Petro-Based and Bio-Based Plasticizers: Chemical Structures to Plasticizing Properties

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ABSTRACT: Polymeric materials, in particular PVC, can find various industrial utilizations thanks to the use of plasticizers added during their processing. The most famous applications include wires and cables, coatings, flooring, paintings, packaging... After some generalities concerning plasticization theories and the description of plasticized petro- and bio-based polymers, this review details the well-known different petro-based plasticizers and more particularly phthalates which represent the most important category of PVC plasticizers. Owing to migration problems, impact on the human health and the environment, alternative candidates have been developed by researchers. Renewable resources and their wastes offer a large platform for the design of bio-based plasticizers using polysaccharidic or lipidic structures. In an in-depth analysis, the bio-based plasticizer structures, their groups and substituents (ester groups, alkyl chains, aromatic rings...) are gathered and examined in order to be able to predict their plasticizing efficiency and design new molecular and macromolecular plasticizers from natural resources. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *54*, 11–33

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INTRODUCTION The number of industrial polymers is limited compared to the millions of organic compounds available. To extend the number of polymers and respond to the very large scope of applications, plastics were modified by various additives. For instance, rubber was stiffened by Goodyear applying crosslinking using sulphur under the denomination of vulcanization. Other properties including flame retardancy, UV protection, and electrical conductivity may be added. Plasticizers represent the most common plastics additives[1] (Global volumes about 10 billion lb and valued at about $5 billion). They make polymers more flexible and ease their processability. In the 1800s, the first example concerned the plasticizing of celluloid or celluloid lacquers using natural camphor and castor oil[2] as illustrated in Figure 1. In the early 1900s, triphenyl phosphate substituted the camphor oil. This molecule was a significant turning point that led to ester based plasticizers.[2] Phthalic acid esters also named phthalates found applications as plasticizers for the first time in 1920 and are still running the largest class of plasticizers in the 21st century and particularly for PVC.[3] Before World War II, most plasticizers were used for coatings and safety glasses. However, during the war, the demand in high performing plastics and plasticized plastics increased.[4] In 1968, 550 plasticizers were listed. Nowadays, only around 60 of them are really employed.[5,6] During the last decade, the worldwide production of plasticizers was around 6,4 million tons per year,[7] 1, 0.8, and 3.5 million of which in Europe,[7,8] North America,[7] and Asia,[7,9] respectively. The global annual demand for the plasticizers market is projected to exceed more than 13.2 million tons per year till 2018.[10] The search for new plasticizers stays a current goal to satisfy the numerous applications of plastic products.

Nevertheless, concerns and controversy have been raised regarding the use of common plasticizers, and more specifically phthalates. They exhibit a migration phenomenon toward elements in contact with them (medical and childcare articles). Moreover they are suspected to produce bioaccumulation in the environment[11,12] justifying restrictive regulations in several countries about the use of phthalates as plasticizer for flexible PVC (polyvinyl chloride) products.[13] Both European and American regulations define six banned phthalates derivatives[14] (diethylhexyl phthalate (DEHP), dibutyl phthalate, benzyl butyl phthalate, diisobutyl phthalate (DIBP), di-isodecyl phthalate, and di-*n*-octyl phthalate) for content above 0.1 wt %.[15] With the growing interest for plasticizers with low migration levels and low toxicity as an alternative to phthalates,[16] researchers are paying more attention to bio-based plasticizers (*a priori* less toxic) made

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from vegetable oils, citrates, and sugar derivatives able to plasticize either petro- or bio-polymers.[17]

In this review, some generalities about the plasticization theories will be briefly reported before describing the plasticized petro- and bio-based polymers. The historical petro-plasticizers will be then described before focusing on the more recent bio-based plasticizers having polysaccharide, lipid and sugar structures. Some molecules can directly be used without prior modifications (e.g., water, glycerol, and cardanol) whereas others need chemical modifications for better compatibility with polymeric matrices (vegetable oils

and sugar derivatives). In an in-depth analysis, the petro- and bio-based plasticizers structures were analyzed in terms of groups and substituents (ester groups, alkyl chains, aromatic rings...) to find a relationship between the structure and the plasticizing efficiency. The ultimate goal is to be able to design bio-based molecular and macromolecular plasticizers for an optimum plasticizing efficiency.

GENERALITIES ABOUT PLASTICIZERS

According to the IUPAC council, a plasticizer is defined as "a substance or a material incorporated into a plastic to
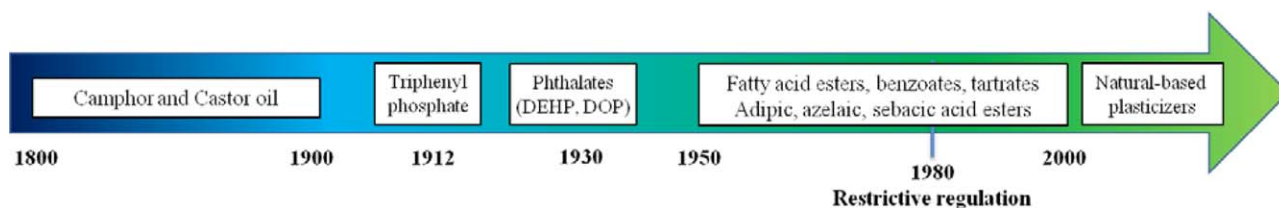
FIGURE 1 Evolution of plasticizers.

increase its flexibility, workability or distensibility."[6] Nevertheless numerous other definitions of plasticizers are based on the molecular weight, the nonvolatile character of the compounds…. Plasticizers include many organic compounds: oil derivatives, animal fats, vegetable oils, and so forth described later in this review.

Main Functions Performed by Plasticizers

The primary role of plasticizers is to enhance the flexibility[18] and the processability of polymers by decreasing the glass transition temperature (Tg).[19] Plasticizers allow processing on different types of equipment (injection molding, extrusion, calendering), optimizing experimental parameters, shortening the mixing time, and the pressure of extrusion. They also reduce physical properties like hardness, elastic modulus, and increase fracture and impact resistance. Viscosity, density and dielectric constant are also impacted by the polymer chain flexibility.[20] Numerous other properties are affected by the use of plasticizers: crystallization, melting and gelation temperatures, interactions with water, fire behavior, gas permeability, degradation rate…[3]

Plasticizing Theories

The first plasticization theories were developed in 1930–1950. Three of them are still used nowadays: the lubricity theory and the gel theory that were developed in a parallel way, and finally the free volume theory[3] which originated some years later than the other two (Fig. 2). In general it is recognized that the low molecular weight of a plasticizer allows reducing secondary forces (hydrogen bonding, van der Waals forces…) between the polymer chains by occupying intermolecular spaces. Thus, plasticizers change the three-dimensional molecular organization of polymers, decreasing the energy required for molecular motion. The lubricity theory provides that the plasticizer diffuses into the polymer, inserting into the polymer chains and reducing the intermolecular frictions. The macromolecules slip over each other when a plastic part is flexed. Then, the plasticizer lubricates the movement of the molecules reducing their internal resistance to slide and to prevent the re-formation of the rigid matrix. Thus, according to this theory, a plasticized plastic can be represented as parallel alternating layers of polymer and plasticizer.[3,21] The gel theory is based on the assumption that the plasticized polymer is considered to be a three-dimensional network with plasticizer molecules bonded to resin chains by weak secondary forces. The plasticizer acts by breaking the polymer–polymer bonds and interactions, masking these centers of attachment from each other and preventing their reformation.[3,21] To sum up, the lubricity theory assumes that the rigidity of polymers comes from internal frictions and that plasticizers act by lubricating the layers of polymer whereas the gel theory supposes that
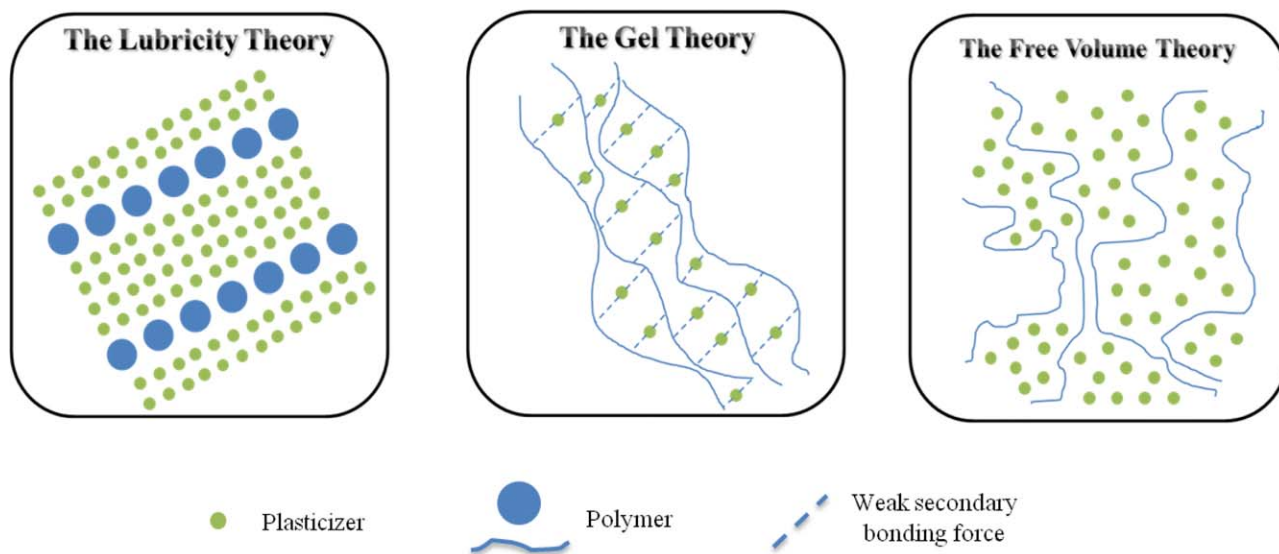

FIGURE 2 Mapping of plasticization theories.

it comes from points of attachments of polymer to polymer and that plasticizers reduce the number of these sites. The free volume is the internal space available within a polymer. A rigid polymer possesses very little free volume. When a plasticizer is added, it increases the free volume making the polymer soft and rubbery, increasing motion of polymer molecules. This free volume is maintained when the resin-plasticizer mixture is cooled down after melting. Free volume comes from three principal sources: motion of chain ends, motion of side chains and motion of the main chain.[3,21] The free volume theory allowed Chandola and Marathe to predict the behavior of 25 PVC plasticizers.[22] This theory is the one giving more precise explanation on plasticization since it is based on relationships between properties (specific volume, viscosity…) and variables (molecular weight, terminal groups content…) of polymers that were not yet explained at the time the other two theories appeared.

