



Review article

Natural-based plasticizers and biopolymer films: A review

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ABSTRACT

In recent years, much attention has been focused on research to replace petroleum-based commodity plastics, in a cost-effective manner, with biodegradable materials offering competitive mechanical properties. Biopolymers have been considered as the most promising materials for this purpose. However, they generally present poor mechanical properties regarding processability and end-use application, since the fragility and brittleness exhibited during thermoformation can limit their potential for application. In order to overcome this problem, plasticizers are added to provide the necessary workability to biopolymers. This class of products became more visible when biodegradable additives and plasticizers also became the focus of material scientists. The use of natural and/or biodegradable plasticizers, with low toxicity and good compatibility with several plastics, resins, rubber and elastomers in substitution of conventional plasticizers, such as phthalates and other synthetic conventional plasticizers attracted the market along with the increasing worldwide trend towards use of biopolymers. Here we discuss the main results and developments in natural plasticizer/synthetic and biopolymer-based films during the last decades.

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1. Introduction

Plasticizers are an important class of low molecular weight non-volatile compounds that are widely used in polymer industries as additives [1]. The primary role of such substances is to improve the flexibility and processability of polymers by lowering the second order transition temperature, the glass transition temperature (T_g). The council of the IUPAC (International Union of Pure and Applied Chemistry) defined a plasticizer as "a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility". These substances reduce the tension of deformation, hardness, density, viscosity and electrostatic charge of a polymer, at the same time as increasing the polymer chain flexibility, resistance to fracture and dielectric constant [2]. Other properties are also affected, such as degree

of crystallinity, optical clarity, electric conductivity, fire behavior and resistance to biological degradation, amongst other physical properties [3].

During the last decade, the worldwide production of plasticizers was around 5 million tons per year. These were applied to around 60 polymers and more than 30 groups of products [3]. The use of plasticizers for plastic products manufacture is not a new practice. Its application to modify polymer characteristics began in the 1800s. In these early days, manufacturers of celluloid or celluloid lacquers used natural camphor and castor oil for plasticization purposes, but these were unsatisfactory for many end uses. Later, in 1912, triphenyl phosphate was tested to substitute camphor oil, representing the beginning of the ester plasticizers era. Phthalic acid esters found applications as plasticizers for the first time in 1920 and continue to be the largest class of plasticizers in the 21st century [4]. Di(2-ethylhexyl) phthalate (DEHP), also known as dioctyl phthalate (DOP), was introduced in 1930 and has been the most widely used plasticizer since the 1930s. The great variety of plastic products and its numerous applications have led to the development of new and improved

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plasticizers in order to meet product quality and specification requirements. Over the last half century, legislation and health safety issues have led to the development of a wide range of currently-available commercial plasticizers. They include some fatty acid esters, benzoates, tartrates and chlorinated hydrocarbons, esters of adipic, azelaic and sebacic acid.

As the plastic industry continuously grows, the demand for plasticizers goes in the same direction. The current market offers numerous choices of plasticizers with a range of attributes that can be selected for specific applications to meet critical material requirements. However, since the early 1980s, there have been concerns, and even controversy, regarding the use phthalates and their effects on human health and the environment [5]. Thus, the use of plasticizers is being questioned due to their possible toxicity problems, related to the migration of phthalates. This fact has caused some countries to develop new and restrictive regulations regarding the use of phthalates in flexible PVC products [6,7]. Currently, there is a trend towards replacing DOP by either diisononyl phthalate (DINP) or diisodecyl phthalate (DIDP), which are higher molecular weight phthalates and therefore are more permanent, have lower solubility and present slower migration rates [8]. In addition, other alternative plasticizers and mixtures, with low migration levels and low toxicity have been widely used in the last decades to overcome these problems. These alternative plasticizers could be very useful for applications that are especially sensitive to this phenomenon [9].

Nowadays, there is increasing interest in the use of natural-based plasticizers that are characterized by low toxicity and low migration. This group includes epoxidized triglyceride vegetable oils from soybean oil, linseed oil, castor-oil, sunflower oil, and fatty acid esters (FAEs) [10].

In addition, this search for natural-based plasticizers is also related to the increased interest of material researchers and industries in the development of new bio-based materials, made from renewable and biodegradable resources with the potential to reduce the use of conventional plastic goods. It is reasonable to suppose that plasticizers for biopolymers should preferably also be biodegradable [11].

