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Review

Processing and shelf life issues of selected food packaging materials and structures from renewable resources

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Use of polymers from renewable sources for food packaging applications is steadily growing. However, as compared to thermoplastic synthetic polymers, they present problems when processed with traditional technologies and show inferior performances in terms of functional and structural properties. This review paper focuses, in its first part, on current issues related to processing, such as thermoplasticization of starch and proteins, extrusion of films and foams. In the second part, the strategies for the technological advancements aimed to improve barrier properties, to promote active antimicrobial functionality and to apply these materials also in demanding high pressure processing of packaged foodstuff are discussed.

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Introduction

Polymeric materials derived from renewable resources can be biodegradable or compostable under specific environmental conditions. They are classified according to the method of production or their source:

- Polymers directly extracted or removed from biomass such as polysaccharides and proteins.
- Polymers produced by classical chemical synthesis starting from renewable bio-based monomers such as polylactic acid (PLA).
- Polymers produced by micro-organisms or genetically modified bacteria such as polyhydroxyalkanoates, bacterial cellulose, xanthan, pullulan.

In order to tailor physico-chemical properties of plastics obtained from renewable resources to meet specific processing requirements, functional and structural demands, several types of chemicals and additives, such as stabilizers, antioxidant, plasticizers, fillers and processing aids, are added to the polymeric macromolecules. Moreover, with the aim to expand the range of applications of these products, blends, composites and laminates have been developed by combining polymers obtained from renewable sources with other synthetic polymers.

The potentials and challenges of using biodegradable polymers from renewable resources, that we will from now on call biopolymers for the sake of simplicity, in large scale food packaging applications, have been discussed in previous reviews (Mahalik & Nambiar, 2010; Siracusa, Rocculi, Romani, & Dalla Rosa, 2008). In this paper we will focus on some critical aspects related to the use of extrusion technologies to produce films and foams from selected materials based on proteins, starches and PLA. Moreover, we have looked in the state of the art in the area of the possible strategies employed to improve the shelf life of food packaged by using such biopolymers.

Starch is the most important polysaccharide, it is the most abundant in nature and relatively inexpensive. Natural starch exists in granular form and, as such, it has been used as a filler in polymers, but it can also be processed with classical plastic processing technologies such as extrusion, foaming and film blowing after thermoplasticization, as it will be described in the following. The main limitation for starch is its hydrophilic nature, which limits its use in high moisture environments (Brouillet-Fourmann, Carrot, Lacabanne, Mignard, & Samouillan, 2002).

Several protein sources have been proposed for the preparation of new thermoplastics (Cuq, Gontard, & Guilbert, 1998). In particular, cereal proteins could be available in large amounts as by-products arising from agricultural and biofuel processing activities such as ethanol production. These protein-rich products include spent grain from the brewing and distilling industries, cereal bran streams from milling and protein residues from starch extraction activities. Protein-based films can act as barriers to oxygen, carbon dioxide, oil and fats, while mechanical and water vapour barriers properties of films produced from these materials are typically inferior to those of synthetic origin (Krochta, 1994). One of the film-forming proteins which has been the object of extensive research activity as well as of industrial interest is zein, the prolamine of corn, mainly for its unique hydrophobicity, which is due to its high content of non-polar amino acids, (Augustine & Baianu, 1987; Reiners, 1973). Zein is a substantially better moisture barrier than any other proteins like casein, or polysaccharides such as starch (Lia & Padua, 1999).

Polylactic acid (PLA) is a highly versatile biodegradable polymer whose properties, such as degree of crystallinity, melting temperature and glass transition temperature can be tailored by controlling the monomer composition of the two optical isomeric forms, L and D. In this way, different resin grades and, in turn, a wide spectrum of products can be obtained. The structural, thermal, crystallization and rheological properties of PLA have been recently reviewed in relation to its processing properties. Specific process technologies such as extrusion, injection molding, injection stretch blow molding, casting, blown film thermoforming, foaming, blending, fiber spinning and compounding have been discussed by Lim, Auras, and Rubino (2008). Nevertheless, there are also a number of functional properties that need to be improved, especially in applications where PLA is intended to be used as a substitute for existing thermoplastics. With specific reference to packaging applications, for example, PLA shows much lower barrier properties than polyethylene terephthalate and it is difficult to heat seal. Some of these challenges are expected to be addressable by blending PLA with other polymers, by using micro and nanocomposites, by coating it with high barrier materials and by polymer modification.