Plasticizer Classifications

Plasticizers can be classified according to several categories. First of all, they can be defined as internal or external.[19] An external plasticizer is a low volatile substance added to a polymer without any chemical bonds with the polymer chains; only secondary interactions maintain the additive in the matrix. Even though these plasticizers can be lost by migration, evaporation, or extraction phenomena, this type of plasticization is the most widespread. Internal plasticizers are chemically attached to polymer chains by primary bonds according to copolymerization or reaction with the initial polymer. The presence of internal plasticizers dangling in the matrix decreases the Tg. For example, Ding et al. grafted a polymeric plasticizer (an acrylic copolymer) onto LDPE in order to change the rheological properties.[23] Zhang and Fang introduced internal plasticizer based on poly(ethylene oxide) (PEO) onto polydimethylsiloxane (PDMS) using hydrosilylation reaction.[24] This chemical approach of plasticization is less common and will only be briefly described in this review.

Another classification splits the plasticizers into two classes: primary or secondary.[19] A plasticizer needs to gather all the following requirements to be defined as primary: (i) be totally soluble in the polymer even at high concentration, (ii) not exude from the final material, (iii) be used as the single plasticizer. On the contrary, secondary plasticizers lead to a slow gelation process, have limited compatibility with the polymer and exude or cause surface tackiness if used in excess. They are often used in addition to primary plasticizers to reduce cost or to improve product properties.

A last classification system categorizes plasticizers for biopolymer-based films as water soluble and water insoluble.[25] Polymeric aqueous dispersions (polymer in water) are used in various applications such as adhesives, inks, paints, coatings, and so forth.[26] Thus, water-soluble plasticizers can dissolve a polymer in the aqueous dispersion. At high concentration it increases the water diffusion in the polymer.[19] During plasticization, the plasticizer diffuses into the colloidal polymer particles, with a diffusion rate depending on its water solubility and affinity for the polymer phase.[27] On the other hand, with water-insoluble plasticizers, a three-phase system is formed, composed of the water phase, the polymer particles and the emulsified droplets. During plasticization, the plasticizer diffuses from the emulsion droplets through the water phase and is absorbed by the polymer.[27]

PLASTICIZED POLYMERS

Plasticizers were applied to 60 polymers and more than 30 groups of products.[3] The most common plasticized polymers are based on polyvinylics, acrylics, cellulose compounds and polyamides. Some polymers like elastomers, polyurethanes are intrinsically flexible whereas others cannot be plasticized owing to a high crystallinity rate preventing the spreading of the plasticizer into the amorphous phase (polyolefins for instance).[28]

Petro-Based Polymers

This class of plasticized polymers includes poly(vinyl alcohol) (PVA), poly(vinyl acetate) (PVAc), poly(vinyl butyral) (PVB), poly(vinylidene chloride) (PVDC) and particularly poly(vinyl chloride) (PVC) which is the most widespread plasticized polymer with about 80% of all plasticizers consumed (88% in Europe and 85% in North America).[14] PVC is one of the most common thermoplastic materials applied in packaging, toys, wire and cables, clothes and healthcare devices.[29] Its inertness, high transparency, facility of sterilization and strength make it an interesting candidate for the medical market. However, the inherent rigidity of PVC precludes certain applications. Thus, the PVC market is divided in 70% for rigid materials and 30% for soft and flexible ones (P-PVC). The most widely used PVC plasticizers are phthalates, particularly DEHP which dominates the market. Other types of plasticizers are used according to requirements related to properties (low temperature (dihexyladipate), flame retarding (isopropylphenyldiphenyl phosphate),[30] etc). Epoxidized soybean oil (ESBO) stays an important plasticizer in many formulations due to its dual role as plasticizer and stabilizer[13] whereas trimellitates seem to gain more applications in the medical field owing to their biocompatibility. The American company Eastman also produces a large range of PVC plasticizers from benzoates, under the trade name Benzoflex®.

PVDC is another plasticized chlorinated polymer, often blended with PVC for food-grade overwrapping or rewrapping with flexible films. Citrates,[31] polyadipates, and trimellitates[32] are used in PVDC/PVC films.

The plasticization of PVB is mainly performed by adipates (dihexyl, hexyl, and cyclohexyl), sebacates (dibutyl), and glycol esters [polyethylene glycol and triethyleneglycol di-(2-ethylhexanoate)].[17,33] They are used in extrusion throughput processes where a low viscosity is required. In the case of PVA, water-soluble plasticizers are used (ethylene and propylene glycol, glycerine, and soy lecithin) for improvement of film flexibility, gas permeability, and biodegradability.[34] The
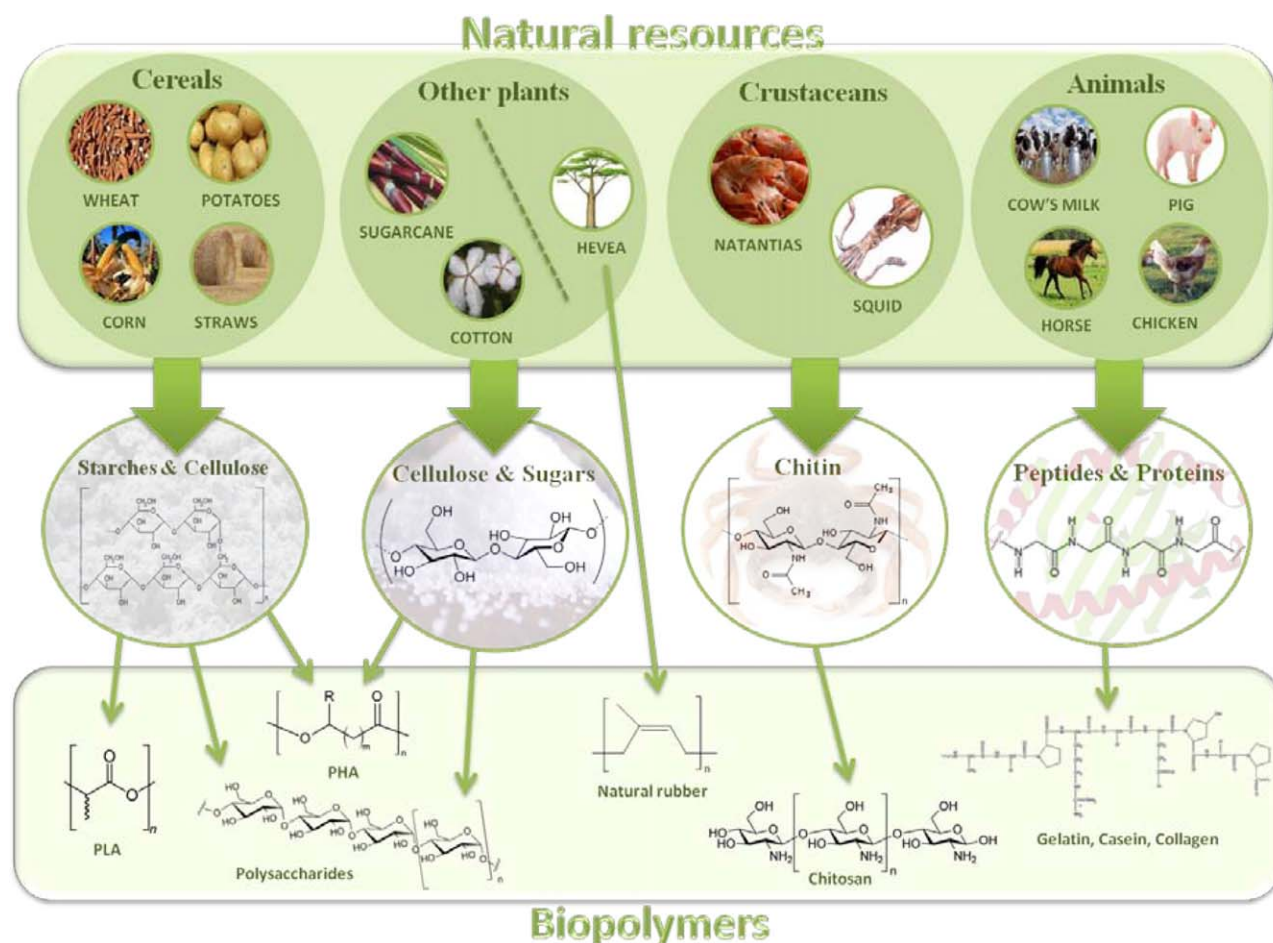
FIGURE 3 Overview on the biopolymers and their natural origin.

last polyvinylic is PVAc which can be "self-plasticized" by a partial hydrolysis or by the use of phthalates, citrates, and water-soluble plasticizers containing ethylene and propylene glycol and glycerine.[35]

Among acrylics, poly(butyl methacrylate), poly(ethyl methacrylate), and poly(methyl methacrylate) (PMMA)[36] are frequently plasticized with phthalate and adipates to produce sealants, adhesives and coatings.

Semicrystalline polyamides (PA6, PA6,6, PA11, and PA12) can be modified by sulfonamides[37] or benzoates in order to improve fatigue resistance, toughness or impact strength.[38] These plasticized thermoplastics are most often applied in electric cables or hot melt adhesives.

Many other polymers are plasticized by bio-based or petro-based plasticizers. These polymeric materials ranged from elastomers[39] (EPDM, nitrile rubber, polybutadiene, etc), olefins, cyanoacrylates, polyurethanes, polycarbonates, silicones, polyesters (polylactide,[40] poly(3-hydroxybutyrate), perfluoropolymers,[41] bio-based polymers (protein, chitosan, starch, natural rubber,) to thermosets (epoxy resins).[42]

Bio-Based Polymers

Bio-based polymers come from various natural resources ranging from animals (pig, cow's milk...), crustaceans (squid, natantias) to cereals (wheat, corn, straws...) and other plants (cotton, sugarcane, hevea) as illustrated in Figure 3. From these natural resources, biopolymers are directly extracted while other biomolecules need some chemical modifications to produce biopolymers. Thus, peptides, proteins, natural rubber (latex), and polysaccharides (starches, cellulose, chitin and sugars) are directly obtained from natural resources. These macromolecules then lead to chitosan, gelatin, casein, and collagen that can be used as biopolymers. On the other hand, biopolymers such as poly(lactic acid) (PLA) and poly(hydroxyalkanoate)s (PHA) are produced starting from biomass under bacterial fermentation, for instance.