In this respect, most of the traditional plasticizers used in synthetic polymer processing are not suitable for some biodegradable thermoplastics such as poly(3-hydroxybutyrate) (PHB), reinforcing the need for further investigations and developments in this area. Although a total replacement of synthetic plasticizers by natural-based plasticizers is just impossible, at least for some specific applications such a replacement seems obvious and useful.

2. Attributes and performance of plasticizers

Plasticizers are, in general, high boiling point liquids with average molecular weights of between 300 and 600, and linear or cyclic carbon chains (14–40 carbons) [12,13]. The low molecular size of a plasticizer allows it to occupy intermolecular spaces between polymer chains, reducing secondary forces among them. In the same way, these molecules

change the three-dimensional molecular organization of polymers, reducing the energy required for molecular motion and the formation of hydrogen bonding between the chains. As a consequence, an increase in the free volume and, hence, in the molecular mobility is observed [14]. Thus, the degree of plasticity of polymers is largely dependent on the chemical structure of the plasticizer, including chemical composition, molecular weight and functional groups [15]. A change in the type and level of a plasticizer will affect the properties of the final flexible product [4,16]. The selection for a specified system is normally based on the compatibility between components; the amount required for plasticization; processing characteristics; desired thermal, electrical and mechanical properties of the end product; permanence; resistance to water, chemicals and solar radiation; toxicity and cost [16,17].

Compatibility between plasticizer and polymer is of major significance for effective plasticization and various parameters can indicate this feature, including polarity, hydrogen bonding, dielectric constant and solubility parameters [11,18]. Other important factor is solvation, as plasticizers with solubility parameters close to those of the polymer require less energy to fuse or solvate the polymer. The temperature of fusion or gelation is related to the solvation strength of the plasticizer and to the size of its molecule [4].

Permanence is related to volatility and resistance to migration and extraction in water, solvents and oils. Therefore, the plasticizer should have low vapor pressure and a low rate of diffusion in the polymer [13].

The majority of plastic products are prepared by so-called “hot compounding” techniques, where the formulated ingredients are combined under heat and shearing forces that bring about a state of molten plastic (fluxing) which is shaped into the desired product, cooled and allowed to develop ultimate properties of strength and integrity. Hot compounding includes calendaring, extrusion, injection and compression molding. The ease or difficulty of processing plastic can be significantly influenced by the plasticizer type and concentration as well as other formulating additives. So, as they do not only modify the physical properties of polymers but can also improve processing characteristics, plasticizers can also be considered as processing additive. Plasticizers can influence processing by inducing lower viscosity, faster filler incorporation, easier dispersion, lower power demand and less heat generation during processing, better flow, improved release and enhanced building tack. For example, as a property modifier, plasticizers can reduce the second order transition temperature and the elasticity modulus, as a result cold flexibility is improved. The softening effect of plasticizers leads mostly to improve processing through easier filler incorporation and dispersion, lower processing temperatures and better flow properties [19].

In biopolymer-based films and coatings production, plasticizers are also essential additives since they can improve flexibility and handling of films, maintain integrity and avoid pores and cracks in the polymeric matrix [20]. Incompatibility is commonly evidenced by phase separation between the biopolymer and plasticizer, presented in the form of exudated drops on the surface of the product

immediately after its blending or during final product application [13].

3. Plasticizer classification

In polymer science, plasticizers can be either defined as internal or external. External plasticizers are low volatile substances that are added to polymers. In this case, plasticizer molecules interact with polymer chains, but are not chemically attached to them by primary bonds and can, therefore, be lost by evaporation, migration or extraction. On the other hand, internal plasticizers are inherent parts of the polymer molecules and become part of the product, which can be either co-polymerized into the polymer structure or reacted with the original polymer [21]. Internal plasticizers generally have bulky structures that provide polymers with more space to move around and prevent polymers from coming close together. Therefore, they soften polymers by lowering the T_g and, thus, reducing elastic modulus. For both types, although more pronounced for internal plasticizers, a strong temperature dependence of material properties is observed. The benefit of using external plasticizers, compared to internal ones, is the chance to select the right substance depending on the desired product properties [22].

Plasticizers can also be classified as primary and secondary [23]. If a polymer is soluble in a plasticizer at a high concentration of the polymer, it is said to be a primary plasticizer. This type of plasticizers are used as the sole plasticizer or as the main element of the plasticizer, they should gel the polymer rapidly in the normal processing temperature range and should not exude from the plasticized material. Secondary plasticizers, on the other hand, have lower gelation capacity and limited compatibility with the polymer, they are typically blended with primary plasticizers, to improve product properties or reduce the cost [24].