The present paper is structured in two parts. In the first we discuss the main issues associated to the processing of macromolecules directly extracted from biomass such as starch and proteins. In the second, are discussed open scientific questions related to strategies to prolong the shelf life of packaged foodstuff by using starch, proteins and PLA-based films. In particular, the improvement of their barrier properties, the development of active antimicrobial systems and the potential use in high pressure Pasteurization/sterilization treatments are analysed, with specific reference to some of the results obtained within the EU project NovelQ (Integrated Project NovelQ; contract grant number: FP6-CT-2006-015710).

Processing issues

The class of materials described above finds nowadays use only in niche segments of the market or is still at a stage of potential interest in packaging applications. In fact, the packaging field is still dominated by plastics derived from petrochemical sources, such as polystyrene, polypropylene, polyethylene and polyethylene terephthalate, which are produced in large production plants, and, as such, are relatively inexpensive due to economy of scale and relatively low unit processing costs. Conversely, biopolymers have not yet found wide use in food packaging, the main reasons for that being high cost, low performance and difficult processing (Petersen *et al*., 1999). In this section, this latter issue will be analysed by describing the challenges and hurdles for utilizing conventional, high-productivity technologies to process starch and proteins based packaging systems in the form of films and foams.

Processing problems are particularly relevant for biopolymers directly extracted from biomass such as cellulose, polysaccharides and proteins, mainly due to reduced plastic-flow properties of these polymers and the intrinsically difficult reproducibility and control over the molecular architecture and spatial conformation of the natural macromolecule. Conversely, synthesis of polymers from fermentation or bioproduction has now reached good standards to allow for reproducible processing. We will then focus, in the following, on the issues related to processing of protein and polysaccharides, analyzing the most recent developments in films and foams processing technologies.

Thermoplasticization of proteins and starches, access route to large scale processing

Thermoplastic synthetic polymers can be melt-processed by simply applying heat and shear; unfortunately, the high crystallinity and the strong intermolecular interactions present in the proteins and polysaccharides lead to thermal degradation of the material before achieving melt flow. The flow of these natural occurring macromolecules is however possible if a thermoplasticization process, based on a combination of heat, mechanical shear and suitable plasticizers occurs. The plasticizer is needed as it acts as an internal lubricant, leading to an increase of molecular mobility, necessary to promote the melt flow; before the occurrence of degradation phenomena. In this way, several products can be formed by using traditional shaping methods, such as extrusion, compression molding, thermoforming, calendering, injection molding and film blowing (Ha & Padua, 2001; Wang, Filo, Geil, & Padua, 2005). The thermoplasticization process involves several complex phenomena, which promote the intimate contact of the plasticizer with the protein macromolecules and, eventually, with the help of shear stresses, the denaturation of the hierarchical structure thus favoring the development of molecular entanglements. Process variables and formulations that enhance the spreading of the plasticizer and the shear stresses induce an improvement in terms of achieved final properties of the

thermoplasticized material and a shortening of the whole thermoplasticization process. Thermoplastic starches (TPS) have been widely studied and successfully applied at an industrial level as blends with other synthetic polymers to reduce the final cost of the product or to improve its biodegradability. Only recently, thermoplasticization of proteins has been investigated. These include zein (Di Maio, Mali & Iannace, in press; Oliviero, Di Maio, & Iannace, 2010; Selling, 2007; Wang & Padua, 2003), gelatin (Salerno, Oliviero, Di Maio, & Iannace, 2007) and gluten (Pommet, Redl, Guilbert, & Morel, 2005).

