Review Article

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Role of plasticizers in bioplastics

Abstract

Currently, a variety of petroleum based plastic materials are dominating the packaging industries owing to their durability, versatility, light-weight and most importantly their cost-effectiveness. This trend is being overcome by the growing concern towards environmental pollution caused by the production as well as the disposal of these materials and the presence of toxic substances that could migrate from the packaging material to the product causing potential risk to human health while using the product. Biopolymers, is a promising green alternative to synthetic, non-degradable polymers. These natural polymers (polysaccharides, proteins and lipids) are much more suitable components for food as well as non-food packaging applications due to their qualities of renew-ability, degradability and edibility. However, poor water vapour barrier properties of carbohydrates (polysaccharides) and proteins, and low elasticity of lipids are the main limitations for their use as commercial packaging materials. In this regard plasticizers provide the necessary workability to biopolymers. This review gives a brief insight into their plasticization effects, types, properties along with their effect and recent applications on bio-based materials, with special reference to a new class of plasticizers, Ionic liquids.

Keywords: degradability, elasticity, plasticizers, Ionic liquids, biopolymers

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Introduction

Over the last few years, there has been a gradual shift in focus from petroleum based plastics to biopolymers. Though, biopolymers are considered best biodegradable and green alternative, they still have a long way to go in terms of various characteristics to be able to replace plastics in market. The fragility and brittleness exhibited during thermo-formation leads to poor mechanical properties with regards to process-ability and end-use application thereby limiting their potential for various packaging applications. In order to overcome this limitation of biopolymers, the use of various types of plasticizers has gained momentum quite recently. Plasticizers have been widely used in the modification of polymers since the early 1800s. These are a class of low molecular weight, relatively non-volatile organic molecules that improve workability and durability of polymers since they help in the reduction of polymer-polymer contact leading to decrease in rigidity of the three dimensional structure of polymers thereby enhancing the deformation ability without rupture.[1]

Plasticization

In general, this process denotes a change in the mechanical and thermal characteristics of a polymer, involving:[2]

a. lowering of inelasticity at room temperature
b. lowering of temperature- at which substantial distortions can be achieved without needing enormous forces
c. enhanced elongation to break at room temperature
d. increase in impact strength (toughness) to the lowest temperature of serviceability

These characteristics can be accomplished via: external and internal plasticizers, as well as, primary and secondary plasticizers.[3]

External and internal plasticizers

External plasticizers are low volatile constituents added to polymers. These plasticizers are not chemically attached to polymer chains by primary bonds, although, there is interaction between the two. Since they are not chemically bound they are easily lost by extraction, migration or evaporation. Conversely, internal plasticizers are integral part of the polymer chain, which can be either be reacted with the native polymer or co-polymerized into the polymer arrangement. These plasticizers eventually become a part of the final product. The bulky structure of the internal plasticizers offer more space for the polymers to move and also prevents them from coming close together, thereby softening the polymers by reducing the glass transition temperature (Tg) and ultimately elastic modulus. Although, more prominent for internal plasticizers, a strong temperature dependence of material properties is observed for both internal as well as external plasticizers. Compared to internal plasticizers, the use of external plasticizers gives the opportunity to choose the right material according to the desired product properties.[1,3]

Primary and secondary plasticizers

When a polymer, at high concentration, is soluble in a plasticizer, it is considered as a primary plasticizer. These plasticizers gel the polymer rapidly in the normal processing temperature range are considered the sole plasticizer or as the core component of the plasticizer and they should not leach out from the plasticized material. Whereas, secondary plasticizers have restricted compatibility with the polymer and reduced gelation capacity. They are, generally, combined with primary plasticizers to reduce the cost or improve product properties.