Plasticizers, for biopolymer-based films, can be divided into water soluble and water insoluble [25]. The type and the amount of plasticizer strongly affect the film formation from polymeric aqueous dispersions [26]. Hydrophilic plasticizers dissolve in the aqueous medium when they are added to polymer dispersions and if added in high concentration they can lead to an increase in water diffusion in the polymer. In contrast, hydrophobic plasticizers may close the micro-voids in the film, leading to a decrease in water uptake. However, water insoluble plasticizers can cause phase separation leading to flexibility losses or yet to the formation of discontinuity zones during film drying. As a consequence, water vapor permeability rates are increased. Complete uptake of insoluble plasticizer by the polymer can be achieved by an optimum stirring rate of the polymeric dispersion with the plasticizer [27].

4. Commercially available plasticizers

Currently, there are numerous available options, with specific strips of attributes, which can be selected for certain applications. The current database of commercially-manufactured plasticizers contains more than 1200 items; however, only 100 products have achieved noticeable

market significance. The plasticizers produced have been applied in 60 polymers and more than 30 groups of products. Industrially, the most common plasticized polymers are PVC, poly(vinyl butyral) (PVB), poly(vinyl acetate) (PVAc), acrylics, cellulose molding compounds, nylon, polyamides and certain copolyamides. PVC processing is by far the most important use of plasticizers, consuming over 80% of production [3,4]. Esters of phthalic acid constitute more than 85% of the total plasticizer consumption. Most of them are based on carboxylic acid esters with linear or branched aliphatic alcohols of moderate chain lengths (predominantly C6–C11) [3]. In relation to the classic plasticizers, the phthalate esters [6,11,28], adipates [29], citrates [11] besides acids esters, alkane-dicarboxylic, glycols and phosphates are used.

5. Biodegradable polymers: sources and classification

Biodegradable polymers can be classified in four categories depending on the synthesis and on the sources [30–32]:

- (a) Polymers from biomass such as the agro-polymers from agro-resources;
 - (I) polysaccharides, e.g., starches (wheat, potatoes, maize) [20,33,34], ligno-cellulosic products (wood, straws, ...) [35] and others (pectins, chitosan/chitin, gums) [36],
 - (II) protein and lipids, e.g., animals (casein, whey, collagen/gelatin) [37–48], and plants (zein, soya and gluten) [49,50],
- (b) polymers obtained by microbial production, e.g., polyhydroxyalkanoates (PHA) such as poly(hydroxybutyrate) (PHB) and poly(hydroxybutyrate co-hydroxyvalerate) (PHBv);
- (c) polymers chemically synthesized using monomers obtained from agro-resources, e.g., poly(lactic acid) (PLA);
- (d) polymers whose monomers and polymers are both obtained by chemical synthesis from fossil resources, e.g., polycaprolactones (PCL), polyesteramides (PEA), aliphatic co-polyesters (e.g., PBSA) and aromatic co-polyesters (e.g., PBAT).

Only the last category is obtained from non-renewable resources. The first category is considered as agro-polymers and the others are called biodegradable biopolyesters [50]. Synthetic polymers are gradually being replaced by biodegradable materials especially those derived from natural resources, due to its biodegradability. Recent innovations in edible and/or biodegradable polymer films are widely discussed in the literature [32,51–54], presenting improvements in food packaging, surgery, pharmaceutical uses.

6. Plasticizers to biopolymer films

The use of natural-based polymers films depends on several features including cost, availability, functional attributes, mechanical properties (strength and flexibility), optical quality (gloss and opacity), barrier requisites (water vapor, O₂ and CO₂ permeability), structure resistance to

water and sensorial acceptance. These characteristics are greatly influenced by parameters such as the type of material used as structural matrix (conformation, molecular mass, charge distribution), film manufacturing conditions (solvent, pH, concentration, temperature, etc.) and the type and concentration of additives (plasticizers, crosslinking agents, antimicrobials, antioxidants, etc.) [55–56].

The dehydration of these structures produces strong cohesive films that usually require plasticizers. The addition of plasticizer leads to a decrease in intermolecular forces along polymer chains, which improves the flexibility and chain mobility. These are added to enhance film flexibility, decrease brittleness and avoid shrinking during handling and storage [30,55,57]. Several studies, however, have also reported adverse effects of plasticizers on edible film attributes. Most of these describe an increase in gas, solute and water vapor permeability and the decrease in cohesion affects mainly mechanical properties. The characteristics of films, based on biopolymers, depend therefore on an equilibrium between the degree of cross linking of the polymer matrix (sometimes necessary to reduce the solubility in water, but induces brittleness) and the addition of plasticizers for better workability [58]. Above a critical concentration, the plasticizer can exceed the compatibility limit with the biopolymer, and phase separation with plasticizer exclusion is usually observed [59].