Film blowing of proteins and starches

Very few reports have been published on the application of extrusion technology for the production of proteins based films. Wang and Padua (2003) produced zein sheets plasticized with fatty acids by extruding a moldable, dough-like resin prepared by precipitating zein and oleic acid from aqueous-alcohol solutions, to finally prepare films by extrusion through a blowing head. Oliviero *et al.* (2010) studied the feasibility of preparing thermoplastic films of zein by film blowing without the time consuming and expensive solubilization step. The zein powder was plasticized directly in the extruder, without the use of solvent and of a premixing phase. However, as evidenced by the authors, the most important problem in the use of biopolymers is the difficulty in having "standard" raw materials. In fact, it is known that the molecular structure of natural polymers strongly depends on several factors such as sources and extraction technique and conditions. By comparing thermal and structural features of the films produced from different batches, authors correlated molecular structure, rheological behaviour in uniaxial elongation to film blowing properties, evidencing a rather important effect of the molecular structure on the elongational viscosity and, in turn, on filmability. Blown films from zein/polyethylenglycol (PEG) 400 mixtures were produced and sufficiently low thickness (80 μm) was achieved.

The preparation of films based on thermoplastic starches (TPS) by using the film blowing technique is also challenging, when thicknesses adequate for packaging applications are required. In effect, most of the studies on film blowing have been conducted on blends of thermoplastic starch with other biodegradable or not biodegradable polymers (Matzinos, Tserki, Kontoyiannis, & Panayiotou, 2002), with TPS usually being the minor component. In recent works, conversely, film blowing process of TPS were conducted on potato starch with different amylose content and modified potato starches (Altskär *et al.*, 2008; Thunwall, Kuthanová, Boldizar, & Rigdahl, 2008). More recently, Zullo and Iannace (2009) investigated different varieties of starch in order to study the suitability of these materials to be processed in a film blowing line. Again, the increase of the melt deformability and the elongational properties of the melt were assessed to be crucial in the film blowing process.

Foaming technology of proteins and starches

Foaming of natural polymers has been mostly studied in the context of food engineering, in the preparation of bread and cooked snacks (Glenn, Orts, & Nobes, 2001; Shogren, Lawton, & Tiefenbacher, 2002), other examples include ice creams, puff-dried fruits and vegetables, egg white and beer (Goof, Verespej, & Smith, 1999; Hagolle, Relkin, Popineau, & Bertrand, 2000). The technologies employed in these cases are different from the gas foaming technology typically used for thermoplastic polymers. Classical polymer science approach aimed at improving material properties, such as matrix rheology, matrix density, interfacial and strain hardening properties, has been successfully applied to optimize food final sensation and texture (de Cindio, Gabriele, Pollini, Peressini, & Sensidoni, 2002a; de Cindio, Gabriele, Pollini, Peressini, & Sensidoni, 2002b; Thièband, Dumay & Cheftel, 1996). Recently, plastic processing technologies such as steam-based extrusion have been used to produce foams with different materials including starch for different applications such as packaging and insulation (Willet & Shogren, 2002). Gas foaming technology to produce foams from thermoplasticized proteins has only recently been reported in the scientific literature by Salerno *et al.* (2007). They batch-foamed both zein and gelatin proteins by using nitrogen and carbon dioxide as blowing agents. In particular, the effects of blowing agent composition, foaming temperature, pressure drop rate and type of blowing agent on the mean cell dimension and final density of the resulting thermoplastic zein and gelatin foams were investigated. Foams with density as low as 0.1 g/cm^3 and mean cell diameter of 10 μm were successfully obtained.

Strategies for shelf life improvement

Improvement of barrier properties

The features that packaging materials should display as far as mass transport properties are concerned, include the control of food products respiration, the supply of a selective barrier to gases and water vapour, the capability of maintaining, as long as possible, a modified atmosphere in the package headspace, the reduction of the migration of lipids, the possible release of food additives such as flavour, colours, antioxidants and antimicrobial agents (Tharanathan, 2003). As a matter of fact, in general, biopolymers display performance problems under this respect in comparison with synthetic polymers, which are even more pronounced in the case of polymers directly extracted from natural materials (Petersen *et al.*, 1999). In fact the barrier properties of these materials, mainly with reference to moisture barrier properties, are inferior to existing packaging materials. Moreover, gas, vapours and aroma barrier properties are unpaired by the presence of sorbed moisture. In Figs. 1–3, O_2, CO_2 and water vapour permeabilities of petrochemical-based plastics (referred to as *common polymeric packaging materials*) are compared to those of selected biopolymers, evidencing the lower performances of the latter. In this comparison we also included polycaprolactone (PCL) which, thanks to its

