Protein-based bio-plastics: formulation, processing, properties and applications

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Introduction

Recently, research on protein based bioplastics have boomed as a result of the fresh interest in renewable and biodegradable raw materials [1,2,3].

Many industrial sources of proteins can be used as raw materials to produce films, molded materials, and various hollow items either by "casting" techniques or by "thermoplastic processing". Plant proteins are generally inexpensive, widely available and relatively easy to process. Animal proteins are more expensive, but sometimes have no functional substitutes. Combining proteins with natural fibbers, paper or biodegradable polyesters is very promising to form biodegradable composites witch take advantage of the barrier and mechanical properties of each component. Using nano-fillers to form nanocomposites has also been shown to be interesting to improve properties. Production, with low transformation cost, of protein based materials to form biodegradable materials with controlled functional properties for food uses, medical uses, packaging, agriculture, controlled release systems, etc. is discussed.

Formulation, processing and related properties

The heterogeneous structure of proteins provides many reaction sites for potential cross-linking or chemical grafting. It facilitates modification of the material-forming properties and end-product properties. protein based materials cross-linked via heat treatments, or radiation treatments (UV, gamma, etc.) form insoluble and infusible networks, characterized by elastomeric or thermosetting thermo-mechanical behavior according to the covalent cross-linking density. It is important to notice that physically induced treatments has similar effects on protein structuration (cross linking degree) than chemically induces ones (*e.g.* thermal cross linking of wheat gluten matrix can be as important as formaldehyde one). In addition the activation energy of thermally induced cross linking is strongly reduced when mechanical energy is applied [4].

The mechanical mixing/shearing strengthens the effect of the temperature by provoking the split of intermolecular disulfur bonds but also peptidic ones and by favoring the mechanisms of free radical and thiol / disulfur exchanges [5,6].

Formulation of blends, composites and nano-composites have given good test results and could be used to modulate protein based materials mechanical and transport properties.

The functional properties (especially optical, barrier and mechanical) of these protein-based materials are often specific and unique, and they could thus be used as raw materials for bioplastics with a wide range of agricultural, agrifood, pharmaceutical and medical industry applications.

Protein-based materials have slightly lower mechanical properties than reference materials such as low-density polyethylene or plasticized PVC [7], but the addition of fibers (composite materials) can considerably improve them. The thermoplastic properties of proteins and their water resistance (for insoluble proteins) are especially interesting for natural resin uses to produce particleboard type materials. [8]

The water permeability of protein-based films is very high (water permeability around 5 10-12 mol.m-1.s-1.Pa-1) but affected by crosslinking density and material formulation. This high moisture permeability is especially attractive for cheese, fruit and vegetable packaging, and for agricultural material and cosmetic applications. The gas barrier (O2, CO2 and ethylene) properties of protein based materials are highly interesting as they are exceptionally low under low relative humidity conditions. O2 permeability (around 1 amol.m-1.s-1.Pa-1) properties are close to those of EVOH (0.2 amol.m-1.s-1.Pa-1) and much lower than those of low density polyethylene (1000 amol.m-1.s-1.Pa-1). The gas barrier properties are closely dependent on the material structure, relative humidity and temperature. The CO2/O2 selectivity coefficient, which can rise from 3 to more than 50 when the relative humidity increases from 0 to 100% and the temperature rises from 5 to 45°C. This property can be utilized in designing selective or active materials for modified atmosphere packaging of fresh products such as fruit, vegetables, cheese, etc. [9].

Solute retention properties (especially antimicrobial and antioxidant agents) have been studied and modeled, thus paving the way for potential applications involving controlled release of beneficial agents (phyto-chemicals, bioactive compounds, …) for food, agriculture (e.g. coated seed), pharmacy (drug delivery) and cosmetic industries [10].

Environmental performance and applications

The environmental performance of wheat gluten materials was conducted following the life cycle analysis methods of the ISO 14040 family [11]. The results were very positive (energy use=10 MJ/ kg and emission of green house gasses=0.72 kg CO2-eq/ kg). Both values are very low compared to starch or PLA based biodegradable polymers. This without any chemical additives. Mechanical properties can then be adjusted from thermoplastic material with high elongation at break up to elastomeric like material. Barrier properties can also be designed for the controlled release of entrapped solutes (phyto-chemicals, bioactive compounds, …). Whatever the physical treatment severity performed (and the important consecutive change in the protein network structure) gluten materials were fully degradable (after ISO 14852) within 36 days and no microbial inhibition due to toxic metabolites during the mineralization process was observed. In vitro enzymatic digestion tests confirmed that a decrease of the protein network hydrolysis rate became significant only at very high gluten crosslinking degrees [12].

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