Usually, biopolymers and plasticizers are hygroscopic and therefore film moisture content is affected by ambient conditions. Besides, water is the main solvent in the natural biopolymer technology. Its molecules reduce the T_g and increase the free volume of biomaterials, and thus are considered as plasticizers. Indeed, water is the most powerful “natural” plasticizer of hydrocolloid-based films [17,60]. The plasticization action of water molecules on biopolymers has been widely reported in the literature [17,60–67].

In addition to water, the most commonly used plasticizers are polyols, mono-, di- and oligosaccharides. Polyols have been found to be particularly effective for use in plasticized hydrophilic polymers [68]. Glycerol (GLY) was, thus, nearly systematically incorporated in most of the hydrocolloid films [41]. GLY is indeed a highly hygroscopic molecule generally added to film-forming solutions to prevent film brittleness [60,64].

Recently, many studies have focused on the use of polyols such as GLY [17,33,36,38,39,47,61,62,65,68–77], ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol and polyethylene glycol (PEG) [16,36,39,41,61,78,79], propylene glycol (PG) [61], sorbitol [16,20,41,61,64,65,68,70–72,74,76,77,80,81], mannitol [82] and xylitol [68,71]; fatty acids [20,45,83–85]; monosaccharides (glucose, mannose, fructose, sucrose) [41,68,77,86]; ethanolamine (EA) [87]; urea [76]; triethanolamine (TEA) [39]; vegetable oils; lecithin; waxes [20,85]; amino acids [88]; surfactants [89] and water [17,60,62,64] as plasticizers of edible and/or biodegradable films.

The basic materials used to form edible and/or biodegradable films are polysaccharides, proteins and lipids compounds. Polysaccharides have good film-forming properties, providing efficient barriers against oils and lipids, although their moisture barriers are poor. Protein-based films have highly interesting properties: mechanical and barriers prop-

erties are generally better than those of polysaccharides-based films. Lipid compounds have been used to make edible films for their excellent moisture barrier properties, but they can cause textural and organoleptical problems. In the last years, several studies have been dedicated to form composite films, combining one or several lipid compounds with one hydrocolloid-based structural matrix [51–53,90]. In this context, this paper aims to highlight some developments regarding the use of natural plasticizers currently used in polysaccharides-, proteins-, lipids-films and other films obtained from microbial sources.

Some natural plasticizers currently used in edible and/or biodegradable films from biomass products (polysaccharide-, protein-, and lipid-based films) and other films obtained from microbial sources are summarized in Table 1.

6.1. Polysaccharide-based films

Generally, polysaccharide films are made from starch, alginate, cellulose ethers, chitosan, carrageenan, or pectins and exhibit good gas barrier properties. Linear structure of some of these polysaccharides, for example, cellulose (1,4-b-d-glucan), amylose (a component of starch, 1,4-a-d-glucan), chitosan (1,4-b-d-glucosamine polymer), renders their films tough, flexible and transparent. Their films are resistant to fats and oils [32]. However, due to their hydrophilic nature, they are poor water vapor barriers. Among polysaccharide and biopolymers in general, starch is considered to be one of the most promising materials for use in biodegradable plastics [91].

Different approaches have been carried out to use this polysaccharide as a natural biopolymer for the production of biodegradable thermoplastics and different types of starch were processed in blend systems with natural plasticizers and commercial fibers by conventional extrusion and injection molding techniques [92].

Hydrophilic compounds, such as polyols (GLY and sorbitol) are commonly used in starch films [17,20,33,68,71,72,74,76,79,82], but some sugars [77,86], surfactants [89,92,93], amino acids and fatty acids [81] could also be employed to improve their mechanical and barrier properties. However, a limiting barrier to the development of starch materials is the brittle nature of blends containing high concentrations of starch. The re-crystallization of starch restrains starch from coming into real practical use, because it easily becomes rigid and brittle during long-term storage, and therefore loses its value in use [87].

Overcoming the brittleness of starch while achieving full biodegradability in blends, can be accomplished with the addition of biodegradable plasticizers [89]. An ideal plasticizer for starch-based materials should impart flexibility and suppress retrogradation to thermoplastic starch (TPS) during aging [34]. The crystallization of GLY-containing potato starch plastic sheets revealed a significant influence on their mechanical properties. The changes in crystallinity were clearly related to the initial amount of plasticizer and moisture migration during aging. The differences in material properties could be attributed to the formation of an entangled starch matrix and by starch chain-to-chain associations that are related to plasticizer content [92].