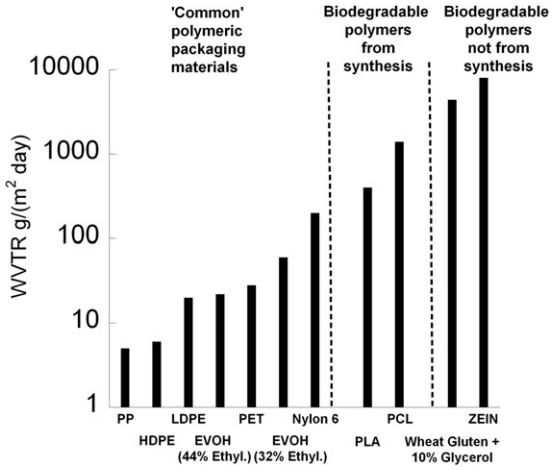

Fig. 1. Water vapour transmission rate (WVTR) for several biopolymers and synthetic polymers as evaluated for 25 μm thick films at 38 °C and 90% relative humidity. Data for nylon 6, polyethylene terephthalate (PET), polypropylene (PP), high density polyethyelene (HDPE) are taken from Comyn (1985). Data for low density polyethylene (LDPE), polylactic acid (PLA) and polycaprolactone (PCL) are taken from Sansone (2008). Data for wheat gluten additivated with 10% of glycerol (WG + 10% glycerol) are taken from Tunc *et al.* (2007) (measurements performed at 25 °C and 70% RH). Data for zein (performed at 25 °C) are taken from Ghanbarzadeh *et al.* (2007).

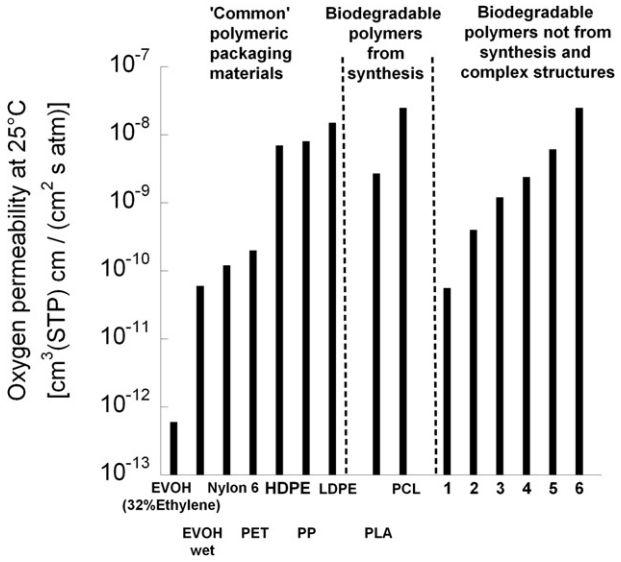

Fig. 2. Oxygen permeability for several biopolymers and synthetic polymers as evaluated at 25 °C. Data for nylon 6, polyethylene terephthalate (PET), polypropylene (PP), high density polyethyelene (HDPE) are taken from Comyn (1985). Data for low density polyethylene (LDPE), polylactic acid (PLA) and polycaprolactone (PCL) are taken from Sansone (2008). Data for film '1' (wheat gluten additivated with 30% glycerol and 3% NaOH) are taken from Ullsten *et al.* (2009). Data for film '2' (zein/polyethylenglycol (PEG) blend with 20%PEG, measurement in dry conditions), film '3' (zein/polyethylenglycol blend with 20%PEG, measurement at 53% RH), film '4' (blend 40% zein/60% PCL) and film '5' (PCL/zein-PCL blend/PCL 1:2:1 thickness ratios multilayer structure) are taken from Oliviero (2008). Data for film '6' (wheat gluten + 10% glycerol at 70% RH) are taken from Tunc *et al.* (2007).