Polyesters: Poly(Lactic Acid) and Poly(3-Hydroxybutyrate)
Poly(Lactic Acid)

PLA is nowadays the most famous environmentally friendly polymer. Its production and consumption drastically increased and it is now a competitive material applied in

convenience products but also in high value niche markets. PLA exhibits excellent optical properties and high tensile strength. This biodegradable polymer (polymer degraded by the action of microorganisms and/or enzymes) derives from various renewable resources such as corn-starch and can also be obtained by synthetic route (ring-opening polymerization of lactide for instance). Physical properties of PLA depend on the ratio of L- to D- isomers in the backbone. Poly(L-lactic acid) (PLLA) is a semicrystalline material with a melting point close to 170-180 °C and a Tg around 60 °C whereas copolymers from L- and D- monomers can be totally amorphous materials according to the ratio of the two monomers. The high crystallinity of PLLA leads to rigid materials. The plasticization by its own monomers (lactic acid,[43] lactide and PLA oligomers) was investigated. These additives improve ductility, exhibit good stability to storage and lead to materials adapted to food packaging.[44–46]

PEO[47,48] (the most popular plasticizer for PLA) or PPO oligomers and their copolymers were described as plasticizers.[49] In the case of PPO, an easier plastic deformation was observed.[50,51] Diethyl adipate,[52] acetyl triethyl, triethyl, tributyl citrate, or acetyl tributyl citrate[52,53] have also been described and were efficient in reducing Tg values.

Vegetable oils and lipidic derivatives such as fatty acids have been extensively used in the area of processing. These natural oils improve the ductility of the materials up to 200% at a plasticizer loading of 5 wt %.[54–57] Some authors explained this by possible hydrogen bonding between PLA and oxirane groups.

Polyesters coming from adipic or succinic acid such as poly(diethylene glycol) adipates, poly(diethylene glycol-co-neopentylglycol) adipates, or poly(butylene succinate)[58] are reported to be good PLA plasticizers giving high impact strength as well as break strain close to 480%.[59] However, it must be pointed out that these compositions are similar to binary blends and not to usual plasticized polymers where the plasticizer is used in a minor content.[48,59,60] Finally, some malonate oligo(esteramide)s have shown a plasticizing effect leading to flexible films. However, thermal annealing of the material favors the phase segregation.[61]

Other molecules like glycerol,[62,63] glycerol triacetate (triacetin), and malonates have been described in the modification of PLA. Diethyl bishydroxymethyl malonate drastically decreased the Tg of PLA, but the blends showed no morphological stability over time.[61,64,65] Finally, some commercially available plasticizers are specially dedicated to PLA like Hexamol® DINCH (1,2-cyclohexane dicarboxylic acid diisononyl ester)[66] or Lapol 108.[67,68]

Poly(3-Hydroxybutyrate)
Poly(β-hydroxyalkanoate)s (PHA), obtained from sugar, are the most advanced materials for biodegradable or biocompatible items. Poly(3-hydroxybutyrate) (PHB) is one of the well-studied polymers since its properties can be compared to that of some degradable oil-based polyesters. However, still too expensive, poly(3-hydroxybutyrate)-co-poly(3-hydroxyvaler-ate)s (PHBV) are preferred. Choi and Park tested ESBO and triethyl citrate as plasticizers and showed that they decreased the Tg of PHBV, with greater effect for triethyl citrate.[17] Yoshie et al. showed that adding small quantities of low molecular weight molecules (dodecanol, lauric acid, tributyrin and tri-laurin) results in a plasticizing effect and an improvement of biodegradation.[69] Polymeric additives like PEO were revealed to be efficient.[70–72] Unfortunately, a variation of the performances in respect with time was observed. PEO increases the rate of biodegradation whereas a less hydrophilic additive like oxypropylated glycerine diminishes it. Triacylglycerols with short linear chains (glycerol triacetate, glycerol tripropionate, glycerol tributyrate) and monoacylglycerols with a long alkyl chain (glycerol monostearate) act as plasticizers with PHB. Finally, glycerol triacetate (GTA) seems to be the best plasticizer for PHB with a Young's modulus decreased from 1620 to 280 MPa.[73]

Polysaccharides
Starch
Starch is a very abundant material extracted from plants such as wheat, potatoes, maize, rice, and so forth. The European production is of about 8 million tons per year and the main use concerns the food industry where starch is used as additives. Starch is also used in the paper industry, cosmetology and as additives for oil based polymers or biodegradable ones, and so forth. This cheap polymer is totally biodegradable, hydrophilic, and exhibits high molecular weights. It is composed of two main monomeric structures: amylose (amorphous slightly branched polymer) and amylopectin (partially crystalline and branched polymer). Starch cannot be used directly since its decomposition appears before its melting point; it is too hydrophilic and brittle in dry atmosphere. Plasticizing appears as a solution to make it thermoplastic and enlarge the field of applications.

First of all, starch has been studied in blend with PLA to give easily processed materials.[52,62] The most famous plasticizers are: glycerol,[74,75] triacetin,[76] vegetable oils,[77] fatty acids,[78] PEO,[79] polyadipates, polysuccinate,[80] and citrates.[81] These additives exhibit net effects on the properties of starch permitting its use as thermoplastic materials processed with usual extruders.

The use of polyols has also been extensively studied: sorbitol,[74] maltose,[75,82] xylitol,[83] glucose,[84] and mannitol.[74] Tg ranging from 15 to 80 °C were reached except for sorbitol which induces an anti-plasticization effect.[85,86] At last, some formamide such as ethylene-bis-formamide and N,N-bis(2-hydroxyethyl)formamide or amine like ethanol amine have revealed a plasticizing effect. Materials with elongation at break close to 100% were obtained.[87–89] Finally, some authors showed the plasticizing effect of ionic liquids (IL) which greatly modify the native crystallinity of starch giving more flexibility but inhibit the material biodegradation.[90]

Ligno-Cellulosic Polymers
Cellulose is the most abundant polymer on Earth and is mainly made up of β-(1-4) D-glucopyranose units with very

high molecular weights giving the coexistence of amorphous and crystalline domains. The crystallinity and the existence of intra and intermolecular hydrogen bondings make the polymer solubilization difficult as well as its melting. This hydrophilic polysaccharide has a high Tg and its melting cannot be observed due to the hasty decomposition. Its availability justifies its use in various applications such as coatings, membranes, filters, various molded articles, and so forth. However, the modification of the backbone structure is required to improve its solubility in various solvents, its melting and its molding to make it usable in industrial processes. The esterification of hydroxyl groups (to give cellulose acetate for example) with organic acids or with mineral acids has largely been investigated to limit hydrogen bonding.

The plasticization has been first investigated using usual plasticizers such as dioctyl, diethyl, and diphenyl phthalates.[91,92] The substitution of these compounds by less hazardous ones such as triethyl citrate, tributyl citrate, tributyl 2-acetyl citrate, triacetin, tripropionin, and low molecular weights PEO have been largely studied. These plasticizers increase the weight loss of the materials[93] and decrease the Tg of cellulose acetate.

Phosphates like triphenyl or tricresyl phosphate have been applied in specific applications like fire retardancy and birefringence properties of cellulosic esters.[94,95] Furthermore, some polyesters from succinic, glutaric, and adipic acids have been used to modify cellulosic derivatives to give material with good mechanical properties.[96,97]

Internal plasticization is an interesting route preventing any migration of the additive. Thus, cellulose backbone has been grafted by cardanol oil derivatives which greatly improved the mechanical properties and water resistance of this polysaccharide.[98]

IL have also been used for cellulose derivatives plasticization. For instance, 1-butyl-3-methylimidazolium chloride was shown to be a good plasticizer with an efficacious decreasing of the crystalline regions. Tensile test and Young's modulus were affected and confirmed that the ionic liquids destroy the interactions between the polysaccharide chains.[99,100]

At last, it must be mentioned other cellulosic derivatives such as cellulose nitrate that can be plasticized by alkyd resins,[101] phthalates,[102] carboxymethylcellulose, sorbitan monopalmitate, and ethyl cellulose by ESBO[103] or triethyl citrate.[104]

Chitosan
Chitosan comes from the deacetylation of chitin which is mainly found in the exoskeleton of crustaceans and in mushrooms. It is nowadays more and more studied for biomedical applications, agricultural uses, various consumer items, and so forth.

Glycerol is the most common plasticizer for chitosan.[105] It has been frequently mixed with other compounds (oleic acid,[106–108] PEO[109]) to give additional properties. Corn oil with or without glycerol gave materials with high elongation at break and tensile strength.[110] Moreover, the combination lactic acid and glycerol drastically decreases the crystallinity of the chitosan.[111] Other polyols such as sorbitol have also been tested for their ability to plasticize chitosan, giving good efficiency.[112,113]

Finally, imidazolium-based IL have been shown to be efficient to modify chitosan thanks to ionic interactions between amine groups and polar groups of IL.[114]

Proteins
Proteins are very interesting abundant raw materials even if their use in materials such as membranes, biodegradable and edible films, remains a challenge. Water is a good plasticizer, greatly modifying their physical and mechanical performances. Some authors tried to modify their hydrophilicity by adding other chemical compounds.[115,116]

In the case of gluten, glycerol stands the most used modifier but the final material absorbs water and leads to a plasticized material with decreased mechanical properties.[117–119] Other polyols such as sorbitol, PEO, PPO or genipin have been tested in place of glycerol and revealed efficiency giving flexible films with permeability to water vapour.[120,121] Hydrolyzed wheat gluten can be used as plasticizer of gluten with similar effect than glycerol.[122] Of course, phthalates have also been largely used to modify gluten.[123]

Casein is easily available and has been processed with glycerol to give thin edible films. Their properties are affected by glycerol content and moisture levels.[124]

In the case of zein, glycerol is also commonly used to make casted films.[125,126] Sometimes, oil derivatives can be added to give homogeneous films.[127] PEO and oleic acid have also been applied to give materials with good tensile properties.[128,129] At last, PEO, lactic acid, lauric acid and stearic acid have been tested to give transparent and flexible materials with properties similar to that of petroleum based polymers.[130]

Natural Rubber
Natural rubber is mainly applied to tires and tubes manufactures. Most often, paraffinic, aromatic and naphthenic oils are integrated in the formulations as plasticizers. Several authors tried to replace usual phthalates by less toxic compounds. Thus, glycerol has been tested to plasticize rubber for materials devoted to drug delivery[131] such as patches. Some polymers based on PEO, sebacic acid or triethyl citrate were investigated for the design of pharmaceutical devices where adhesive properties are required.[132]

Lipidic derivatives[133–136] were applied to obtain films. Epoxidized vegetable oils from soybean, linseed,[137] coconut,[138] castor, and sunflower oils and esterified fatty acid[19] have also been tested with good results even if some improvements are needed for specific applications.

Cardanol oil has been proved to be an efficient plasticizer for natural rubber.[139,140] This natural oil has also been radically grafted onto natural rubber modifying strongly its viscosity and plasticity.[141,142]

All these petro- and bio-based polymers described in this paragraph, as well as their plasticizers are summarized in Table 1. A global analysis shown the versatility of phtalates, adipates, sebacates, azelates, glycol esters, and citrates (all except citrates belong to diesters family) able to plasticize petro- and bio-based polymers. By contrast, the plasticizers based on lipidic derivatives (glycerol, vegetable oils), sugar derivatives, lactic acid and PPO selectively proceeded on bio-based polymers. A peculiar position concerns PVC, plasticized by numerous compatible bio- and petro-plasticizers bearing various molecular structures.