Table 1

Natural plasticizers used in biodegradable films from biomass products (polysaccharide-, protein-, and lipid-based films) or other films obtained by extraction of micro-organisms.

Type	System of application	Plasticizer	Refs.
Polysaccharide-based films	Citric acid-modified pea starch (CAPS) and citric acid-modified rice starch (CARS)	GLY	[91]
	γ -Carrageenan edible films	GLY and water	[60]
	Potato starch	GLY and EG	[78]
		GLY, xylitol and sorbitol	[71]
		GLY	[92,93]
	Waxy maize starch, maize starch and amylo maize starch	GLY, sorbitol and water	[94]
	Soluble starch/gelatin	GLY, sorbitol and sucrose	[53]
	Corn starch	Ethanolamine	[87]
		Caproic acid, lauric acid and glycerol triacetate (triacetin)	[95]
		GLY, acetamide, formamide, anhydrous glucose and urea	[34]
		Sorbitol and GLY	[20,74]
		GLY and amino acids	[88]
	Cassava starch	GLY	[33]
		GLY and sorbitol	[72]
	Oat starch	GLY, sorbitol and urea	[76]
		GLY, sorbitol and urea, sucrose and glycerol-sorbitol mixture	[77]
	Pea starch	Mannose, glucose, fructose, GLY and sorbitol	[68]
	Chitosan films	GLY, EG, PEG and PG (PG)	[36]
	Hydroxypropyl methylcellulose (HPMC)–beeswax (BW)	GLY and mannitol	[82]
	Cellulose from sugarcane bagasse and cellulose acetates	Residual xylan acetate	[35]
	Konjac glucomannan	Sorbitol and GLY	[17]
	Alginate/pectin	GLY	[58]
	Protein-, lipid-based films	Zein	Oleic and linoleic acids
Caseinate-pullulan		Water and sorbitol	[64]
Whey protein		GLY and sorbitol	[65]
Whey protein/beeswax emulsion		GLY	[47]
β -Lactoglobulin		Sorbitol, GLY and PEG	[40]
		Sorbitol, GLY, EG, PEG 200 and PEG 400	[42]
		Propylene glycol (PG), GLY, sorbitol, PEG 200, PEG 400 and sucrose	[48]
		GLY, EG, DEG, TEG and PG	[49]
Sunflower protein		Saturated fatty acids (FA)	[45]
Peanut protein		Glycerin, sorbitol, PEG, PG	[61]
Wheat gluten		Glycerin	[43]
Feather keratin		GLY	[69]
Fish mince from Atlantic sardines (<i>Sardina pilchardus</i>)		Sorbitol, GLY and sucrose	[41]
Fish skin protein		Fatty acids (FA) and sucrose esters (FASE)	[83]
Water-soluble fish proteins		GLY and PEG	[36]
		GLY, PEG, EG, sucrose and sorbitol	[44]
Fish muscle proteins		GLY, PG, DEG and EG	[96]
Fish myofibrillar protein		Glycerin and water	[62]
Gelatin		GLY and sorbitol	[70]
		Sucrose, oleic acid, citric acid, tartaric acid, malic acid, PEG of different molecular weights (300, 400, 600, 800, 1500, 4000, 10,000, 20,000), sorbitol, mannitol, EG, DEG, TEG, EA, diethanolamine (DEA) and TEA	[16]
Pigskin gelatin		GLY	[38]
		Sorbitol	[80]
Bovine gelatin		Fatty acids	[50]
	Sorbitol	[80]	
	GLY	[67]	
Other films (from microbial sources)	<i>Amaranthus cruentus</i> flour edible films	GLY	[75]
	Poly(3-hydroxybutyrate) (PHB)	Dodecanol, lauric acid, tributyrin and trilaurin	[97]
	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)	Soybean oil (SO), epoxidized soybean oil (ESO), dibutyl phthalate (DBP) and triethyl citrate (TEC)	[11]

Ethanolamine is a novel plasticizer that can be used for thermoplastic starch processing, destroying the native starch granules and making them come into a uniform

continuous phase. Ethanolamine plasticized thermoplastic starch (ETPS) could restrain the re-crystallization of traditional thermoplastic starch plasticized by GLY (GTPS),

improving their mechanical properties and thermal stability [87].

