



Review

Plasticizer design strategies enabling advanced applications of cellulose acetate

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ABSTRACT

Plasticized cellulose acetate (CA) is one of the most applied bio-based polymers due to its structural properties and easy processing. Plasticizers are added to CA to increase workability, prevent degradation under processing conditions and ensure thermo-mechanical properties suitable for the intended final application. Moreover, inexpensive and non-toxic solvents enable its processing into fibers, films, and solid blocks. However, when incorporated in the polymer matrix, plasticizers are prone to migration. CA products can suffer embrittlement, cracking, warping, or discoloration during their life cycle, affecting the material's integrity and durability. The design of new plasticizers compatible with the polymer at high concentrations, tailored to be effective in lowering the glass transition temperature, and with a low tendency to migration could considerably reduce material degradation over time.

This review offers a perspective on the current plasticizers and comprehensively depicts the plasticization mechanisms in CA for internal and external plasticization. Understanding the plasticization mechanisms paves the way to identify a rationale for designing new plasticizers for this polymer.

1. Introduction

Cellulose acetate (CA), a cellulose ester derived from the partial acetylation of cellulose, has numerous applications in a wide range of industrial fields due to its transparency, high gloss, colorability, warm and pleasant feel, and suitability for direct and prolonged contact with

human skin. The main applications of CA include eyewear frames [1,2], tool handles, cigarette filters [3–6], safety glasses and shields, protective films for LCD polarizing panels [7–10], costume jewelry, buttons, sequins [11] and decorations. Other applications of CA include drug delivery systems [12–17], membranes [18–24], battery separators [25,26], biodegradable films [27], foaming applications [28], and

Abbreviations: AC, Acetyl chloride; AGU, Anhydroglucose unit; AmimCl, 1-allyl-3-methylimidazolium chloride; ATBC, Acetyl tributyl citrate; ATEC, Acetyl triethyl citrate; BA, Benzoic acid; BDP, Biphenyl diphenyl phosphate; BMIMBF₄, 1-butyl-3-methylimidazolium tetrafluoroborate; BMIMCl, 1-butyl-3-methylimidazolium chloride; BMIMOTF, 1-butyl-3-methylimidazolium trifluoromethanesulfonate; BMIMPF₆, 1-butyl-3-methylimidazolium hexafluorophosphate; C-Dp, Cellulose diphenyl phosphate; CA-Dp, Cellulose acetate diphenyl phosphate; CA, Cellulose acetate; CAB, Cellulose acetate butyrate; CA-g-PHA, Cellulose acetate-graft-polyhydroxyalkanoates; CAP, Cellulose acetate propionate; CB, Cellulose butyrate; CDA, Cellulose diacetate; CDA-g-PLA, Cellulose diacetate-graft-poly(lactic acid); CL, ε-caprolactone; CMT, Cellulose mixed triesters; CP, Cellulose propionate; Cpp-Ac, Phenyl propyl cellulose acetate; CST, Cellulose simple fatty triesters; CTA, Cellulose triacetate; DBP, Dibutyl phthalate; DCP, Diphenyl chlorophosphate; DEP, Diethyl phthalate; DMA, Dynamic Mechanical Analysis; DMAc, N,N-Dimethylacetamide; DMAP, 4-dimethylaminopyridine; DMF, N,N-Dimethylformamide; DMP, Dimethyl phthalate; DOP, Dioctyl phthalate; DS, Degree of substitution; DSC, Differential Scanning Calorimetry; GDA, Glycerol diacetate; Gly, Glycerol; GPA, Glucose pentaacetate; GPB, Glucose pentabutylate; GPP, Glucose pentapropionate; GTA, Glycerol triacetate; HFC, 5-Hydroxymethyl-2-furancarboxylic acid; IUPAC, International Union of Pure and Applied Chemistry; LA, L-lactide; LCD, Liquid crystal display; MAH, Maleic anhydride; MEP, Methyl ethyl phthalate; MFR, Melt flow rate; MS, Molar substitution; PAA, 3-Pentadecylphenoxy acetic acid; PCL, Polycaprolactone; PEG, Polyethylene glycol; PICC, Pentadecylcyclohexyl (6-isocyanatoethyl) carbamate; PLA, Polylactic acid; PPG, Polypropylene glycol; PVC, Polyvinylchloride; ROP, Ring-opening polymerization; SA, Stearic acid; TBC, Tributyl citrate; TBTM, Tributyl trimellitate; TCP, Tricresyl phosphate; Td, Decomposition temperature; TEC, Triethyl citrate; TETM, Triethyl trimellitate; Tf, Flowing temperature; Tg, Glass transition temperature; TMTM, Trimethyl trimellitate; TPP, Triphenyl phosphate.