PETRO-BASED PLASTICIZERS

1200 commercially manufactured plasticizers are available. As previously described, the first plasticizers were used in the 1800s with natural camphor and castor oil.[2] In the 1930s the largest class of plasticizers appeared: phthalates. Regarding the increasing demand in plasticizers, the development of a wide range of plasticizers occurred over the last 50 years including fatty esters, benzoates, tartrates, adipates, azelates and sebacates. Since the 1980s, the toxicity of some plasticizers such as di-*n*-butyl phthalate (DBP) related to its migration through the polymer was proved, thus the interest in natural-based plasticizers significantly increased as detailed in § 4.[19]

Phthalates represent 80% of all plasticizers production (Fig. 4). Di-(2-ethylhexyl)phthalate (DEHP) is by far the most widely used one representing 50% of the worldwide phthalates production,[143] but is suspected of endocrine-disruption activity.[144] That is why alternative high molecular weight phthalates (85% of phthalates) such as di-(2-ethylhexyl)terephthalate (DEHT), di-isononyl (DINP), di-isodecyl (DIDP), di-*n*-octyl phthalates (DNOP) and low molecular weight phthalates such as DBP, butylbenzyl phthalates (BBP) have been produced. These plasticizers combine most of the desirable properties: excellent compatibility, high gelling capacity, low volatility, water resistant, and low cost. The industrial applications ranged from medical plastics, floors, wall coverings, toys, cables to food packaging.

Trimellitates have a similar structure to that of phthalic acid with the exception of a third carboxylic functionality on the aromatic ring. Tris-2-ethylhexyl trimellitate (TOTM) is the most often used one, and supplied by Eastman, for example, for its high gas exchange capacity, which is beneficial for blood platelet survival.[145] The main characteristics of trimellitates are low volatility, good water resistance, high temperature stability even if they are expensive. PVC tubes and medical devices are their main industrial applications.

Adipates, azelates and sebacates are aliphatic plasticizers bearing a central aliphatic chain in C6, C9, and C10, respectively. They have an excellent low temperature performance affording high flexibility as well as high plasticizing effectiveness. Adipates are often used in combination with phthalates. They plasticized numerous petro-based (PVC, PVA, PVB, elastomers)[132] and bio-based polymers (PLA,[52,59,146,147] PHB,[33,148,149] starch, cellulose).[96,97] The drawbacks of these plasticizers are the low compatibility with many polymers and its price.

Benzoates are mainly produced by Velsicol Chemical and Eastman as previously said (Benzoplast® and Benzoflex®).[150,151] Glycol dibenzoates revealed excellent properties in terms of stain and UV resistance and low moisture sensitivity even if their use is limited owing to their high viscosity and processability difficulties. The industrial applications ranged from flooring to PVA adhesives, PVC,[152] polyamides, and PU sealants.

Linear saturated, unsaturated aliphatic or cycloaliphatic chain terminated with two carboxylic ester groups represent another class of plasticizers. Di-2-ethylhexyl maleate (DEHM) is an interesting substituent to DEHP in dental applications because of its low toxicity and good plasticization properties.[153] By contrast, fumarates produced low plasticization. Promising alternative plasticizers for PLA and PVC are cyclohexane derivatives, such as di(isononyl)-cyclohexane-1,2-dicarboxylate produced by BASF under the trade name Hexamoll DINCH®.[154] Compared to DEHP, it offers a tendency to migrate three to ten times lower, has lower environmental persistence and higher biodegradability. Other cycloaliphatics were synthesized such as dialkyl and dicycloalkyl of 2(3)-methylcyclohexene dicarboxylic acid and dimerates and trimerates which were proved to be good plasticizers.

Heterofunctional plasticizers gather phosphorus, sulfurous and aminated derivatives. The most important and historical class are phosphates[155] (tricresyl phosphate, 2-ethylhexyldiphenyl phosphate, tris(2-ethylhexyl)phosphate). They have excellent properties: flame retardancy,[156] heat resistance but are not suitable for low temperature and food-contact applications. They are used in calendering, extrusion and plastisol with various petro-based (PVC, polyacrylates) and bio-based polymers (cellulose,[94,95] rubber).[141,142] Sulfonates,[157] and sulfamides[37] represent the last categories of heterofunctional plasticizers and the widespread candidates (*n*-butylbenzenesulfamide, toluenesulfamide Mesamoll®) are produced by Lanxess. Sulfamides are specially used with polyamides[158] and cellulose derivatives[37] for their aging resistance, low volatility even if they tend to discolor and are not compatible with PVC.

Several technical challenges have been addressed to improve formulations. The use of polymeric plasticizers can be a way of improving their properties. On the one hand, the high molecular weight of polymeric plasticizers generates high viscosity but significantly improves leaching and volatility issues and avoids demixing and migration through the polymeric material.[11] On the other hand, their low performance in terms of processing and mixing with the polymer limited their use. Moreover, they increase tensile strength and reduce elongation at break. They are mainly used in specific

TABLE 1 Main polymers and their plasticizers

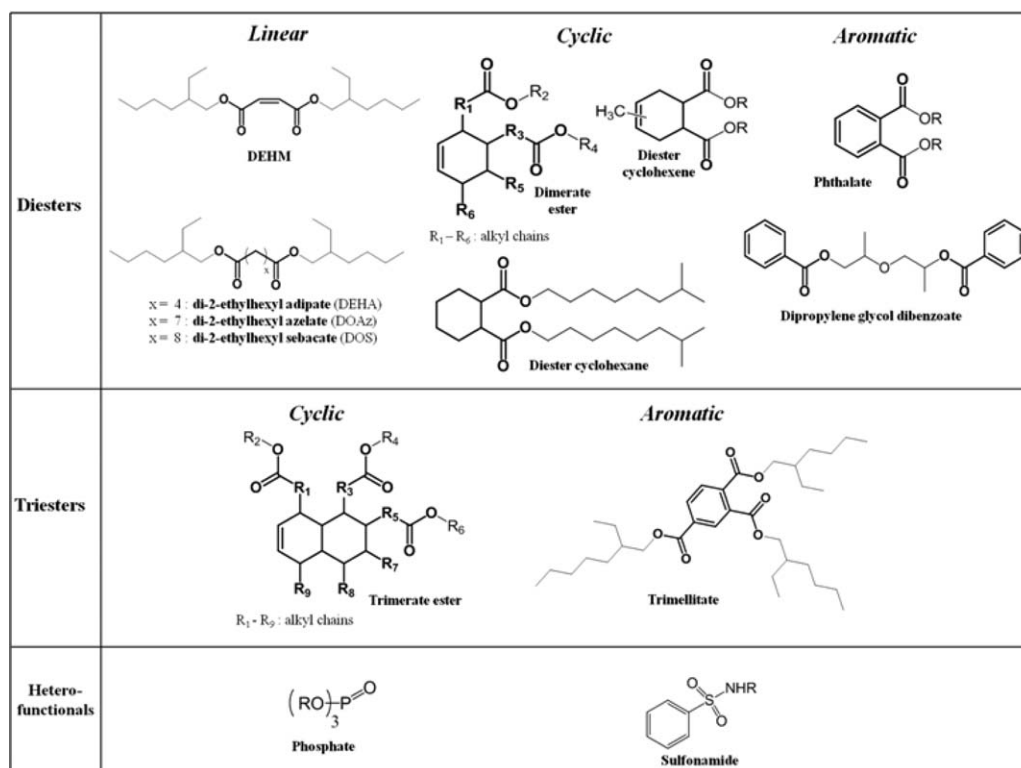| Plasticizer type	PVC	PVB	PVA	PVDC	PVAc	PMMA	Poly-amides	PLA	Starch	PHBV	Cellulose	Chitosan	Gluten	Zein	Natural rubber
Phthalates	X	X			X	X[36]					X[91,92,102]		X[123]		
Adipates, sebacates, azelates	X	X		X		X[36]		X[52]	X[80]						X[132]
Citrates	X			X[31]	X[35]			X[52,53]	X[81]	X[17]	X[93,104]				X[132]
Cardanol	X										X[98]				X[135–138]
Glycol esters		X[17,33]	X[34]					X[47,48]	X[79]	X[70–72]	X[89]	X[109]	X[120,121]	X[128,130]	X[132]
Lactic acid								X[39–42]				X[111]		X[130]	
PPO								X[45–47]					X[120,121]		
Glycerol and its derivatives								X[62,63]	X[74,75]	X[73]		X[105,111]	X[117–119]	X[125,126]	X[131]
Vegetable oils derivatives	X[13]							X[54–57]	X[77,78]	X[17]	X[103]	X[106–108,110]		X[127,129]	X[19,129–134]
Sugar derivatives	X								X[74,75,80–82]			X[112,113]	X[120,121]		
Phosphates	X[30]										X[94,95]				
Trimellitates	X			X[32]											
Polyesters	X														
Sulfonamides							X[37]								
Benzoates							X[38]								

FIGURE 4 Chemical structures of the main petro-based plasticizers.

applications where high temperature resistance is required. Among polymeric additives, polyesters such as poly(1,3-butyleneglycol adipate), poly(phthalate-*co*-butyl acrylate), PCL,[159] PEO[50] are the most studied. Others concern elastomers [acrylonitrile-butadiene copolymer, ethylene-vinylacetate copolymer (EVA)][160] and ethylene-propylene copolymers named Elvaloy® by DuPont de Nemours which satisfactorily plasticized PVC but is expensive.[161]

BIO-BASED PLASTICIZERS

As said before, the use of petro-based plasticizers is being questioned because of toxicity issues coming from plasticizer migration. This concerns a large demand for new low-toxicity and low-migration natural-based plasticizers[162,163] to replace petro-based ones. The ideal "green" plasticizer should: 1) be nontoxic as for its metabolites, 2) have a good miscibility with the polymer, 3) be as efficient as usual plasticizers, 4) have high resistance to leaching from the polymer and 5) be relatively low cost. The most natural plasticizer for hydrophilic and biopolymers (PLA, polysaccharides, proteins) is water, as it is widely reported in the literature.[164–168] Its molecules reduce the Tg and increase the free volume of biomaterials.[19]

Natural-based plasticizers can be obtained from the agricultural industry by-products and wastes that are sustainable, low cost, and largely available resources.[169] As illustrated in Figure 5, many plasticizers can be prepared from different

agricultural resources: cereals, oleaginous plants, trees, fruits, and vegetables or their wastes. For example, starches and cellulose obtained from wheat, corn, straws or potatoes lead to several sugars and saccharidic derivatives that can be used as plasticizers (mannose, glucose, fructose, sorbitol,[170] xylitol,[171] mannitol).[172] Vegetable oils coming from soybean, linseed, palm, castor bean, permit to elaborate several plasticizers after chemical modifications. Tall-oil, obtained as a by-product of the Kraft process of wood pulp manufacture, leads to bioplasticizers as those produced by Gerflor. Finally, citric acid coming from sugarcane, beetroots or citrus fruits, is a very attractive precursor leading to many different citrates and itaconates used as plasticizers. Other molecules like amino acids, waxes or lecithin have also been studied as plasticizers for eatable or biodegradable films.[19] Be careful, the term biodegradable does not mean the plasticizer is "good".