Different plasticization systems for starch acetates (caproic acid, lauric acid and glycerol triacetate (triacetin)) were prepared to investigate internal and external plasticization of starch acetates [81]. The presence of fatty-acid esters is shown to decrease T_g , and the T_g depression effect may be enhanced by increasing the size of the substituent or the proportion of the fatty-acid.

The formulation of films (lipid addition, type of starch and plasticizer) can cause changes on their microstructure, water vapor and gas permeability properties. Two types of starch (commercial corn starch and high amylose corn starch), two plasticizers (sorbitol and GLY) and sunflower oil were tested in different concentrations (1–8 g/L), aiming at reducing water vapor and gas permeability of films. Plasticizer addition improved starch-based coatings performance by increasing barrier properties to water vapor, maintaining the selective gaseous permeability. GLY and sorbitol showed to be compatible with amylose and improved mechanical properties of films, by decreasing intermolecular attraction and interfering with the amylose packing [20].

The interactions between plasticizer and starch can be very specific. In crystalline amylose and crystalline and amorphous amylopectin systems with plasticizers (GLY or EG), the plasticizers interact through hydrogen bonding with crystalline amylose and crystalline and amorphous amylopectin when the temperature is increased and also during film storage at room temperature. Crystalline amylopectin and amylose showed similar behaviors, with a slower rate of plasticizer/polymer interaction, compared to amorphous amylopectin. A marked interaction occurred by increasing the temperature, probably due to H-bond formation. As a consequence, matrix mobility increases, viscosity reduces, and the material behaves like a rubber [78].

Plasticizers containing amide groups (urea, formamide and acetamide) were tested for TPS plasticization, using GLY as a reference. Amide groups seem to have an interesting effect on TPS retrogradation suppression. The effects of TPS films on mechanical properties and retrogradation were observed to rely mainly on the hydrogen bond-forming ability between plasticizers and starch molecules, increasing in the following order urea > formamide > acetamide > polyol [34].

The effect of the type and the concentration of the most conventional natural plasticizers such as polyols (e.g., GLY), sorbitol, amongst others on polysaccharide-based films [20,33,36,53,58,71,72,74,77,79,82,89] has been extensively investigated. Plasticizer concentration and hydrophilic nature were found to be important factors in determining the moisture affinity of cassava starch films [74]. GLY-containing films adsorbed more water and at a higher rate during their storage, compared to sorbitol films. In addition, the analysis of the mechanical properties of these films indicated that GLY alone exerted a more effective plasticization. In another study [33], GLY addition caused an increase in the mobility of amylase and amylopectin chains, which overcame the opposite effect of re-crystallization, and increased the film flexibility.

The increase in GLY concentration on the formulation of transparent and homogenous alginate/pectin composite films decreased their tensile strength and increased their solubility in water, moisture content and the elongation at break. As a compromise between film mechanical resistance and flexibility, to maintain low solubility and swelling in water, the use of 5–10% glycerol in the finishing crosslinking step was recommended. Concentrations lower than 3% glycerol produce brittle films and phase separation was observed on the film surface when concentrations higher than 12% glycerol were used [58].

The properties of biodegradable oat starch films, combined with different plasticizers. Hydrophilic plasticizers (GLY, sorbitol and urea) increased the permeability and water sorption properties of biodegradable oat starch films [76], without changing their mechanical properties. In another study, the same research group investigated the effect of sucrose and a mixture of GLY/sorbitol, besides GLY, urea and sorbitol as plasticizers on the microstructure, moisture sorption, water vapor permeability and mechanical properties of oat starch films kept at different relative humidity conditions [77]. Plasticizer type did not significantly affect the equilibrium moisture content of films. Sucrose added films were the most fragile at low RH, while GLY films were the most hygroscopic. However, at RH of 76–90%, sucrose films showed similar resistance compared to other plasticized films. Films without plasticizer adsorbed less water and showed higher water vapor permeability, indicating the antiplasticizing effect. Other study also investigated the effect of sucrose or inverted sugar addition on mechanical properties, hydrophilicity and water activity of cassava starch films was studied [86]. Compared to inverted sugar, sucrose addition resulted in films with higher elongation at break. Results suggested that sucrose could replace inverted sugar as a plasticizer for cassava starch films. However, the effect of such substitution on material microstructure during storage should be investigated.

The effect of polyols such as GLY, EG, PEG and PG on mechanical and surface properties of chitosan films was evaluated considering the plasticizer volatility [36], since it may influence film properties and stability during application and storage, i.e. the less volatile the plasticizer, the better it is for use. Besides, considering the plasticization efficiency and storage stability for chitosan films, GLY and PEG showed to be more suitable than EG and PG. Furthermore, a plasticizer concentration of 20% (w/w) with GLY or PEG was sufficient to obtain flexible chitosan film, exhibiting good stability for 5 months of storage.