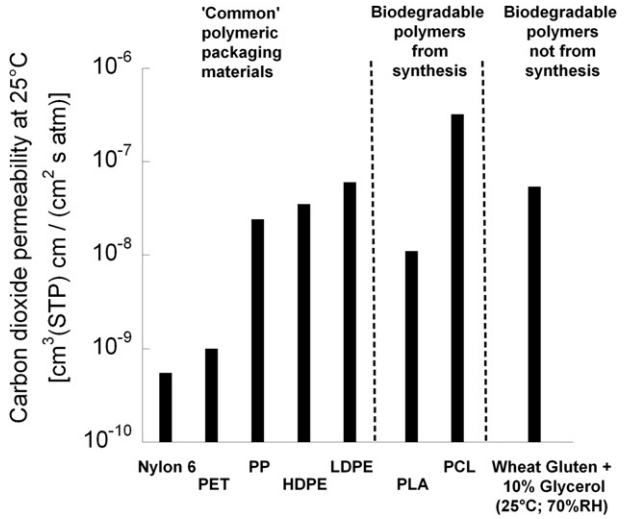

Fig. 3. Carbon dioxide permeability for several biopolymers and synthetic polymers as evaluated at 25 °C. Data for nylon 6, polyethylene terephthalate (PET), polypropylene (PP), high density polyethyelene (HDPE) are taken from Comyn (1985). Data for low density polyethylene (LDPE), polylactic acid (PLA) and polycaprolactone (PCL) are taken from Sansone (2008). Data for wheat gluten additivated with 10% of glycerol (WG + 10% glycerol) are taken from Tunc *et al.* (2007) (measurements performed at 25 °C and 70% RH).

low processing temperature, can be used in combination with polymers from renewable sources to prepare biodegradable packaging structures with reduced hydrophillicity.

To improve the barrier properties of biopolymers, several approaches are available, i.e. (Petersen *et al.*, 1999):

i) use of coating with materials which would add hydrophobicity to the packaging material,
ii) lamination of two or more biopolymers (co-extrusion),
iii) use of an edible coating with the required barrier properties for the food and subsequently use biopolymers as primary packaging,
iv) development of blends of biopolymers with different properties (Cabedo, Feijoo, Villanueva, Lagarón, & Giménez, 2006). Some examples include polylactic acid (PLA) − polyethylene glycol (PEG) blends, PLA − polyhydroalkanoates (PHA) blends and PLA − PCL blends,
v) chemical and/or physical modification of biopolymers,
vi) development of micro and nanocomposites based on biopolymers.

Co-extruded laminated films are already widely used in food packaging applications. They are mainly applied in the packaging of products such as fresh pasta, meats and cut vegetables to extend their shelf life. Commercial multilayer films currently comprise a number of layers (3–9) of different polymers derived from fossil fuels. In comparison to these commercial products, the performances that can be obtained with packaging materials based on biopolymers are still very far from the barrier performances achieved

with common polymers and, at the moment, it is certainly impossible a total replacement. A food group amenable for packaging with biopolymers are "high value" fruit and vegetables with short shelf-life: use of laminates of biopolymers is possible for the preservation of respiring products by modified atmosphere packaging (MAP) where important factors are not only the permeabilities per se, but also their ratios. Packaging structures based on biopolymers display carbon dioxide/oxygen permselectivities which are well suited for MAP applications and are unattainable with synthetic polymers. As an example, wheat gluten based films exhibit a wide range of selectivity values (between 3 and 28) (Pochat-Bohatier, Sanchez, & Gontard, 2006) as compared with the selectivity of most synthetic films which is usually between 4 and 6.

Other examples of laminates based on biopolymers are those reported by Fang *et al*. (2005). Modified starch and PLA were co-extruded with the aim of combining the PLA's mechanical strength and hydrophobic properties with the gas barrier properties of starch. Chemical modification of starch was employed in this case to improve the adhesion with the more hydrophobic layer of PLA. A different approach to enhance the adhesion between hydrophobic and hydrophilic layers in a laminated structure is to use a blend as a compatibilizing layer. For example, the use of PCL and thermoplastic zein (TPZ) blends has proved to have excellent adhesive capability in laminated PCL and TPZ packaging structures (Oliviero, 2008). These laminated structures were found to be suitable for high pressure Pasteurization treatments (Sansone, 2008).