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photographic films [29–31]. CA has also been proposed for sensors of metal ions [32], gases [33], humidity [34,35], formaldehyde [36], and ascorbic acid [37].

CA features a strong dipolar interaction network, which gives it a high glass transition temperature (T_g) and a narrow window between flow temperature (T_f) and decomposition temperature (T_d) [38,39]. To overcome this issue, CA has traditionally been blended with low molecular weight organic compounds that act as plasticizers to broaden the processing window and increase its workability [40]. This method is generally termed external plasticization. [41] CA thermoplastic processing commonly uses 15–35 wt% plasticizers. [11] Other cellulose esters with longer chains, such as cellulose propionate (CP), cellulose butyrate (CB), or longer substituents, are more flexible and require lower quantities of plasticizer to reach the same flowability at a given temperature due to an internal plasticization effect [11,42]. Copolymerization with a small amount of a second monomer or grafting substituents with high side chain flexibility is called internal plasticization [43]. However, external plasticization is the more generalized approach.

As the other relevant cellulose ester, CA is processed using most of the plastic production methods, such as injection molding [44], compression molding [45], blow molding [46], extrusion [47], film casting [48] and fiber spinning [49]. CA is subjected to solvent dissolution in acetone in the last two industrial processes. In the case of fiber production, the dope solution is dry spun to produce textile filaments or cigarette filters. It is worth recalling that the traditional solvent block process is still employed for obtaining thick patterned and multicolored sheets for applications in the eyewear and fashion industry (Fig. 1) [11].

Although industrial processes are optimized by incorporating a certain amount of plasticizers, plasticized CA products are generally subject to plasticizer migration and volatilization to such an extent that CA becomes prone to cracking, warping, discoloration, and powdering as it ages [50,51]. Moreover, plasticizers that migrate out of the material could harm human health and contaminate the environment [27,52]. In this regard, understanding the mechanisms of CA plasticization is crucial to find room for improvement in tailoring cellulose acetate properties with a well-designed plasticizer molecule.

Even though numerous works in the literature focus on plasticizer design for polymers [53–59], there are no recent studies on the development of plasticizers for CA. In one recent work, six plasticizer

candidates with slight structural variations were designed to evaluate the effects of the inclusion of oligolactide segments, in combination with variations in end groups (hydroxyl or levulinate ester) and structural differences in the alcohol cores on the thermal, mechanical, and migration patterns of plasticized poly(lactic acid) (PLA). The plasticizer candidates were designed from potentially renewable chemicals using a flexible (1,4-butanediol) or rigid (isosorbide) core and combined with three different types of flanking groups [53]. The same authors [60] further studied eugenol, a natural aromatic compound: bio-based resources such as levulinic and valeric acids were combined to produce dual-functioning plasticizers, with different plasticizing and antibacterial performances, depending on phenol-, carboxyl-, and alcohol group content.

In this scenario, fundamental parameters such as solubility, compatibility, polarity, molecular weight, and functional groups of plasticizers play a crucial role in determining the success of plasticized systems while mitigating the drawbacks of the external plasticization [61]. Internal plasticization of pure cellulose or CA is an interesting approach to prevent plasticizer migration, but lower plasticizing efficiency and technological limitations hinder its industrial scaling-up [62,63]. However, the substituent structure seems to lower glass transition temperature, and acylating reagents consisting of bulky terminal moieties spaced from CA chains by a linear chain efficiently separate macromolecular chains without generating detrimental stiffening interactions [64,65].