Water–GLY and water–sorbitol interactions on Konjac glucomannan films influenced their mechanical properties. In the concentration range studied (0–50%), the incorporation of GLY and sorbitol did not significantly reduce film tensile strength, but enhanced their flexibility and extensibility [17].

Surfactants could also be incorporated into film formulations in order to reduce the surface tension of the solution, improving the wettability and adhesion of plasticized film [89]. The surfactants Tween 20, Span 80 and soy lecithin and GLY were used as a plasticizer in potato starch films [92]. In the absence of GLY, surfactants had a

significant effect on mechanical properties, but they did not significantly modify the water vapor permeability. Films with GLY and a high level of any surfactant behaved as films with larger amounts of plasticizer (with lower tensile strength and higher elongation at break and higher water vapor permeability). Tween exhibited the most intense synergistic effect with GLY.

Cellulose acetate films could be prepared through acetylation of cellulose from sugarcane bagasse [35]. The hemicellulose content (5%) present in bagasse was used as an internal plasticizer of the acetate cellulose films. Furthermore, residual xylan acetate acted as a plasticizer for cellulose acetate and films exhibited good mechanical properties without addition of an external plasticizer.

6.2. Protein-, lipid-based films

Proteins have a unique structure (based on 20 different monomers), which confers a wider range of functional properties, especially a high intermolecular binding potential [41]. Protein-based edible films can form bonds at different positions and offer high potential for forming numerous linkages [40,98]. Molecular weight, number and positions of hydroxyl groups of a plasticizer are all variables that affect its ability to plasticize a protein-based polymer [40]. Zein, the prolamine of corn, was investigated as a raw material for packaging materials [84]. Oleic and linoleic acids were added as plasticizers resulting in flexible sheets of high clarity, low modulus, and high elongation and toughness, although low tensile strength. Fatty acid separation caused zein aggregation, resulting in loss of flexibility and increased water absorption. Linoleic acid was more effective than oleic acid at reducing water absorption of sheets. However, plasticization of zein with oleic acid resulted in relatively tough and water-resistant sheets that may find application in thermoformed packaging trays.

The plasticizing effect of traditional natural plasticizers such as polyols (GLY, PEG, EG, DEG, TEG and PG), sorbitol and sucrose, varying type and concentration of plasticizer, on protein- or lipid-based film properties is widely reported in the current literature [39,41–44,46–49,61,62,64,83,90,96,99].

The increase in GLY content caused an increase in film solubility in water and a decrease in mechanical resistance of whey protein-based films [47]. On the other hand, the plasticizing effect of sorbitol, GLY and sucrose in myofibrillar protein-based films prepared with fish mince from Atlantic sardines (*Sardina pilchardus*) did not cause significant differences in film properties when were introduced at the same molecular concentration due to structural similarities between sorbitol, GLY and sucrose [99].

GLY was used as plasticizer for fish protein films, reducing opacity, color and T_g [43]. Similarly, another study verified that an increase in plasticizer (GLY and PEG) concentration decreased the tensile strength with a concomitant increase in elongation at break and water vapor permeability of water-soluble fish protein-edible films [40]. Other studies corroborate with those results [42,44]. Films plasticized with EG, sucrose and sorbitol were too brittle and fragile to handle, making then unfeasible to

prepare. PEG concentration influenced the tensile strength of films, whereas elongation at break is more affected by GLY. Results clearly demonstrated the plasticizing effect of GLY, which acted by reducing internal hydrogen bonding within the protein, due to its highly hydrophilic characteristics, thereby decreasing the internal forces and increasing the inter-molecular spacing. The addition of combined plasticizers (GLY and PEG) can modify the mechanical properties and water vapor permeability [44].

β -Lactoglobulin films were plasticized with different plasticizers (PG, GLY, sorbitol, PEG 200, PEG 400 and sucrose) aiming at improving the mechanical properties. GLY and PEG 200 were the plasticizers that most efficiently achieved desirable mechanical properties for films [48].

The use of five compounds (GLY, EG, DEG, TEG and PG) as plasticizers for sunflower protein isolate films, producing soft, brown and smooth films, with good mechanical properties and a high level of impermeability to water vapor [49]. No marked loss of GLY or TEG was observed over the 3-month aging period, being both substances the most suitable plasticizers for sunflower proteins. GLY, as a totally non-toxic plasticizer, is indicated for use in the food industry.