Another typical investigative approach is the use of nanometric additives, which have been reported to dramatically change rheological properties of polymer melts and to improve functional properties such as barrier to gases and vapours, mechanical properties and thermal stability. Potentials and problems associated to the use of nanoscaled fillers to biopolymers including PLA and TPS have been recently reviewed (Bordes, Pollet, & Avérous, 2009; Lee *et al*., 2005; Sinha Ray & Bousmina, 2005; Sorrentino, Gorrasi, & Vittoria, 2007). The research and development of bio-nanocomposite materials for packaging applications is expected to grow in the next years, due to the possibility of improving both packaging performances and process technology of biopolymers. Up to now, only few research works have dealt with the preparation of nanocomposites made from layered silicates and thermoplasticized proteins. Nanocomposites from montmorillonite (MMT) and wheat gluten (Angellier-Coussy, Torres-Giner, Morel, Gontard, & Gastaldi, 2008) as well as from MMT and zein prepared by using thermo-mechanical processing have been recently investigated in the framework of the EU project NovelQ. In particular, MMT without any organic modification was mixed with the plasticizer and then added to the zein powder directly in the mixing chamber employed for the thermoplasticization process at controlled heat and shear conditions, by using the procedures described in Oliviero *et al*. (2010).

Mechanical properties of TPZ and TPZ/MMT nanocomposites are summarized in Table 1. As already shown in many polymer/clay nanocomposites, the tensile moduli of the TPZ/MMT systems were remarkably improved, especially at low concentration of clay. In most conventionally filled polymer systems, the modulus increases linearly with the filler volume fraction, whereas for these nanoparticles much lower filler concentrations increase the modulus sharply and to a much larger extent (Sinha Ray & Okamoto, 2003). These results are in agreement with the only published work, so far, on zein nanocomposite films with nanoclay (Luecha, Sozer, & Kokini, 2010). In this specific work, the development of the zein-based nanocomposites was achieved not using directly the thermoplastic processing but rather by using the solvent casting and the blown extrusion technique of a resin obtained by the precipitation of zein proteins from an aqueous ethanol solutions.

Even though nanoparticles results in materials with improved properties, further research is needed to better understand how plasticizers, biomacromolecules and nanoplatelets interact to give rise to materials with potentially improved barrier and structural properties and with extended range of applicability due to the increase of thermal stability. Moreover, the possibility of using bio-nanocomposites to achieve materials from renewable resources with longer stability during storage and usage for food packaging applications should also be investigated. As a matter of fact, plasticizer migration and/or retrogradation phenomena, usually occurring in thermoplasticized biopolymers, could be extensively reduced by using the bio-nanocomposite approach.

Antimicrobial packaging systems

Antimicrobial packaging films are developed with the aim to prolong the shelf life of packaged food products by slowing down or inhibiting those mechanisms that are

Table 1. Tensile properties of TPZ/MMT nanocomposites

Material	Young modulus [MPa]	Stress max [MPa]	Stress at break [MPa]	Strain at break [mm/mm]
TPZ	296 ± 31	6.93 ± 0.57	6.68 ± 0.5	0.07 ± 0.0066
TPZ + 1%MMT	444 ± 25	8.93 ± 0.45	8.5 ± 0.3	0.052 ± 0.01
TPZ + 2.5%MMT	552 ± 31	9.46 ± 1.23	9.46 ± 1.23	0.042 ± 0.005
TPZ + 5%MMT	1205 ± 41	12.9 ± 0.06	12.9 ± 0.06	0.015 ± 0.002
TPZ + 10%MMT	1478 ± 351	13.98 ± 5.12	13.98 ± 5.12	0.01 ± 0.003

responsible for packaged food products unacceptability. Extended literature works has dealt with starch, zein and PLA-based antimicrobial films produced *via* solvent casting technique (Cutter, 2006; Jin & Zhang, 2008; Joerger, 2007; Ku & Song, 2007; Mecitoglu, Yemenicioglu, & Arslanoglu, 2007; Sanjurjo, Flores, Gerschenson, & Jagus, 2006). However, the use of extrusion based processing, industrially employed for the manufacturing of packaging films, could affect the functionalities of antimicrobial compounds embedded in the polymeric matrix. These substances are generally heat sensitive and thermally unstable, thus, they may be inactivated by processing, mainly because of the high temperature, high shear rates and high pressure that can be reached into the extruder (Brody, Strupinsky, & Kline, 2001). For these reasons, processing issues related to the achievement of active films based on zein, starch, and PLA using traditional technologies such as extrusion are discussed below.