This review provides an overview of CA plasticization approaches and sets general principles and guidelines for selecting a suitable plasticizer or designing a new molecule. After an introduction to the general properties of cellulose and its derivatives, mainly CA, and the main plasticization theories, we thoroughly present the modification strategies of internal plasticization and the more common external plasticizers used for CA. Through a more detailed analysis of effective plasticizer molecules, we then investigate molecular structures for a possible future design of new molecules to be used in CA, focusing on some critical aspects such as substituent moieties (ester groups, hydroxyl groups, alkyl chains, aromatic rings), as well as molecular weight. We finally provide the reader with guidelines for proper CA plasticizer design.

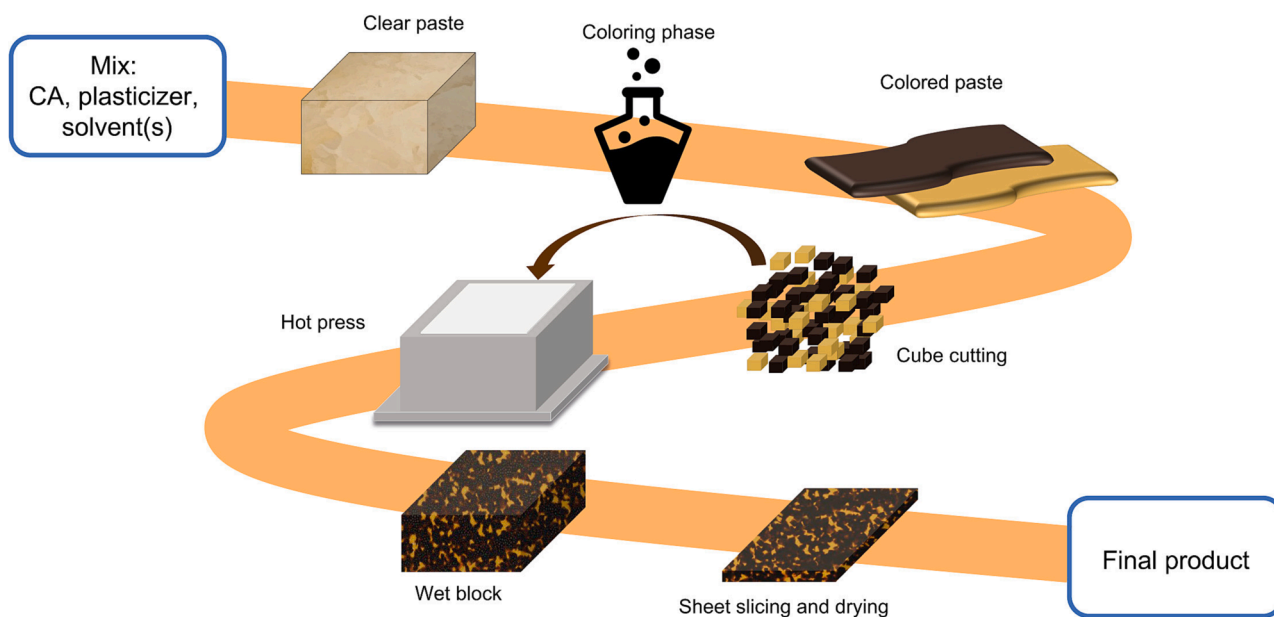


Fig. 1. Solvent block process: CA flakes are mixed with the plasticizer and the solvent(s) to produce a transparent paste. The paste is colored by adding pigment and pressed in a calender to produce CA sheets. These colored sheets are then cut into cubes, randomly reassembled in a mold, and hot pressed to generate the wet block. The wet block with the desired pattern is then cut into sheets. Finally, the sheets are dried, flat-pressed, and trimmed for subsequent processing.

2. Cellulose acetate: Structure and properties

2.1. Cellulose

Cellulose is the most abundant natural polymer on Earth [66]. The cellulose used in industry derives from two primary sources: cotton linters and wood pulp. Different types of cellulose can also be obtained from corn fibers or other agricultural sources, biomass waste, and bacteria (bacterial cellulose) [67,68]. These sources can be further combined in a circular economy perspective: bacterial cellulose, for instance, can be produced using agricultural waste such as fruits, vegetables, or lignocellulosic materials [69,70]. Crystalline cellulose from agricultural waste and forest residues is also reported in the literature [71]. Some sources contain pure cellulose, as in the case of cotton linters, or are mainly but not completely made of cellulose, as is the case of wood (40–60 %). In the latter case, chemical extraction and further purification are required to isolate the cellulose fraction via subsequent industrial processes.