From Vegetable Oils

Vegetable oils represent a promising route to renewable plasticizers since they are readily available, biodegradable and have low toxicity. They are extracted from oleaginous plants and trees as shown in Figure 5. They have various compositions of fatty acids depending on the plant and the growing conditions.[173] Chemically, they are mainly composed of triglycerides or triacylglycerols made up of glycerol and various fatty acids (Fig. 6).
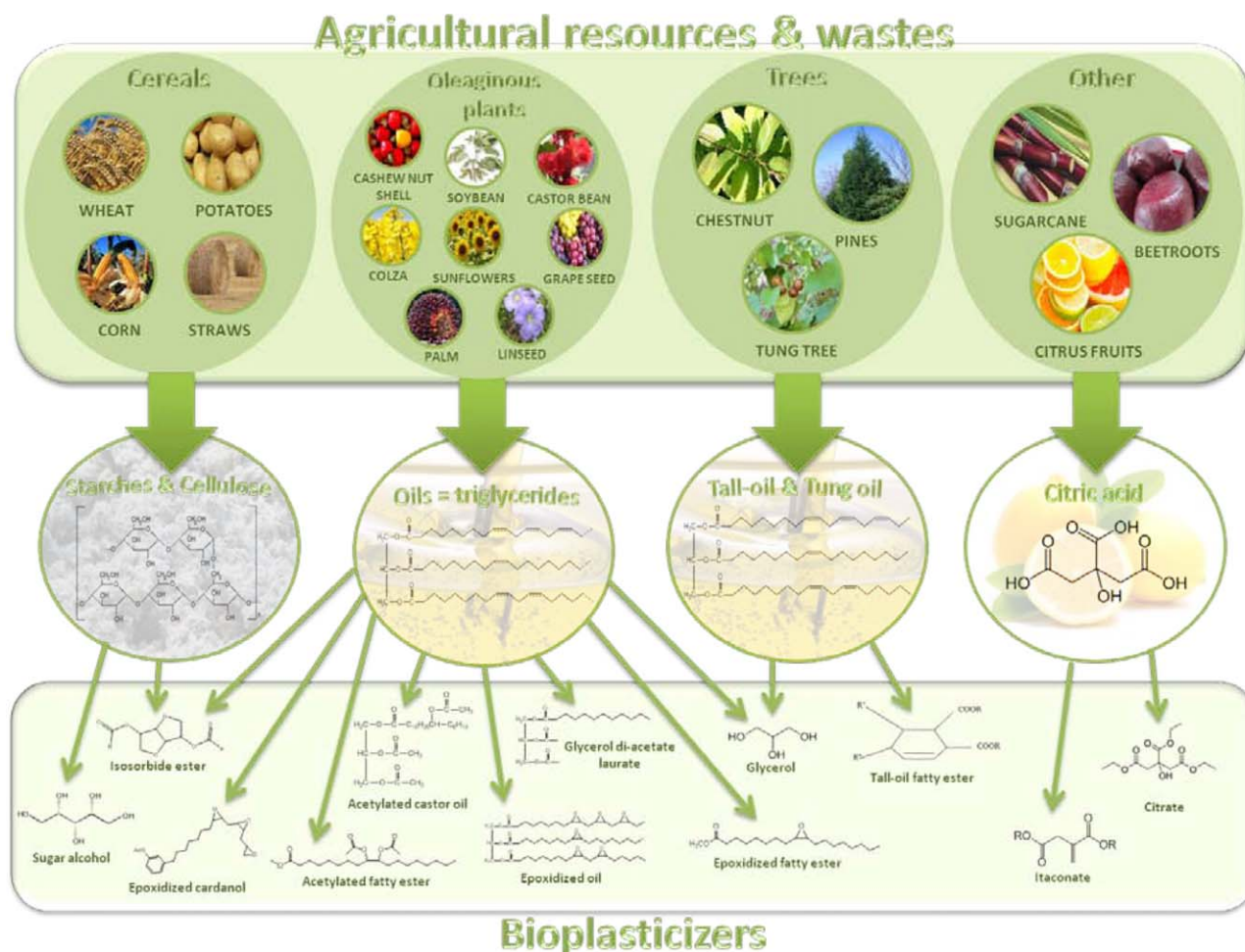
FIGURE 5 From agricultural resources to bio-based plasticizers.

Vegetable oils have two chemicals characteristics that make them potentially good plasticizers: (1) the fatty chains can intersperse and intercalate between polymer chains, increase intermolecular spacing and bring mobility, and (2) the ester groups can interact with polymer chains (van der Waals interactions for instance) and bring compatibility. Two major reactive sites can be found on triglycerides structures: the ester groups and the double bonds. A modification of these reactive sites is required to increase the compatibility of vegetable oils with polymers (Fig. 6). Thus, modified glycerol and fatty esters can be used as plasticizers after *trans*-esterification of ester groups. The fatty esters or triglycerides double bonds can also be epoxidized and further acetylated as well as react in Diels-Alder reactions.

Epoxidized, Acetylated and Esterified Oils

The use of ESBO as secondary plasticizer in PVC has been known for a long time. An advantage of ESBO is the ability of the epoxy groups to scavenge HCl molecules generated during the thermal degradation of PVC.[174] During the 1950s and 1960s, ESBO was tested as primary plasticizer. It has been reported that the plasticizing effect is acceptable but

that exudation occurs after a longer time of UV-exposure, resulting in sticky surfaces.[175] One reason might be that the epoxidation was incomplete, unreacted double bonds remaining.[176] A reduction of the residual unsaturations increased the plasticizer lifetime in PVC. Other plasticizers have also been prepared from epoxidation of olive, corn, cottonseed,[177] and sunflower[178] oils although the last one could only be used as secondary plasticizer in combination with DEHP.[179] By contrast, epoxidized palm oil was not effective as PVC plasticizer,[180] since it has very few double bonds. In order to develop plasticizers for PVC from palm oil, Gan et al. prepared a large variety of esters and their epoxidized counterparts, thinking they would offer better compatibility. They highlighted that epoxy esters of palm stearin had poor compatibility with PVC and could be used only as secondary plasticizers whereas epoxy esters of palm olein were found to be good plasticizers.[180]

Once epoxidized, other lipidic plasticizers can be produced by ring-opening of epoxidized vegetable oils giving acetylated vegetable oils (Fig. 5). These bio-based plasticizers have properties as good as phthalates. Fogassy et al. compared
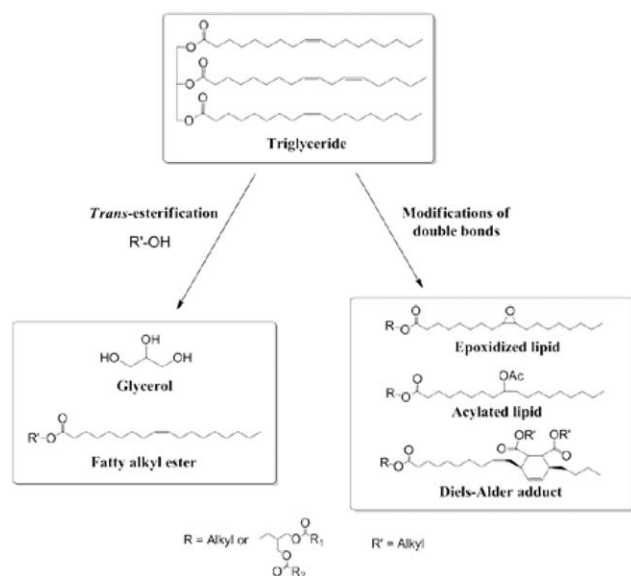
FIGURE 6 Lipidic derivatives coming from vegetable oils.

the use of different catalysts for the epoxy ring-opening.[181,182] Quaternary ammonium salts were found to be excellent ones as Novance and Serge Ferrari companies claimed it.[183]

Besides epoxidation and acetylation, some other chemical modifications can be done on vegetable oils. Biermann et al. studied triesters as PVC plasticizers, synthesized in two steps: the first reaction occurs between maleic anhydride and Tung oil giving the corresponding Diels-Alder adduct which was converted into triester by ring-opening reaction with various alcohols[184] (Fig. 6). These compounds showed excellent compatibility with PVC even better than DEHP for some of them. Various companies are trying to develop bio-based plasticizers made from vegetable derivatives in order

to compete with the petro-based ones (Table 2). For instance, Vandeputte Oleochemicals, Varteco and Nexdeum produce epoxidized linseed, soybean and rapeseed oils for plasticizing purposes. Danisco patented a fully biodegradable plasticizer produced by acetylation of castor oil: Grindsted® Soft-N-Safe®.[185] Three to four times more expensive than phthalates, the European Union allowed its use for food applications. The Gerflor group used esterified fatty acids coming from tall-oil and epoxidized fatty acids coming from sunflower oil to plasticize PVC.[186] Arkema proposes a range of plasticizers named Vikoflex® based on ESBO and epoxidized esters as PLA plasticizer[54–57,187] and PVC plasticizer.[188] The Hallgreen company creates Hallgreen® plasticizers composed of fatty esters to plasticize bio-plastics like PLA and petro-based ones.[189] Novance mainly developed plasticizers for PVC based on soybean and rapeseed oil and fatty esters (unsaturated or epoxidized) under the trade name Radia®.[190–192] The plasticizers Resiflex® K50, PLS Green® 9 and Lankroflex® ED6 were also produced by Resypar, Petrom and Akcros Chemicals, respectively. Soybean oil-based plasticizers such as Kalflex® 14A, Nexo® EO1 and Resiflex® K50 represented in 2011 already 65% of plasticizer consumption in Argentina and about 20% in Brazil.[193] Finally, Jayant-Agro-Organics elaborates from castor oil a fully bio-based plasticizer named DSC®. Many bio-based polymers can be plasticized by vegetable oils including starch,[77,78] cellulosic derivatives,[103,127–130] PHB,[69] and rubber.[133–138]

Glycerol

Glycerol is a simple polyol composed of three hydroxyl groups responsible for its water-solubility (Fig. 6). It is widely used in food, cosmetic and pharmaceutical formulations because of its properties and its low toxicity. Approximately 950,000 tons are produced per year in the USA and Europe as a by-product of biodiesel synthesis. It is one of the most used polyols for plasticization of edible and