To the best of our knowledge, no zein-based antimicrobial films have been developed using extrusion process, while only few and very recent works describe the obtainment of antimicrobial packaging films based on starch and PLA using this technology. Pelissari, Grossmann, Yamashita, and Pineda (2009) proved the antimicrobial effect of cassava starch-chitosan films containing oregano essential oil produced by an extrusion process against *Bacillus cereus, Escherichia coli, Salmonella enteritidis,* and *Staphylococcus aureus*. Nam, Scanlon, Han, and Izydorczyk (2007) studied the antimicrobial properties of lysozyme embedded into extruded pea starch prepared under different extrusion conditions. They found that processing parameters strongly influenced lysozyme recovery into the active film. In particular, lysozyme recovery decreased with increase of extrusion temperature, whereas the moisture content of the dough had the opposite effect. Notwithstanding, the retained lysozyme in extrudates still exhibited effective antimicrobial activity against the test microorganism *Brochotrix thermosphacta*. Del Nobile *et al*. (2009) studied the effect of manufacturing conditions on the antimicrobial effectiveness of, among others, active PLA extruded films loaded with natural antimicrobial compounds such as lemon extract, thymol and lysozyme. They found that both thymol and lemon extract loaded into PLA films did not reduce to a great extent the growth kinetic of the selected cocktail of *Pseudomonas* spp compared to the control films. This is likely due to the high processing temperature used to extrude these active PLA films. On the contrary, PLA films containing lysozyme exhibited a good antimicrobial action against *M. lysodeikticus*. Therefore, it is reasonable to assume that, due to its higher thermal stability and high molecular weight, the residual concentration and activity of lysozyme after film formation was not significantly affected by the processing conditions. In other works (Liu, Jin, Coffin, & Hicks, 2009; Liu, Jin, Coffin, Liu, & Hicks, 2010) PLA and nisin, with and without ethylene diamine tetraacetic acid, were co-extruded to obtain antimicrobial membranes. They highlighted that PLA melts at around 160 °C, whereas the maximal temperature at which nisin retains its bioactivity is 120 °C. For this reason PLA/nisin films showed little or no antimicrobial activity whereas, PLA/lactide and PLA/glycerol triacetate blend membranes containing nisin prevented bacterial growth in brain–heart infusion broth inoculated with *Listeria monocytogenes*. Thus, in order to obtain active nisin-based films with enhanced antimicrobial activity, plasticizers such as lactide and glycerol triacetate must be added during extrusion processing to lower the temperature profile.

Biopolymers and high pressure treatments

High pressure processing (HPP) is steadily gaining as a food preservation method that maintains the natural sensory and nutritional attributes of food with minimal quality loss. HPP applies high pressure, typically in the 300–800 MPa range over a period of several minutes to foodstuff, to greatly reduce the number of micro-organisms and also to deactivate enzymes by mechanical action allowing Pasteurization and sterilization treatments at rather lower temperatures. HP Pasteurization is conducted at 25–40 °C while HP sterilization is conducted at 90–110 °C. Packaged foods processed by using these techniques maintain most of their original texture, nutritional and sensory qualities with extended shelf life. Moreover, the lower temperature for Pastuerization and sterilization could allow for the use of biopolymers, that are usually less thermally stable as compared to tradition petroleum based plastics.

Selecting the correct packaging material for this treatment is crucial since the packaging material has to be flexible enough to withstand the compression forces, while maintaining physical integrity (Caner, Hernandez, & Harte, 2004; Hernandez, Harte, & Pascall, 2000). Ideally, HPP should not affect the integrity of the package to any degree. Packaging materials need to show sufficient flexibility and resilience to compensate for the reduction in volume to preventing irreversible deformations. Several researchers have reported various effects on mechanical as well as barrier properties of a number of petroleum based packaging materials, including polyolefins, polyesters, polyamides, ethylene vinyl alcohol, after exposition to HPP (Fairclough & Conti, 2009; Galotto *et al*., 2008; Yoo, Lee, Holloman, & Pascall, 2009). No research work on the effects of HPP on packaging materials based on biopolymers have been reported, except one recent work on the effect of HP treatment on thermal properties of polylactides (Ahmed, Varshney, Zhang, & Ramaswamy, 2009). Pressure–temperature-induced changes in the materials should not affect the barrier, mechanical and mass-transfer (sorption and migration) properties of the package in a significant manner. Most of these issues on petroleum based polymers as well as on biopolymers were investigated within the framework of the EU project NovelQ. Here we