Cellulose consists of β -D-glucopyranose units covalently linked by β -1,4-glycosidic bonds, i.e., repeated anhydroglucose units (AGUs) ($C_6H_{10}O_5$) form a linear polymer chain (Fig. 2). The number of AGUs forming the cellulose macromolecule, also referred to as the degree of polymerization (DP), depends on the extraction source and the treatment of the raw material [72]. Different molecular weights can considerably differ in mechanical properties and chemical reactivity [73,74]. The structure of the polymer also depends on the cellulose source used and its treatment. Industrial cellulose processing aims to modify cellulose macromolecules' spatial arrangements to obtain the desired properties.

Each AGU has three reactive hydroxyl groups (C2, C3, and C6) (Fig. 2). These groups form intramolecular hydrogen bonds (interaction of the hydroxyl groups within the same molecule) and intermolecular hydrogen bonds (interaction of the hydroxyl groups with neighboring cellulose molecules) [75]. Cellulose macromolecules form highly ordered crystalline regions, mainly due to the intramolecular bonds, but regions with a low degree of order can also be found. The high degree of crystallinity (i.e., 40–60 %) [76] leads to highly packed zones, thus limiting the interaction of cellulose with common solvents or reagents [77].

The main drawback of this strong network is the processability of cellulose for industrial applications. To achieve better processability and modulate material properties, cellulose –OH groups are generally replaced, entirely or partially, with substituent –OR groups to obtain different cellulose derivatives. In this regard, the degree of substitution (DS) refers to the average number of substituents per AGU. Since cellulose contains three hydroxyl groups per AGU, the DS is between 0 and

3. The most important chemical modifications on an industrial scale involve the three reactive hydroxyl groups of individual AGUs (at C2, C3, and C6 positions), supporting etherification and esterification reactions, usually under heterogeneous conditions [78].

2.2. Cellulose esters

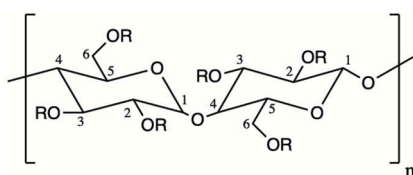
Esterification of cellulose is one of the most employed chemical modifications as it provides sub-products with a bio-based content. Cellulose esters are obtained by reacting cellulose with organic acids, anhydrides, acid chlorides, and catalysts [79]. In principle, any organic acid can react with the available hydroxyl groups of cellulose for esterification, even if only esters of acids with two to four carbon atoms are of industrial interest. In this process, the final reaction product is the cellulose triester of the involved organic acid. Hydrolysis is then achieved by adding a water-acid mixture to the cellulose triester to obtain the desired DS. Finally, water is added to precipitate the polymer and remove reaction by-products. DS is a statistical mean value where unsubstituted, mono-, bi-, and tri-substituted anhydroglucose units coexist. [80].

For a cellulose derivative, the total DS and the distribution of the substituent among positions C2, C3, and C6 of the AGU are relevant to the final material properties, namely solubility, permeability to gases and liquids, and water vapor sorption [81–83]. Regarding cellulose esters, the DS refers to the substituent, such as acetyl for CA, propionyl for cellulose propionate (CP), butyryl for cellulose butyrate (CB) (Fig. 2). Still, it can be alkanoyl with a variable number of carbon atoms, usually from 2 to 10.

Nowadays, only esters of carboxylic acids with two to four carbon atoms and mixed esters are considered technically and economically relevant due to their properties and ease of production [84]. On this same topic, due to technical limitations (i.e., slow reaction rates and competitive cellulose chain cleavage in heterogeneous esterification), esters of aliphatic acids containing more than four carbon atoms have not achieved commercial relevance [82]. Moreover, cellulose esters of aliphatic diacids and aromatic acids are also difficult to prepare because of the poor reactivity of the corresponding anhydrides with cellulose [85]. Mixed esters of different partial DS of each acyl moiety, in particular cellulose acetate/propionate and acetate/butyrate, result in different thermal behavior and solubility compared to their simple esters (i.e., a single substituent). They are prepared commercially by reacting the respective anhydrides simultaneously [79]. The reactivity of these anhydrides toward cellulose is acetic anhydride > propionic anhydride > butyric anhydride as studied under homogeneous reaction conditions [86].

