Natural Deep Eutectic Solvents as plasticizers and mechanical properties modifiers of edible films from dairy by-products

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The development of new bio-based plastics is of growing priority mainly due to health and environmental concerns derived by the petroleum-based plastics. The food industry is one of the main industries that use large amounts of plastics for packaging thus the renewable and sustainable alternatives in packaging and coating materials is of great interest. Among several types of natural polymers, protein-based films have emerged as potential bio-basted plastics (Hadidi *et al.*, *2022*, Chiralt *et al.*, 2018). The efficient production of bio-based food packaging or coating requires abundant in nature materials thus, the interest is turning into the use of industrial by-products, considering them as valuable resources for the development on novel materials rather than wastes (Wagh *et al*., 2013).

Regarding the dairy industry, the cheese whey consists an important by-product as it occurs in large amounts during the production of dairy products. As it retains many of the nutrients of milk, cheese whey has a high content of organic material, which makes its direct disposal into the environment, prohibitive (Gupta *et al.*, 2017). However, its composition offers the prospect of being treated as a raw material instead of just a waste.

In this context, the aim of this study is the development of bio-based films from casein, whey protein isolate (as the main proteins in milk) as well as cheese whey (as one of the mail by-products of the dairy industry) suitable for food coating and/or packaging applications (such as for cheese, vegetables etc). Since the cohesive energy density of proteins is strong, the protein films are considered to be brittle with poor mechanical properties regarding their end-use application (Hongbo *et al.*, 2019). For this reason, biocompatible and task-specifically designed green solvents such as the natural deep eutectic solvents (NADES) are recently used as plasticizers in order to improve the elasticity and reduce the fragility (Pontillo *et al.*, 2021).

In this work, six NADES were synthesized out of natural and low-cost starting materials such as L-proline, betaine, choline chloride, sodium acetate, glycerol and water. All the NADES were structurally characterized using NMR and FTIR spectroscopy while some of their most important properties, such as their pH and polarity, were also determined.

The protein films were formed using the casting methodology using the NADES in various concentrations as plasticizers. The films were characterized using FT-IR spectroscopy and TGA analysis and their weight, thickness, elasticity, bristliness and water vapor permeability were also evaluated. For comparison purposes, protein films were also formed (a) using glycerol as a well-known plasticizer as well as (b) without the addition of any plasticizer.

According to the founding of this study, the film properties were influenced by the type of the used biopolymer (casein and whey protein isolate), the type and concentration of the used plasticizer. The properties of the NADES-derived films, were improved comparing to the films derived (a) using the conventional plasticizer or (b) without using any plasticizer (Figure 1). Among the studied NADES, the most efficient plasticizers were those derived from glycerol in combination with betaine as well as in combination with L-proline.

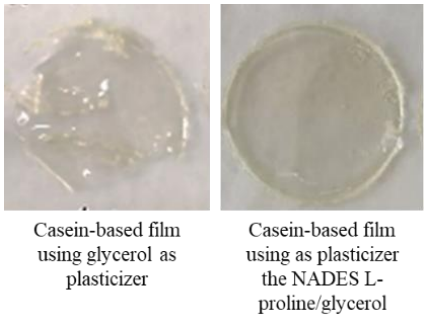

Figure 1. Casein-based films using as plasticizers (left) glycerol and (right) the NADES L-proline/glycerol.

Furthermore, in order to study the development of an active coating system, the selected as optimum NADES in respect of the film forming process, was used as an extraction solvent for the extraction of

bioactive compounds from Greek chamomile, and then the added-value NADES-extract was effectively used for the formation of a protein film with desirable properties.

Overall, in this work, the utilization of dairy by-products in combination with the use of task-specifically designed NADES for the formation of edible bio-based plastics promotes the sustainability using the green chemistry principles and fulfils the demands of circular economy.

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