The first successful class of plasticizers to be used, dating back to the 1920s, were phthalic acid esters or phthalates. The most commonly used phthalates are di(2-ethylhexyl) phthalate (DEHP), diisodecyl phthalate (DIDP), and diisononyl phthalate (DINP), which have been used until recently. However, the use of phthalates is now regulated and restricted in various products when found to be toxic to human health as well as environment due to their migration ability.[4]

Properties of plasticizers

Typically, plasticizers have linear or cyclic carbon chain with an average molecular weight of 300 to 600. These are high boiling point liquids with a low molecular size that helps them to penetrate into the intermolecular spaces in the polymer chains leading to lowering of secondary forces between the chains. This changes the three- dimensional network of the polymer chains which eventually gives higher mobility by increasing the free volume. Therefore, the chemical structure of the plasticizer along with the molecular weight, functional groups, chemical composition plays a vital part in deciding the degree of plasticity of polymers.[3]

The compatibility factor between the system that is the plasticizer and the polymer is of paramount importance which signify a key role in various parameters such as solubility, polarity, dielectric constant and hydrogen bonding.[3]

As commonly desired, plasticizers should have low vapour pressure and diffusion rate into the polymers. This permanence of plasticizers is related to volatility and resistance to migration and extraction in water, oil or any other solvents.[2,3]

Another important factor is the ease or difficulty in processing the polymers, which is majorly tackled by addition of plasticizers. The plasticizer concentration and type not only aid in modifying the properties of the polymer but also influence processing ability by reducing viscosity, heat generation and power consumption and enhance dispersion and flow characteristics.[1,3]

Specific to bio-based coatings and films, plasticizers aid in reducing brittleness/ fragility and enhance flexibility in films making them easier to handle, along with preventing cracks and pores in them.[2]

Overall, the selection of plasticizer for a particular polymeric system depends on their compatibility with each other, desired characteristics of the final product, plasticization properties, migration/ permanence, toxicity and cost.

Plasticization of bio-based materials

The need for low migration as well as low toxicity is now of paramount importance while choosing a plasticizer. Keeping in view the safety concerns as well as biodegradability, new alternatives to the conventional plasticizers are being explored. With respect to, biopolymer-based films, they can be categorised into water soluble and water insoluble plasticizers. The nature of the plasticizer and its amount can vastly affect the film formation from polymeric aqueous dispersions.[2] Based on the nature of the plasticizers; they are classified into two categories: hydrophilic and hydrophobic plasticizers. Hydrophilic plasticizers when added to polymer dispersions dissolve in the aqueous medium such as glycerol, polyethylene glycol (PEG), ethylene glycol. They can lead to enhanced water diffusion in the polymer if added in higher concentrations. Hydrophobic plasticizers such as phenyl ethers, citrate esters, phenyl ester, stearyl esters, on the other hand, can lead to a decrease in water uptake as they close the micro-voids in the films.[3]

Applications of various bio-based plasticizers

Majority of bio-plastics are starch-based biopolymers which are storage polysaccharide of cereals, legumes and tubers and widely available. For processing of starch, flexibilizer and plasticizer such as sorbitol and glycerine are added. After addition of plasticizers and application of thermal and mechanical energy, these constitute thermoplastic starch (TPS) which could be used as a substitute for polystyrene (PS). Starch works as an effective packaging material when it is modified to form films that provide adequate mechanical properties of high percentage elongation, tensile and flexural strength. Starch can be modified by either plasticization, blending with other materials, genetic or chemical modification or combinations of different approaches.[5]