The properties of cellulose esters are strictly correlated with the number of acyl groups per AGU, acyl chain length, and the degree of polymerization (i.e., molecular weight). In cellulose esters with DS = 3 and increasing acyl chain length from C-2 to C-6, physical parameters such as melting point, tensile strength, mechanical strength, and density tend to decrease. Still, moisture resistance and solubility in non-polar solvents increase [42]. Regarding partially substituted cellulose esters, increased solubility in polar solvents and increased moisture absorption result from fewer acyl substituents, which means that polarity increases as apolar alkyl chains decrease [85]. The physical and chemical properties of cellulose esters are a function of the substituents and the ratio of esters if mixed esters are used. For instance, in cellulose acetate butyrate (CAB), where the substituents are either acetyl or butyl moieties, increasing the proportion of acetyl to butyl increases moisture absorption, polar solubility, density, and melting point while reducing flexibility [82].

Cellulose esters with short-chain carboxylic acids (C-2 and C-3) have high glass transition, melting, and low decomposition temperatures. Therefore, cellulose esters are typically melt-processed in the presence of plasticizers that extend the processing window. For the main commercial esters such as CA, cellulose acetate propionate (CAP), and CAB,



Cellulose derivative	Abbreviation	Substituent (R)
Cellulose acetate	CA	-CO-CH ₃
Cellulose propionate	CP	-CO-CH ₂ -CH ₃
Cellulose butyrate	CB	-CO-CH ₂ -CH ₂ -CH ₃
Cellulose acetate propionate	CAP	-CO-CH ₃ or -CO-CH ₂ -CH ₃
Cellulose acetate butyrate	CAB	-CO-CH ₃ or -CO-CH ₂ -CH ₂ -CH ₃

Fig. 2. Chemical structure of cellulose (R = H) and main cellulose esters (R partially substituted with other chemical groups).

the softening point and the region with the rheological properties required for each specific processing technique depend on an appropriate degree of ester substitution and plasticizer content. The bonding of more extended chain ester groups should provide an effective internal plasticization, potentially eliminating the need for external plasticizers that may be prone to diffusion, extraction, or volatilization [82]. (This topic will be covered later in the *Internal plasticization* section).

2.3. Cellulose acetate

CA is one of the most relevant organic ester of cellulose in terms of applications. CA can be prepared with different degrees of substitution, possibly ranging from water-soluble monoacetate to fully substituted triacetate, which is completely insoluble in water. Its broad development has been supported by the solubility of partially hydrolyzed (secondary) CA in inexpensive and relatively non-toxic solvents [85].

In industrial processes, CA is typically obtained by heterogeneous reactions, and acetyl substituents are present randomly along the macromolecules [87]. Before acetylation occurs, cellulose is adequately activated with water or an aqueous acetic acid solution. This step aims to increase the reactivity by breaking part of the hydrogen bonding between the polymer chains. For commercial CA, one standard procedure involves using glacial acetic acid with sulfuric acid that will be subsequently used as a catalyst. Sulfuric acid is also employed to reduce the molecular weight of the starting cellulose material by chain scission. The activation of cellulose is influenced by temperature, time, amount of catalyst, and acetic acid-to-cellulose ratio beyond the cellulose source (i. e., wood pulp or cotton linters). Industrial acetylation catalysis is typically based on sulfuric acid to obtain cellulose triacetate with a DS of 3. The following hydrolysis step to remove some acetyl groups is critical to creating the specific CA grade with the desired combined acetic acid content or degree of substitution [84,88]. The most common products are cellulose triacetate (CTA) with DS = 3 and cellulose diacetate (CDA), with DS around 2.45 (ca. 39.5 % in acetyl content), which are odorless, tasteless, and non-toxic. Interestingly, water-soluble cellulose acetate having a total degree of acetyl substitution of approximately 0.8 (which is a cellulose acetate with a low degree of substitution) is reported to be metabolized and decomposed by intestinal bacteria and can be used as appetite suppressants [89].