TABLE 2 Industrial bio-plasticizers made from vegetable oils

Plasticizer trade name	Manufacturer	Feedstock	Bio-based content[193]	Chemical name
Grinsted® SOFT-N-SAFE	Danisco	Castor oil	80%	Acetylated castor oil
Kalflex® 14A	Varterco	Soybean oil	98%	ESBO
Nexo® EO1	Nexoleum	Soybean oil	95%	Methyl epoxy soyate
Resiflex® K50	Resypar	Soybean oil	100%	Amyl epoxy soyate
PLS Green® 9	Petrom	Soybean oil	66%	Nonyl epoxy soyate
DCS®	Jayant-Agro-Organics	Castor oil	100%	Di-caprylsebacate
Radia® 7295	Novance/Oleon	Rapeseed oil	78%	Acetylated ester
Lankroflex® ED6	Akcros Chemicals	Soybean oil	68%	Octyl epoxy stearate
—	Gerflor	Tall oil Sunflower oil	—	Tall-oil fatty esters
Virkoflex® 7010	Arkema	Soybean oil	—	Epoxidized soybean oil fatty esters
Hallgreen®	Hallstar	Linseed, soybean, castor oil	38 – 100%	Fatty ester

—: no data found.

biodegradable films[194–197] and has been approved as a food additive by the FDA (Food and Drug Administration).[198] Glycerol has a high temperature tolerance, is polar and non-volatile.[199] Polyols are known to be effective plasticizers due to their ability to reduce internal hydrogen bonding while increasing intermolecular spacing.[200]

Glycerol is commonly recognized as one of the most suitable plasticizers for starch[74,75,201] thanks to its three hydroxyl groups allowing creating strong hydrogen bonds. Its avail-ability and the mechanical properties[202] of the final "thermoplastic starch" (mixture of starch and glycerol after gelatinization)[203] make it the most widely used plasticizer in the industry. The addition of glycerol diminishes the brittle nature of starch, provides the desired extent of flexibility and increases the onset temperature for gelatinization.[204] Glycerol-plasticized starch has been used to make blends or composites for different applications.[205–207] A solid polymer electrolyte based on starch plasticized with glycerol was cre-ated by Marcondes.[208] Samples plasticized with 30–35 wt % of glycerol presented high ionic conductivity, transparency and conduction stability over 6 months. Bourtoom used glyc-erol as plasticizer to create biodegradable blend films from rice starch-chitosan with good water vapor permeability.[209] Liu et al. also made chitosan-starch blend films and high-lighted that the addition of glycerol resulted in a decrease in tensile strength and an increase in elongation at break. An anti-plasticization effect was observed in polymer films when only 2.5 wt % of glycerol was added.[201]

Hosokawa et al. used glycerol to plasticize chitosan-cellulose composites[210] and stated that the elongation of blended films increased with plasticizer rates but at high content, both tensile strength and modulus decreased. The use of glycerol in chitosan film formulations has also been studied by Suyatma et al. who found that glycerol is a very efficient chitosan plasticizer,[211] better than ethylene glycol and pro-pylene glycol. However, the water barrier and mechanical properties of glycerol-plasticized chitosan films change dur-ing storage.[212]

Tian et al. studied glycerol as plasticizer of soy protein plas-tics.[213–215] Soy protein is the major co-product of soybean oil and is one of the cheapest proteins in nature. In a first study, they used a mixture of ε-caprolactone/glycerol as plas-ticizer to make soy protein plastic sheets.[215] In a second study, soy protein plastics blending with agar was plasticized with glycerol.[214] In their latest study, glycerol plasticized soy protein plastics containing castor oil were prepared.[213] The addition of castor oil led to significant increase in storage modulus as well as Tg. Compared with neat glycerol plasti-cized protein plastics, castor oil improved tensile strength and Young's modulus under high humidity.

Singh et al. investigated the use of unrefined biodiesel co-product stream (mixture of glycerol, methyl linoleate, methyl oleate, linoleic acid, and oleic acid) as a polymer plasticizer. They successfully plasticized cast gelatin films with this by-product instead of pure glycerol.[216]
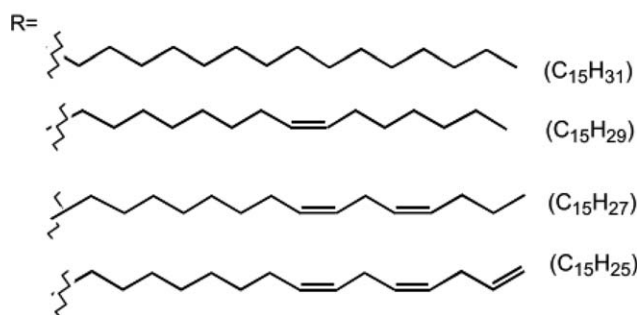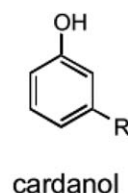

FIGURE 7 Chemical structures of cardonol's components.

Recent studies showed that glycerol derivatives can also be used as plasticizers. For instance, glycerol monostearate was studied as copolyamide solid plasticizer.[38,217] It causes a small lowering of Tg compared to other solid plasticizers like benzene sulfonamide or methyl 4-hydroxybenzoate but its effect on the melting properties is very pronounced. Mos-selman Company produces diacetylated glycerol monolaurate as polymer plasticizer. Finally, unesterified polyglycerols have been described as good plasticizers for starch-based biodegradable thermoplastics. They have a lower volatility and a higher thermal stability than glycerol which allows easier processing. Polyglycerols or blends of glycerol and polyglycerols are claimed to have better plasticizing proper-ties in PVA films than glycerol alone. Diglycerol esters such as diglycerol tetraacetate are also used as plasticizers for cel-lulose acetate and polyester resin compositions based on PLA.[218]

Cardanol

Cardanol and its derivatives are very interesting precursors in order to develop new materials from renewable resources. It is obtained by distillation of the cashew nut shell liquid, a sustainable, low cost nonedible by-product of cashew indus-try.[219] It is a particular vegetable oil since it is not composed of triglycerides as illustrated in Figure 7. It includes more than one compound because the composition of the side chain varies in its degree of unsaturation.[220] Cardanol com-ponents are 48% mono-unsaturated, 16% bi-unsaturated, and 29% tri-unsaturated[221] which represents 2 average dou-ble bonds per chain. Chemical and physical properties of car-danol are very close to those of DEHP. Phosphorylated cardanol was found to be an efficient plasticizer for natural rubber,[140] polychloroprene and polybutadiene rubber,[222]-ethylene-propylene diene rubber,[223] and LDPE/EVA copoly-mer blends.[224] PVC has also been effectively plasticized with cardanol derivatives.[219,225] In order to have a good miscibil-ity with PVC, the hydroxyl group of cardanol needs to be
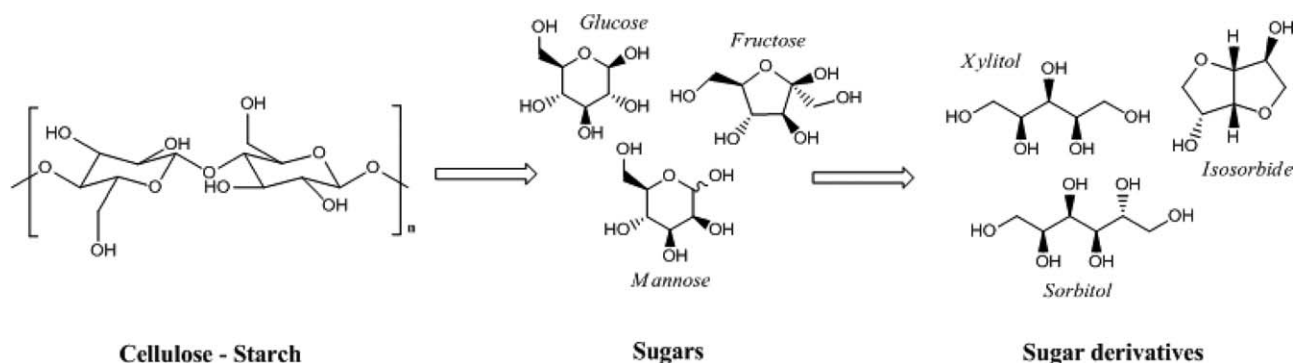
FIGURE 8 Sugar derivatives coming from cellulose and starch.

esterified and the side chain double bonds can be epoxidized for an even better miscibility.[225] Greco et al. showed that cardanol acetate is partially miscible with PVC. It can be used as a secondary plasticizer and then partially replace DEHP. Moreover, they showed that epoxidized cardanol acetate was completely miscible with PVC[219] and exhibited a higher diffusivity than DEHP.[226] However compatibility of cardanol acetate in PVC/wood flour composites was rather poor.[227]

Iji et al.[98] produced cellulose-based bioplastics by bonding cellulose diacetate, a cardanol derivative and additional aliphatic and aromatic components *via* esterification. The resulting thermoplastics have high heat resistance, long elongation at break and good water resistance. All these properties were better than those of cellulose diacetate plasticized with conventional plasticizers. The cardanol phenyl part plays an important role for a good water resistance and a long elongation whereas the linear side chain permits the bonding between cellulose and cardanol. Finally, cardanol can be grafted onto natural rubber using a peroxide initiator. The resulting grafted natural rubber showed lower Tg than natural rubber.[221] Very recently, Yang et al. proposed an interesting grafting of cardanol on PVC via click-chemistry. The synthesized propargyl ether of cardanol was grafted on azide functional PVC and acted as an internal plasticizer, decreasing Tg, exhibiting excellent thermal stability and near-zero migration.[228]

From Starches and Cellulose
Starches are mainly extracted from rice, wheat, maize and potatoes whereas cellulose comes from straws and cotton fibers. After hydrolysis of these polysaccharides, different sugars like glucose or mannose are isolated which further lead to sugar alcohols (xylitol, sorbitol...) and isosorbide after chemical modifications as illustrated in Figure 8.

Sugar Alcohols
Like glycerol, sugar alcohols are bio-based polyols. They are also used for starch plasticization, sometimes as only plasticizer, other times mixed with glycerol. Adhikari *et al.* studied the drying behavior of low-amylose maize starch films plasticized by glycerol and xylitol, separately and in 1:1 combination.[229] Xylitol, with its relatively large molecule size and its

two additional hydroxyl groups, was found to be a more effective plasticizer than glycerol since it can form strong hydrogen bonds with starch molecules. But it was concluded that xylitol plasticized films have higher moisture migration fluxes and effective moisture diffusivity values than glycerol plasticized ones.

McHugh and Krochta used sorbitol to plasticize whey protein edible films and compared it with glycerol.[200] They found that glycerol films showed significantly higher oxygen permeability than sorbitol films. Moreover, at same concentration, sorbitol-plasticized whey protein films have equivalent tensile strengths than glycerol-plasticized ones but exhibited lower elongation values.