Biodegradable films based on starch, sodium caseinate, glycerol and lipids (oleic acid and/or a-tocopherol) have been formulated and evaluated in terms of microstructure, mechanical behaviour, barrier and optical properties and antioxidant capacity. The effect of film storage time on these properties was also analysed.[6] Physical and mechanical properties of edible films based on blends of sago starch and fish gelatin plasticized with glycerol or sorbitol have been investigated by.[7] The thermo-mechanical properties and oxygen permeability of sorbitol–starch–water films have been studied by.[8] The effect of plasticizers, glycerol, sorbitol and poly(ethylene glycol) 400 (PEG 400), on mechanical and barrier properties of rice starch film have been investigated. Sorbitol and glycerol-plasticized starch films appeared homogeneous, clear, smooth, and contained less insoluble particles compared to unplasticized rice starch films.[9] Another study investigated effects of plasticizer (sorbitol) contribution on structural, barrier and mechanical properties of corn starch-based edible films.[10] In a recent study, films from jackfruit seed starch have been developed with glycerol having low opacity, high mechanical characteristics and average water vapour permeability.[11] In another study, aliginate films with glycerol, tributyl citrate (TC) and their blends have been made wherein films with glycerol were less hygroscopic when compared to films with TC or their blends. Meanwhile films with TC and their blends had were observed to be opaque and less homogenous in structure.[12] Cassava starch and lentil protein based films have been developed with glycerol as plasticizer, which showed reduced water vapour permeability and improved breaking resistance due to extrusion.[13] Elephant foot yam starch, whey protein concentrate and *psyllium* husk have been used to prepare biodegradable films wherein glycerol, used for plasticization, overcame the imperfections in physicochemical, mechanical, barrier, surface morphology, optical and thermal properties. These composite films had lower water vapour permeability, higher tensile strength and uniform structural integrity as compared to the control films having only the starch component.[14]

Ionic liquids

Ionic liquids (ILs) are organic salts that are liquid at ambient temperatures, preferably at room temperature (RTIL – room temperature ionic liquids). These are composed of large organic cations and small inorganic or organic anions. Room temperature ionic liquids have emerged as a new class of solvents with a unique combination of low volatility, chemical stability, high conductivity, and wide electrochemical window, ability to dissolve organic and inorganic solutes and gases, and tunable solvent properties. Due to these unique properties and their toxicity profile ranging from low to hazardous, ionic liquids are finding applications in varied arenas, such as in biological processes development (biotransformation processes, as active pharmaceutical ingredients, for lignocellulosic biomass and cellulose dissolution); in extraction, separation and absorption of biomolecules, rare earth, vinyl chloride; in preparation of nanomaterials; in modifications of wool; as herbicide, fungicide and plant growth regulators; and as plasticizers in plastics (PMMA, PVC).[15–17]

Ionic liquid as plasticizers

Another class of plasticizers, gaining momentum nowadays, is Ionic liquids that contribute to flexibility and easy process-ability of films owing to their unique physicochemical properties. Application of imidazolium ionic liquids as plasticizers for poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) has been observed.[18] Ionic liquid plasticizers have displayed much less tendency for leaching and excellent migration resistance.[16] The plasticisation effect of the ionic liquid, 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]), as compared with the traditionally used plasticiser, glycerol, on the characteristics of starch-based films were studied.[19] In another study an ionic liquid (1-butyl-3-methyl imidazolium chloride [BMIM]Cl) was used as a plasticizer in starch, zein and their blends; and compared to glycerol. The characterization of the materials indicated that, compared to glycerol, the use of [BMIM]Cl led to less hygroscopicity, a more efficient plasticization of both starch and zein phases and a compatibilization of starch/zein blends.[20]

Conclusion

The recent sanctions on single use plastics have led to the search for its alternative having properties at least at par if not better. The best way forward, for now, seems to be bio-based polymers that are naturally derived polymers and inherently have film forming characteristics. These characteristics, however, do not match the required propositions as successfully taken care of by plastics. Therefore, it becomes essential to use other processing additives that provide the necessary features to form a usable and commercial product, making the use of plasticizers fairly indispensable. Plasticizers not only make the films more handle-able but also impart and improve properties that are weak or not at all present in the native polymer. However, their migration ability and toxicity range needs to be scrutinized before their large scale applicability. In this scenario, although at the infancy stage of research, ionic liquids present themselves as the ideal option with low migration property and toxicity levels. Proper study of their interaction with biopolymers and environment focussing on their biodegradation ability is of paramount importance for their commercialization. Moreover, further investigation and research, with regards to acute and chronic effects to human health, is required for this class of plasticizers in combination with biopolymers, especially for their applications in food industry.

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Conflict of interest

The authors declare that there was no conflict of interest.

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