A series of saturated fatty acids with different carbon chain length (from 6 to 10 carbons) was added to wheat gluten film in order to evaluate its plasticizing effect [45]. Results were promising and open up new horizons for plasticization and improvement of gluten-based plastics properties.

The thermal and functional properties of pig skin gelatin-based films were improved by adding polyols (GLY, PG, DEG and EG) as plasticizers [90]. The plasticizers were tested in five concentrations and they were compatible with gelatin, producing flexible and easy handling films in the range of concentration studied. No typical phase separation was observed during thermal analyses. In terms of functional properties, GLY presented higher plasticizing effect and efficiency.

Other plasticizers such as sucrose, oleic acid, citric acid, tartaric acid, malic acid, PEG, sorbitol, mannitol, EG, DEG, TEG, EA, diethanolamine (DEA) and TEA were also applied for gelatin films, modifying their mechanical and barrier properties. With regard to mechanical and visual properties, malic acid, PEG 300, sorbitol, EG, DEG, TEG, EA, DEA and TEA presented the most promising plasticizing effect. EG, DEG and TEG films showed the highest water vapor permeability and water content values, while malic acid and sorbitol had the lowest values [16].

6.3. Other films obtained from microbial sources

New biodegradable polymer blends have been developed to enhance the degradation of the final product. Poly- β -hydroxyalkanoates (PHA) have been attracting much attention in recent years as biocompatible and biodegradable thermoplastics with potential applications. Poly(3-hydroxybutyrate) (PHB) is one of the well-known biodegradable PHA. PHB is a natural thermoplastic polyester and has many mechanical properties comparable to synthetically-produced degradable polyesters [100]. Biodegradable plasticizers such as soybean oil (SO),

epoxidized soybean oil (ESO), dibutyl phthalate (DBP) and triethyl citrate (TEC) were added to poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) films, enhancing their thermal and mechanical properties. TEC or DBP presented better plasticizing effects than SO and ESO for PHBV [11].

The use of additives (dodecanol, lauric acid, tributyrin and trilaurin) caused changes on the structure of PHB films [97], decreasing their T_g and T_{cc} (cold crystallization temperature). These additives are miscible with PHB and improved the mobility of the molecules in the amorphous phase. Besides acting as plasticizers, these additives could, in a fairly small amount (1 wt.%), act as accelerators for the enzymatic degradation of the polymer chains. The same effect was also observed by adding a biodegradable plasticizer, di-*n*-butylphthalate (DBP), in PHB films [101].

7. Concluding remarks

Health and environmental concerns, associated with the use of leachable plasticizers such as phthalates, could be approached and minimized by the use of alternative flexible polymers that require less or no plasticizers, by some surface modification techniques and by using plasticizers that have less volatility and leachability, or even by using lower toxicity plasticizers. This latter option refers to the development of natural-based plasticizers and has recently motivated research in various academic and industrial areas. The use of such plasticizers, with low toxicity and good compatibility with several plastics, resins, rubber and elastomers to substitute conventional synthetic plasticizers has become more attractive.

Although there is still not enough scientific data to prove real threats regarding health problems, associated with the use of synthetic plasticizers, there are, however, no doubts that demands made on environmental and toxicological performance will become increasingly stringent. As such, low volatile plasticizers, preferentially new families of oligomeric esters which are also difficult to extract, will become more important in all areas of applications. The challenge to implement this new class of natural-based plasticizers matches the increasing interest of material researchers and industries in new bio-based materials, made from renewable resources with the potential, not to totally replace but to reduce the use of conventional plastic goods.

Thus far, bioplastics cover approximately 5–10% of the current plastic market. Although their development costs are high and they do not yet have the benefit of economic scale, it is believed that, during the next decades, the demand for these products will rapidly increase and they will be widely used in packaging applications. Biopolymers fulfill environmental concerns, but they also show some limitations in terms of performance such as thermal resistance, barrier and mechanical properties, associated with costs. However, bio-based polymers have already found important applications, for example in pharmaceutical and medical fields, where cost is not as important as function itself.

In the scientific literature, an increasing number of publications have reported the production and application of biopolymers with natural and/or biodegradable plasticiz-

ers, such as citrate, polyols, triacetin, oligomeric esters, amides, and fatty acid derivatives. Nevertheless, a deeper understanding of their interactions and fundamental physicochemical and biochemical properties is still needed in order to enable the design and production of desirable and competitive materials using compatible plasticizers.

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