Isosorbide Esters
Isosorbide is a nontoxic, biodegradable and thermally stable heterocyclic diol derived from glucose. Hydrogenation of glucose gives sorbitol which, after a double dehydration, gives isosorbide. Three isomers exist (isosorbide, isomannide and isoidide) according to the hydroxyl groups' chirality.

Historically, isosorbide was produced in a small scale for pharmaceutical and cosmetic applications. In 2007, Roquette started a industrial unit to produce several thousands of tons of isosorbide per year. Isosorbide esters are obtained by double esterification of isosorbide and long chain acids. They are renewable resources and plasticizers with good plasticizing efficiency and miscibility with PVC due to their structure similar to phthalates. Indeed, the two carbonyl groups can form strong secondary bonds with PVC which is required for good miscibility. Yin et al. synthesized three isosorbide esters, oligo (isosorbide adipate) (OSA), oligo(isosorbide suberate) (OSS), and isosorbide dihexanoate (SDH) to evaluate them as PVC plasticizers.[230] PVC films made with SDH showed similar behavior than those made with traditional phthalates. OSA and OSS permit to make plasticized PVC films with higher Tg, lower tensile strain at break and higher tensile stress at break compared to SDH and DIOP plasticized films. OSA and OSS plastisols were more thermally stable compared to SDH/PVC blends. All these three isosorbide esters are potential alternative PVC plasticizers.

Polysorb® ID 37 is a 100% bio-based plasticizer produced by Roquette, constituted of isosorbide diesters coming from fatty acids and isosorbide. It is nontoxic, biodegradable and a high-performance PVC plasticizer with both excellent compatibility and very low volatility. Thus, it is a perfect alternative to conventional phthalates. That is why Roquette launched in 2008 a demonstration unit for the production of Polysorb® ID 37 with a capacity of over 100 tons per year.

Nevertheless isosorbide derivatives possess an important water sensitivity, which can lead to uptake water of the plasticized polymer. It can represent a major drawback for some applications.

From Citric Acid

Citrate plasticizers are tri or tetraesters produced by esterification of citric acid, which is obtained from citrus fruits, sugarcane and beetroots (Fig. 5). The three carboxylic functional sites offer the possibility to create a large variety of citrates. The FDA approved both citric acid and its esters as additives in food.[231] Nevertheless, the price of these esters is about three times higher than that of phthalates. Except for acetyl tributyl citrate commercialized by Jungbunzlauer who was found to be toxic and has only specific applications,[217] citrates are nontoxic and used to plasticize PVC in sensitive markets like medical equipments, food packaging and toys that are to be in contact with young children.[6] For instance, butyryl-n-trihexyl citrate is considered as a safe alternative to DEHP for storing red blood cells in PVC bags, at least for limited periods. Tributyl citrate is particularly used in PVC and its copolymers for food-wrapping films because it is thermally stable and does not cause the products to discolour.[5] Eastman provides several triacetin plasticizers for food applications.

Ghiya et al. plasticized cellulose acetate with triethyl citrate and acetyl triethyl citrate which improved elongation, reduced tensile modulus and accelerated degradation rates in the during composting.[232]

Triethyl citrate,[53] tributyl citrate,[53,233] and triacetin[233,234] are also used to plasticized PLA. They are totally compatible with this polymer. At least 20% of plasticizer needs to be introduced to decrease its Tg and improve the final material ductility.

Some citrates can also be useful for drug delivery. For example, triethyl citrate is used to make films of Eudragit RS, a copolymer of ethyl acrylate, methyl methacrylate and a low content of methacrylate with quaternary ammonium groups in order to create a smart drug delivery system releasing the active molecule in response to a temperature stimulus. Eudragit RS films plasticized with 20% of triethyl citrate possess a Tg close to the body temperature. Water uptake of films and permeation rate of drugs are the best near this temperature.[235]

Finally, citrate plasticizers are also used with PVAc according to a self-plasticization phenomenon,[35] rubber or PHB.[17]

Itaconates are produced by esterification of itaconic acid, which come from the distillation of citric acid. They are sparsely described as plasticizer in the literature. Batzel used itaconic acid and itaconates as dienophile in Diels-Alder reactions with myrcene, to create a PVC plasticizer.[236] For its parts, Brown copolymerized itaconate esters with allyl starch to obtain films with enhanced flexibility and toughness.[237]

From Bio-Based Wastes

Bio-based wastes have also been tested as natural plasticizers in various polymers and materials. Thus, natural and modified polyflavonoid tannin extracts have been shown to behave as super plasticizers of cement and concrete mixes, improving fluidity without any significant retardation of the onset of hardening.[238] Moreover, efficient plasticization was achieved by using tannins such as an additive in the thermal processing of wheat protein-based natural polymers[239] or gelatine.[240] Furthermore, chemical modification of gelatin by a natural phenolic compound tannic acid (TA) at pH 8 was also studied by Zhang et al. The modification due to TA produced an increase in molecular mobility of gelatin matrix, and the materials displayed a behavior similar to that of plasticized protein materials.[241]

Sugarcane bagasse was also used as plasticizer in cellulose acetates. Indeed, Shaikh et al. fractionated sugarcane bagasse and used hemicellulose content (5%) of cellulose bagasse as an internal plasticizer for cellulose acetate.[242] Liquefied wood was also extensively studied as a source of plasticizers. Indeed, wood flour was liquefied to low molecular weight polyols by acid catalysed reaction. The resulting polyol mixture was further utilized for the synthesis of low molecular weight ester plasticizers. Monomeric and oligomeric plasticizers were prepared by esterification of the polyols by hexanoic acid or a mixture of hexanoic and adipic acid respectively. Liquefied wood esters turned to be very good plasticizers for PVC.[243] Moreover, Jasiukaityte-Grojzdek et al. proposed the synthesis of polyesters from liquefied wood by reaction between wood, glycerol, diethylene glycol and adipic acid and successfully used them as plasticizers for PVAc dispersion for flooring applications.[244] Liquefied wood flour and rice bran derived esters were synthesized and evaluated as novel bio-based plasticizers for PLA. If liquefied rice bran esters were not miscible with PLA, liquefied wood flour esters showed good miscibility and good plasticization efficiency with it.[245]

PLASTICIZER DESIGN

Achieve to a structure-property relationship for any functionality, not only plasticization, is a big challenge. For example, Smith et al. demonstrated the relationship between 2,4,6-trimethyl-1,3,5-benzentrisamides which act as ultra-efficient nucleating agents and the nucleation of isotactic polypropylene.[246] Mahesh et al.[247] also showed the relationship between the cyanurate structure and the gelation of melamine-linked tri(p-phenyleneethynylene)s. The physical properties and the morphological features of the
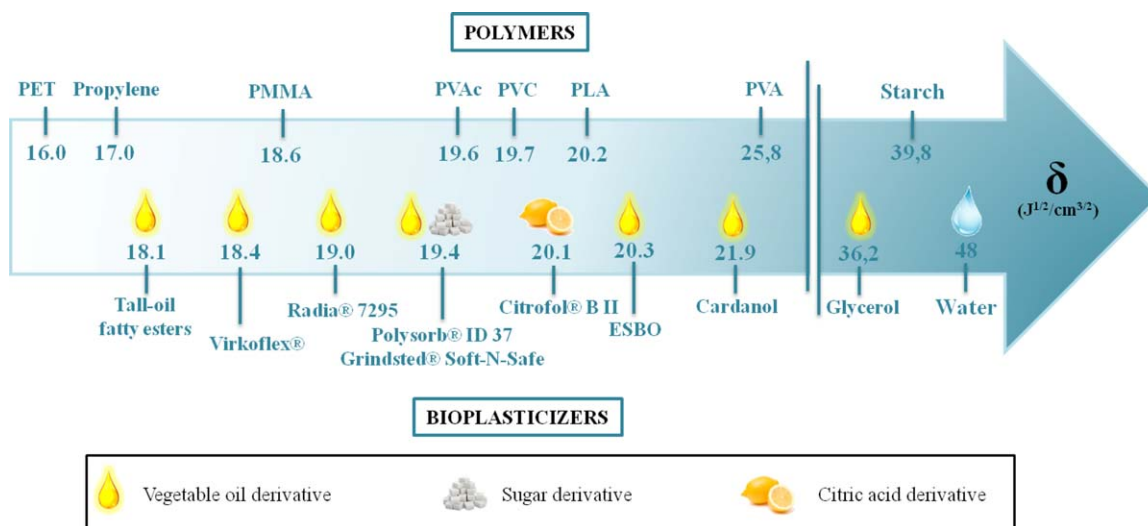
FIGURE 9 Solubility parameters of some polymers and plasticizers.

resultant supramolecular gels result to the ability of cyanurate to generate hydrogen-bondings.

As said earlier, plasticizers act by creating secondary bonds with the polymer, bringing mobility. Its role is also to break the strong interactions existing between polymer chains, even in case of high crystallinity. The compatibility between polymers and plasticizers is then a determining factor to obtain plasticized materials with the desired properties. The compatibility can be defined as the ability of a plasticizer to form a homogenous system with polymer.[248] If plasticizer-polymer compatibility is correct, a homogeneous mixture is formed during processing, the plasticizer remains dispersed in the compound after cooling. Incompatibility is revealed when whitening, tackiness, exudation, and low mechanic properties are observed. Polarity, chemical groups, length of chains, number of hydroxylic groups, molecular weight, dielectric constant, and so forth, are parameters that can influence the compatibility between plasticizers and polymers.

There are several empirical ways for predicting plasticizer/polymer compatibility but most are based on the simple concept that "like dissolves like."[249] For instance, one of the most used predictors is the solubility parameter δ, which is available for a wide range of plasticizers and polymers. In the study of gels, it allows estimating the gelator-solvent interaction. This is defined as the square root of the cohesive energy density,[250] value derived from energies of vaporization at 25 °C for liquids and estimated according to Small's correlations for solids.[251] The solubility parameter is an effective characteristic of the intermolecular interactions. It is possible to predict in which solvents the polymer will not be dissolved by knowing their δ values: it is generally accepted that for a good compatibility the difference in the solubility parameters should be smaller than 3.7 $(J/cm^3)^{1/2}$.[249] This

permits to narrow down a range of plasticizers for a given polymer. However, polymer and plasticizer having the same δ are not always compatible. Therefore the solubility parameter is not sufficient to predict plasticization efficiency. Figure 9 shows the distribution of some polymers and some of the bio-plasticizers aforementioned, according to their solubility parameter value. The δ values are contained between 16 and 40 $(J/cm^3)^{1/2}$ for polymers and between 18 and 48 $(J/cm^3)^{1/2}$ for bio-plasticizers. Most of the values are around 20 $(J/cm^3)^{1/2}$ for both polymers and bio-plasticizers.