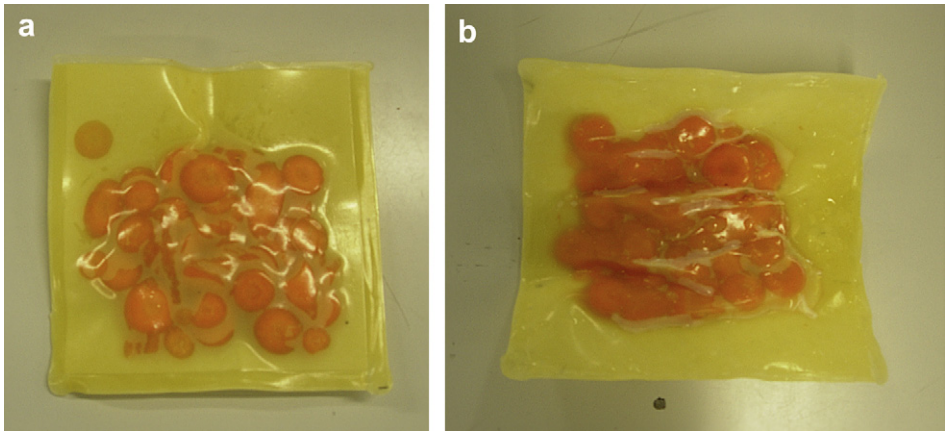

Fig. 4. (a) Multilayer zein-PCL package containing solid carrots before HP treatment; (b) Multilayer zein-PCL package containing solid carrots after HP Pasteurization at 700 MPa.

present some results concerning the use of PLA-based multilayer structures and zein-PCL laminates in HP treatments (Sansone, 2008).

PLA oriented multilayer films, made of two top sealable amorphous PLA layers and of a core of partially crystalline PLA, were used to prepare pouches containing tap water or solid carrots. The pouches were submitted to i) Pasteurization HP treatments, under the following experimental conditions: 5 min at 200, 500 and 700 MPa at temperatures in the 30–40 °C range, and ii) to sterilization HP treatments under the following experimental conditions: 5 min at 200, 500 and 700 MPa at temperatures in the 90–110 °C range. Pasteurization did not promote relevant variations of the barrier properties of PLA, even though there was evidence of some morphological change of the crystalline phase. On the other hand PLA was found to be not amenable to HP sterilization treatment, since this process determined more relevant changes, mainly occurring in the outer layers, which are accompanied by unacceptable brittlening of the material. These effects could be better understood by taking into consideration the dependence of glass transition and melting temperatures with pressure. In the case of HP sterilization the process conditions are such that the material enters the region comprised between glass transition and melting temperature, thus promoting crystallization of the outer amorphous layers.

Tests were also performed on multilayer structures based on PCL and thermoplastic zein. HP Pasteurization performed on carrot juice and solid carrots packaged with multilayer zein-PCL structures, revealed the compatibility of such packaging structure with this type of process. In fact, HP treatment up to 700 MPa did not promote any detectable change of oxygen and water vapour barrier properties. In Fig. 4a,b the appearance of pouches made of zein-PCL multilayer structures containing solid carrots before and after HP Pasteurization are reported.

Conclusions

In this review recent developments related to processing issues and shelf life improvement of packaging materials based on thermoplastic proteins, starch and PLA have been discussed. In particular we have looked in the state of the art in the field of (i) processing of protein and polysaccharides by analyzing the most recent developments for improving films and foams processing technologies and (ii) strategies for the technological advancements aimed to improve barrier properties, to promote active antimicrobial functionality and to apply these materials also in demanding high pressure processing of packaged foodstuff. To this respect, some recent results obtained in the framework of the European Project NovelQ have been also illustrated.

Further scientific and technological developments are still needed to pave the way to the spreading of these materials for food packaging applications. A wider use of biopolymers in food packaging applications, which would certainly lead to a lower environmental impact as compared to polymers from petrochemical sources, will be possible after solution of problems related to processability and performances of these materials.

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