RESEARCH ARTICLE

PLASTICIZERS: PAST, PRESENT AND FUTURE: A REVIEW

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ARTICLE INFO	ABSTRACT
	Plasticizers are indispensable class of polymeric compounds which are non-volatile and low molecular weight in nature and are mainly used as an additive in polymer industries (1). The foremost role of these polymeric material is to improve the plasticity or flexibility and processability of various polymers such as PVC. During last few years it is estimated that almost 5 million tones of Plasticizers are produced worldwide. Different types of Plasticizers are used in PVC, EPDM compounding to give better processability. This paper reviews the different classes of Plasticizers used world wide for various applications.

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INTRODUCTION

Plasticizers are indispensable class of polymeric compounds which are non-volatile and low molecular weight in nature and are mainly used as an additive in polymer industries (1). The foremost role of these polymeric material is to improve the plasticity or flexibility and processability of various polymers such as PVC. Plasticizers improves the flexibility by lowering the second order transition temperature, the glass transition temperature (T_g). It is defined as ''a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility''. These substances decreases hardness, density, viscosity and electrostatic charge of a polymer, also lessen the tension of deformation, but at the same time increases the polymer chain flexibility, resistance to fracture and dielectric constant (2). It also affects other properties such as Fire behavior, optical clarity, degree of crystallinity, electric conductivity, and resistance to biological degradation, amongst other physical properties (3). During the last few years, the estimated worldwide production of plasticizers was approximately 5 million tons per year. These were applied to around 60 polymers and more than 30 groups of products (3). The use of plasticizers started in the year 1800, it was used to modify plastic products manufacture. 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 (TPP) was tested to substitute camphor oil, representing the beginning of the ester plasticizers era.

In 1920 Phthalic acid esters were first used as plasticizers and today in 21 century also they are the largest class of plasticizers (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 its introduction. The great variety of plastic products and its numerous applications have led to the development of new and improved 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 various acids such as adipic, azelaic and sebacic acid. As the plastic industry is growing rapidly, the demand for plasticizers is also increasing day by day. The ongoing market offers countless choices of plasticizers with a wide range of attributes that can be hand-picked for specific applications to meet critical material requisite. However, since the early 1980s, there have been concerns, and even controversy, regarding the use of phthalates as Plasticizers 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. Due to this reason some countries have designed 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 comparatively 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 growing interest in the use of natural 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 re- sources with the potential to reduce the use of conventional plastic goods. It is reasonable to suppose that plasticizers for biopolymers should preferably also be bio- degradable (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), intensifying 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 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 plays a very important role for effective plasticization. This effective 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 ''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 al- lowed to develop ultimate properties of strength and integrity. Hot compounding includes calendering, 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 separa- tion 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).

Classification: PLASTICIZERS

In polymer science, plasticizers can be broadly categorized 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 any type of primary or weak bonds and can, therefore, can be easily removed or eliminated 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 and complex structures that provide polymers with more space to move around and prevent polymers from coming close together. Therefore, they soften polymers by lowering the glass transition temperature (T_g) and, thus, reducing elastic modulus. Although both types of Plasticizers are important but more prominent and strong are 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 comparatively 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). For Bio-Polymers based films plasticizers can be categorized as 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 con- centration 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 in- creased. Complete uptake of insoluble plasticizer by the polymer can be achieved by an optimum stirring rate of the polymeric dispersion with the plasticizer (27).

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 prod- ucts. 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 consti-tute more than 85% of the total plasticizer consumption. Most of them are based on carboxylic acid esters with lin- ear or branched aliphatic alcohols of moderate chain lengths (predominantly C6–C11) (3). In relation to the clas- sic plasticizers, the phthalate esters (6,11,28), adipates (29), citrates (11) besides acids esters, alkane-dicarboxylic, glycols and phosphates are used.

Biodegradable polymers: Sources and classification

Biodegradable polymers can be classified in four catego- ries depending on the synthesis and on the sources (30–32):

Polymers from biomass such as the agro-polymers from agro-resources; polysaccharides, e.g., starches (wheat, potatoes, maize) (20,33,34), ligno-cellulosic products (wood, straws, .. .) (35) and others (pectins, chitosan/chitin, gums) (36), protein and lipids, e.g., animals (casein, whey, collagen/gelatin) (37–48), and plants (zein, soya and gluten) (49,50), polymers obtained by microbial production, e.g., polyhydroxyalkanoates (PHA) such as poly(hydroxy- butyrate) (PHB) and poly(hydroxybutyrate co- hydroxyvalerate (PHBv); polymers chemically synthesized using monomers obtained from agro-resources, e.g., poly(lactic acid) (PLA); polymers whose monomers and polymers are both obtained by chemical synthesis from fossil resources, e.g., polycaprolactones (PCL), polyestera- mides (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-poly- mers and the others are called biodegradable biopolyesters (50). Synthetic polymers are gradually being replaced by biodegradable materials especially those derived from nat- ural resources, due to its biodegradability. Recent innova- tions in edible and/or biodegradable polymer films are widely discussed in the literature (32), presenting improvements in food packaging, surgery, pharmaceutical uses.

