel biomaterials for which a wide range of applications could be envisaged due to their safety, biocompatibility, and biodegradability. In the last decade, among the natural sources to produce hydrogels, starches have been receiving increasing attention as one of the most promising natural biopolymers. Hydrogels are traditionally produced by chemical or physical methods. However, long processing time, high energy consumption, and safety issues related to the synthesis of these products have been identified as important limitations of these methods.

Therefore, to overcome these drawbacks, in this work has been proposed the utilization of high pressure processing (HPP), which has been shown as a promising and suitable technology to obtain the gelatinization of starch suspended in aqueous media in less harsh processing conditions than in conventional methods. HPP treatments consist of subjecting products packaged in flexible containers to a high level of isostatic pressures (100-1000 MPa) in a short period of time (minutes). HPP has been established as a commercially viable food preservation method allowing minimal sensory and nutritional damages of processed products. It is well known that HHP causes the disordering of biopolymers, including proteins and starches, due to the modifications of non-covalent intermolecular interactions such as those inducing pressure-assisted gelatinization. Although the use of HPP has shown evidence in inducing pressure-assisted gelation, there was still a strong need to increase the knowledge on the topic not only to better understand the fundamentals of the gelation process but also to highlight the main factors affecting the production of starch-based hydrogels by high pressure. Moreover, the structural and mechanical properties of the starch-based hydrogels obtained by HPP as well as their performance should be deeply investigated in view of their future exploitation.

The aim of this PhD thesis work was to propose a complete study of the utilization of HPP technology to produce starch-based hydrogels under optimized processing conditions.

To this purpose, different native starches (rice, corn, wheat, potato, and tapioca), which are the most produced and traded natural biopolymers, have been selected as raw materials. The starches have been completely characterized in terms of physical properties, such as particle size distribution, and chemical composition. Hydrogels were produced under pressure and the effects of type of starch, formulation and processing conditions on physical-chemical characteristics were investigated. Among the properties of high pressure starch-based hydrogels, the mechanical and structural characteristics, the stability at different storage conditions, and the in vitro digestibility have been determined, also when bioactive compounds were added to the gelling solution.

All the experiments were carried out in lab-scale HPP units (U111 and U22, Unipress, Poland) and several analytical methods have been used to investigate the properties of the hydrogels, namely

proximate analysis (AOAC guidelines), laser scattering, light microscopy, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), controlled stress and strain rheometer, texturometer, colourimeter, microbiological counts techniques, water activity meter, among others.

The results obtained highlighted the potential use of HPP to produce stable starch-based hydrogels in processing conditions less severe than those utilized in conventional methods. Starch-based HPP hydrogels displayed remarkable mechanical and structural properties even superior to those produced by thermal treatments. Moreover, it was identified different energy requirements of the starches to produce starch-based hydrogels under high-pressure conditions. HPP hydrogels based on corn, rice, wheat and tapioca starch were obtained at 600 MPa for >5 min, while stable potato starch hydrogels were obtained only utilizing the mass fraction with granule size lower than <25 µm and the synergistic effects of pressure and heat treatments at moderate temperature, namely pressure at 600 MPa for 15 min temperature at 50 °C. Rice, wheat and corn HHP-hydrogels showed a cream-like structure while those based on tapioca and potato starch were more compact. With increasing HPP processing time up to 15 min, more stiff tapioca and rice HHP-hydrogels were produced showing higher viscosity, G' values and firmness with respect to those obtained by applying the pressure for reduced residence time. Moreover, a marked influence of starches PSD has been detected. Utilizing starches with small granules size facilitates swelling and gelatinization processes under pressure due to the small particles are more exposed to the action of pressure than bigger particles, but also, being the number of particles per unit volume increased the starch-starch and starch-water interactions are favoured.

Physical and microbiological stability evaluations have shown that a storage temperature of 20 °C granted the best storage condition for all the starch-based HPP hydrogels allowing to reduce evaporation and keep the TPA profiles of products during storage time. The stability analysis allowed also predicting a very good performance of all starch-based hydrogels produced, which are displaying a strength of the network even superior to commercial hydrogels and temperature sensitiveness only at temperatures higher than 40 °C.

In vitro digestion tests demonstrated different behaviours of rice and tapioca hydrogels. Mastication phase was the critical step for rice hydrogels digestion, while the intestinal phases were the critical step for tapioca hydrogels digestion.

The addition of humectants and bioactive compounds influenced the structural and mechanical properties of starch-based hydrogels as well as the occurrence and extent of gelation by high pressure. However, the optimization of processing conditions to produce stable starch-based HHP hydrogels allowed us to demonstrate that stable hydrogels with rheological and structural properties can be produced also in this case.

In conclusions, the approach of this work, which was considering the analysis of the effects of product and process parameters as a fundamental step to understand the gelation phenomenon, has been demonstrated to be sound. The determination of optimal product formulation, preparation and characterization of the hydrogels obtained with different starches represented a clear advancement of the knowledge on the production of starch-based hydrogels by high pressure processing (HPP) technology. However, further research efforts are needed at a fundamental level to unveil the thermodynamic of the gelation phenomenon under pressure, as well as at processing level analyzing how the utilization of more complex formulation affect the preparation of stable starch-based hydrogels by high pressure processing (HPP). Finally, it will be also necessary to scale-up the process in view of the industrial exploitation of the results.