To reach a high degree of compatibility, it is also generally required for the polymer and plasticizer to have approximately the same polarity. If polymer and plasticizer differ greatly in polarity, compatibility is not complete. Thus, nonpolar polymers mix well with hydrocarbon oils but do not mix at all with polar liquids such as water or glycols. The presence of benzene rings in a plasticizer molecule often favors compatibility thanks to entropy factors. On the other hand, highly polar polymers do not mix at all with hydrocarbons or ester but dissolve in water. They have solubility parameter values of more than 20 $(J/cm^3)^{1/2}$. Finally, polymers of average polarity are those with solubility parameter values between 17 and 20 $(J/cm^3)^{1/2}$. They are generally not compatible with water and hydrocarbon oils but mix with diester plasticizers.

A complementary way to predict plasticizer/polymer compatibility is to analyze the plasticizers chemical structures. Indeed, an overview on the plasticizers classes allowed some correlations between the plasticizing phenomenon and the structures' chemical groups including the functionality (ester, epoxide, aromatic groups...) and the nature of the aliphatic chains. It is well-known that dangling chains such as aliphatic chains act as spacers between polymer chains permitting increased free volume and decreased Tg,[252] whereas
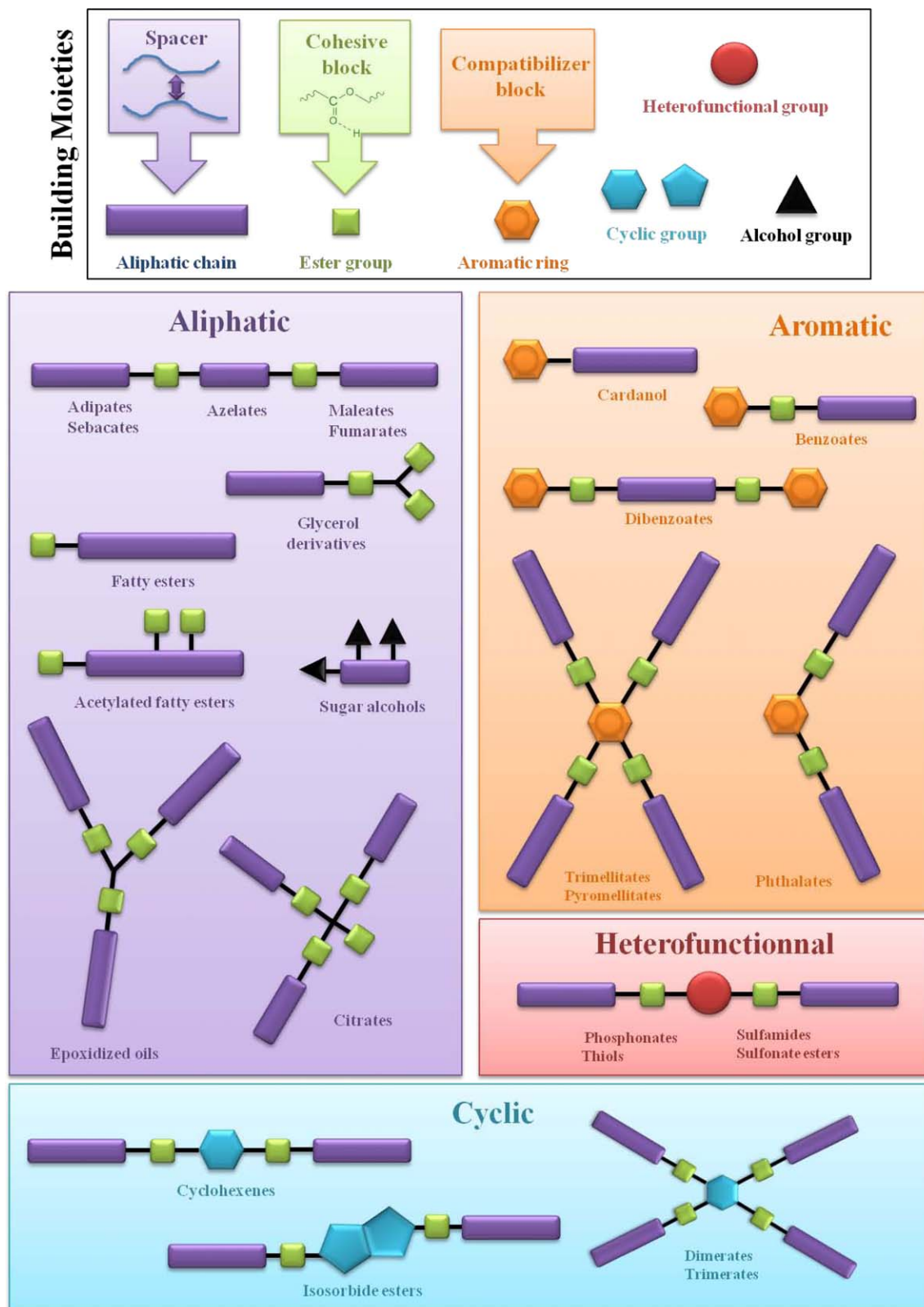
FIGURE 10 Molecular architectures of the bio- and petro-based plasticizers.

polarizable aromatic groups proceed as compatibilizer units with various plastics like PVC affording great flexibility to the polymer chains.

Among petro-based and bio-based plasticizers, those with ester groups are the most used because they allow specific interactions with the polymer (hydrogen bonds, electrostatic,

or van der Waals interactions) acting as cohesive blocks (Fig. 10). Shorter chains are easier to formulate because they diffuse faster but have the drawback to be more volatile. Branched chains reduced the plasticizing effectiveness and if the branches are close to the polar group, the plasticizing is even less efficient. We mentioned that a branched chain defined a main chain bearing a side chain and not a structure bearing more than two chains and a nonlinear architecture. Furthermore, the main chain can become shorter due to branching, also decreasing the plasticizing efficacy and increasing the viscosity. Plasticizers that have low molecular weight and a small number of polar groups generally provide higher flexibility and plasticization.

In this way, there are several tools to design an ideal plasticizer using three essential building blocks: a spacer (aliphatic chains) to bring mobility, a cohesive block (ester groups) and a compatibilizer block (aromatic rings) to bring stability and compatibility. Then, a compromise must be found for the aliphatic chain length: it must not be too short to avoid volatility neither too long to ease formulation. Finally, branching must be limited and a low molecular weight is better. Most of these criteria are found in all the petro- and bio-based plasticizers aforementioned. This is illustrated in Figure 10 where the main plasticizers are classified according to their molecular architectures. A first category, which contains fatty esters, adipates, sebacates, azelates, epoxidized oils, citrates, and so forth, possesses only aliphatic groups. In the case of benzoates, cardanol, phthalates and mellitates, they all have an aromatic ring. The third group represents compounds with cycloaliphatic groups like BASF's plasticizer Hexamoll® DINCH. The last category gathers plasticizers with a heterofunctional group (phosphonates, thiols, sulfonamides). But as shown, almost all plasticizers in each category possess at least one ester function except for cardanol and sugar alcohols, which confirm that the presence of an ester group is nearly necessary to obtain an effective plasticizer. Besides, it can be noticed that there are almost as much ester groups as aliphatic chains in each plasticizer. For example, trimellitates possess three ester groups and three aliphatic chains, phthalates have two ester groups as well as two aliphatic chains... This ratio also seems to be an important criterion.

Finally, the 2-ethylhexyl unit is a particular aliphatic chain that appears in a lot of petro-based plasticizer structures (phthalates, trimellitates, adipates...). This moiety seems then to be an excellent solvator and would be a good choice of aliphatic chain for the design of an effective plasticizer. The influence of 2-ethylhexyl unit in property is not limited to plasticization and extends to others like gelation[253] or liquid crystal organization.[254]

Regarding this whole analysis, other bio-based molecules still not described as plasticizer in the literature, could be good candidates for this purpose (Fig. 11). Cinnamates and p-coumarates come from cinnamic acid, extracted from cinnamon. Coumarin carboxylic acid esters come from coumarin
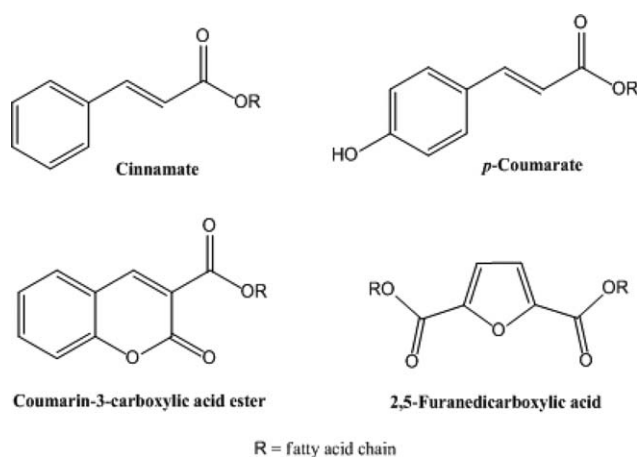

FIGURE 11 Bio-based candidates for plasticizers.

isolated from the tonka bean and furanedicarboxylic acids are sugar derivatives. They all posses ester groups which could bring good compatibility, fatty acid chains for mobility and finally cyclic groups which could bring good stability.

Nevertheless, even if they all seem promising plasticizers according to their chemical structures, parameters like physical state, stability at room temperature and toxicity have to be taken into consideration.

CONCLUSIONS

Health and environment concerns, related to migration problems from leachable plasticizers such as phthalates, can be minimized by the use of alternative plasticizers with low migration level and low volatility. This has recently motivated both academic and industrial research. A large range of platform molecules comes from renewable resources and their wastes, which offer a lot of different structures in terms of functions (polyol and polyester), functionality (di-, tri-, tetra-, and pentafunctional molecules) and molecular weight (molecular, oligomer, and polymer). The challenge concerning the total or partial substitution of petro-based plasticizers by bio-based ones is very attractive and concerns: (i) hydrophilic and hydrophobic polymers, and (ii) petro- and bio-based polymers. Nowadays, the growing number of publications mainly reports the use of plasticizers derived from vegetable oils (epoxidized oils, glycerol, and cardanol), sugar alcohols, and esters (sorbitol, xylitol, and isosorbide), and citrates.

The functionalization of these natural compounds to elaborate effective plasticizers is now well known by chemists, and numerous parameters allow designing efficient plasticizers. For example, the solubility parameter δ is an important data to predict the compatibility between the plasticizer and the polymer. Moreover, the presence of building blocks (aliphatic chains, ester groups, and aromatic rings) in the plasticizer structure seems crucial to optimize the plasticizer stability, the mobility of the structure, and the plasticizer-

polymer compatibility. New bio-based molecular and macro-molecular plasticizers can still be considered.

However, development costs are higher for new bio-based plasticizers. They have not reached yet the desired objectives in terms of benefits and their performances are still a bit lower than those of synthetic plasticizers. Finally, even if the demand for these products should increase rapidly during the next decades, a deeper understanding of their toxicity must be clarified because bio-based does not mean necessarily nontoxic.

ACKNOWLEDGMENTS

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