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, O_2 and CO_2 permeability), structure resistance to water and sensorial acceptance. These characteristics are greatly influenced by parameters such as the type of mate- rial 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.). The dehydration of these structures produces strong cohesive films that usually require plasticizers. The addi- tion 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 flexi- bility, decrease brittleness and avoid shrinking during han- dling and storage (30). 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 charac- teristics 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 addi- tion of plasticizers for better workability (58). Above a crit- ical concentration, the plasticizer can exceed the compatibility limit with the biopolymer, and phase separa- tion with plasticizer

exclusion is usually observed. Recently, many studies have focused on the use of polyols such as GLY (17,33,36,38,39,47), ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol and polyethylene glycol (PEG) (16,36,39,41), propylene glycol (PG), sorbitol mannitol and xylitol; fatty acids (20,45); monosaccharides (glucose, mannose, fructose, sucrose) (41); ethanolamine (EA) triethanolamine (TEA) (39); vegetable oils; lecithin; waxes (20); amino acids; surfactants and water (17) as plasticizers of edible and/or biodegradable films. The basic materials used to form edible and/or biode- gradable films are polysaccharides, proteins and lipids com- pounds. 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 edi- ble films for their excellent moisture barrier properties, but they can cause textural and organoleptic problems. In the last years, several studies have been dedicated to form composite films, combing one or several lipid compounds with one hydrocolloid-based structural matrix. In this context, this paper aims to highlight some develop- ments regarding the use of natural plasticizers currently used in polysaccharides-, proteins-, lipids-films and other films obtained from microbial sources.

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-glu- can), 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 hydro-philic nature, they are poor water vapor barriers. Among polysaccharide and biopolymers in general, starch is con-sidered to be one of the most promising materials for use in biodegradable plastics. 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 plast-icizers and commercial fibers by conventional extrusion and injection molding techniques. Hydrophilic compounds, such as polyols (GLY and sorbi- tol) are commonly used in starch films, but some sugars, surfactants, amino acids and fatty acids could also be employed to improve their mechanical and barrier proper- ties. 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.

Overcoming the brittleness of starch while achieving full biodegradability in blends, can be accomplished with the addition of biodegradable plasticizers. An ideal plasticizer for starch-based materials should impart flexi- bility and suppress retrogradation to thermoplastic starch (TPS) during aging (34). The crystallization of GLY-contain- ing potato starch plastic sheets revealed a significant influ- ence on their mechanical properties. The changes in crystallinity were clearly related to the initial amount of plasticizer and moisture migration during aging. The dif- ferences 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. 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

Different plasticization systems for starch acetates (caproic acid, lauric acid and glycerol triacetate (triacetin) were prepared to investigate internal and external plasti- zation of starch acetates. The presence of fatty-acid es-ters 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), aim- ing at reducing water vapor and gas permeability of films. Plasticizer addition improved starch-based coatings per- formance by increasing barrier properties to water vapor, maintaining the selective gaseous permeability. GLY and sorbitol showed to be compatible with amylose and im- proved mechanical properties of films, by decreasing inter- molecular 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 amy- lopectin 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.

Plasticizers containing amide groups (urea, formamide and acetamide) were tested for TPS plasticization, using GLY as a reference. Amide groups seem to have an interest-ing effect on TPS retrogradation suppression. The effects of TPS films on mechanical properties and retrogradation were observed to rely mainly on the hydrogen bond-form- ing ability between plasticizers and starch molecules, increasing in the following order urea > formamide > acet- amide > 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 has been extensively investigated. Plasticizer concentration and hydrophilic nature were found to be important factors in determining the moisture affinity of cassava starch films. 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 amylo- pectin chains, which overcame the opposite effect of re-crystallinization, 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. The properties of biodegradable oat starch films, com- bined with different plasticizers. Hydrophilic plasticizers (GLY, sorbitol and urea) increased the permeability and water sorption properties of biodegradable oat starch films. without changing their mechanical properties. In an- other study, the same research group investigated the ef- fect of sucrose and a mixture of GLY/sorbitol, besides GLY, urea and sorbitol as plasticizers on the microstruc- ture, moisture sorption, water vapor permeability and mechanical properties of oat starch

films kept at different relative humidity conditions. 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 plasti- cizer adsorbed less water and showed higher water vapor permeability, indicating the antiplasticizing effect. Other study also investigated the effect of sucrose or inverted su- gar addition on mechanical properties, hydrophilicity and water activity of cassava starch films was studied. 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 substi- tution 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 appli- cation 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. Fur- thermore, 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 incorpora-tion of GLY and sorbitol did not significantly reduce film tensile strength, but enhanced their flexibility and extensi- bility (17).

Surfactants could also be incorporated into film formu- lations in order to reduce the surface tension of the solution, improving the wettability and adhesion of plasti- cized film. The surfactants Tween 20, Span 80 and soy lecithin and GLY were used as a plasticizer in potato starch films. 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 ten-sile strength and higher elongation at break and higher water vapor permeability). Tween exhibited the most in- tense synergistic effect with GLY. Cellulose acetate films could be prepared through acet- ylation of cellulose from sugarcane bagasse (35). The hemi- cellulose content (5%) present in bagasse was used as an internal plasticizer of the acetate cellulose films. Further- more, residual xylan acetate acted as a plasticizer for cellulose acetate and films exhibited good mechanical properties without addition of an external plasticizer.

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 poten- tial (41). Protein-based edible films can form bonds at different positions and offer high potential for forming numerous linkages (40). 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. Oleic and linoleic acids were added as plasticizers resulting in flexi- ble sheets of high clarity, low modulus, and high elonga- tion 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 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 signifi- cant differences in film properties when were introduced at the same molecular concentration due to structural sim- ilarities between sorbitol, GLY and sucrose. GLY was used as plasticizer for fish protein films, reduc- ing opacity, color and T_g (43). Similarly, another study ver- ified that an increase in plasticizer (GLY and PEG) concentration decreased the tensile strength with a con- comitant 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 bond- ing 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). b-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, produc- ing 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. The thermal and functional properties of pig skin gela- tin-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 proper- ties, 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). 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 plasti- cizers 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 re- cently motivated research in various academic and indus- trial 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.

CONCLUSION

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 tox- icological performance will become increasingly stringent. As such, low volatile plasticizers, preferentially new fami- lies 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 mate- rial 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.

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