CA properties depend on the acetyl content and molecular weight, with the former determining the polymer's solubility characteristics and biodegradability [85,90]. The greater the molecular weight, the higher the flow temperature and the heat distortion temperature; however, variations in the typical range (DP~175-360) have less effect than variations in the plasticizer used and degree of acetylation [91]. A specific DS of CA flake is always preferable for different processes [11] (Table 1).

Homogeneous conditions would help efficient control of the DS and distribution of the functional groups in the polymer backbone [92,93], but this is usually performed on a lab scale. For this purpose, cellulose can be dissolved in N,N-dimethylacetamide (DMAc) and LiCl [94-97]. Other strategies are reported in the literature, such as triethyloctylammonium chloride with acetone as a reaction medium [98]. Non-derivatizing solvents, which dissolve cellulose by physical interactions, can be single and multi-component systems. These solvents do not react with the hydroxyl groups, leaving them free for

esterification or etherification processes.

3. Plasticizers

3.1. Plasticizers

A plasticizer is defined by the Council of the International Union of Pure and Applied Chemistry (IUPAC) as a substance or material incorporated into a material (usually plastic or elastomer) to increase its flexibility, workability, or distensibility [99]. Plasticizers are commonly low molecular weight organic compounds, liquid or solid, which promote flexibility and processability of polymers by lowering the glass transition temperature (second-order phase transition temperature) and melting temperature (first-order phase transition) [100]. They usually interact with the polymer matrix reducing the secondary forces between different macromolecules and providing mobility to the chains, which results in a more easily deformable material at the macroscopic level [101]. Plasticizers are usually embedded in the amorphous regions of the polymer, while the crystalline domains remain unaffected. These additives are expected to reduce elastic modulus, tensile strength, hardness, density, melt viscosity, glass transition temperature, electrostatic charging, and volume resistivity of a polymer. At the same time, they increase elongation at break, toughness, dielectric constant, and power factor [102].

Even if many plasticizers are on the market, their choice depends on the polymer and its final application. Chemical and physical properties, safety and environmental profile, miscibility, processing temperature, and required plasticity are the main factors to be considered for selecting the best plasticizing solution. The ideal plasticizer must be highly compatible with the polymer, stable during processing and usage of the plastic product, have a low tendency to migrate, and be nonvolatile, low cost, and non-toxic [50].

Plasticization can be external or internal. In the first case, plasticizers are blended into the polymer, and only secondary interactions occur between the plasticizer molecules and the polymer matrix. Therefore, they can be lost by evaporation, migration, or extraction. On the contrary, internal plasticizers are chemically bonded to polymer chains by primary bonds; they are not prone to migration as part of the polymer. In this regard, copolymerization of side chains or grafting reactions of smaller molecules hinders the polymer chain compaction [103], increases the distance, and decreases the interaction force of the chains, thus increasing their mobility [104].

Plasticizers can also be classified as primary or secondary [105]. A primary plasticizer is required when more than one plasticizer is used (and it can also be used as a single plasticizer.) It must be soluble in the polymer at high concentrations and not exude from the final product [99]. Secondary plasticizers are usually added to a primary plasticizer to modify its performance in terms of costs, improving other features such as behavior at low temperatures or permanence properties. In some cases, secondary plasticizers can induce synergistic effects on plastic properties by enhancing the single effects shown by plasticizer molecules when evaluated individually [59].

3.2. Mechanisms of plasticization

Different theories explaining the mechanism and action of plasticizers in polymeric matrices can be found in the literature: the lubricity theory, the gel theory, and the free volume theory (Fig. 3).

The lubricity theory [106] is attributed to Kirkpatrick, Clark, and Houwink, among others. It asserts that the resistance of a polymer to deformation, i.e., its rigidity, is the result of intermolecular friction: the plasticizer would act as a lubricant between the polymeric chains, like oil between two moving parts, reducing friction and promoting the reciprocal movement of the macromolecules as they slide over each other like contact planes. Due to Van der Waals and London forces, plasticizers lessen the force required to overcome adhesion at contacting

Table 1
Preferred degrees of acetate substitution DS for various plastic processing techniques. (Readapted from [11]).

Processing technique	DS
Blow molding	2.49
Injection molding and casting	2.41
Film extrusion	2.34
Block process	2.28

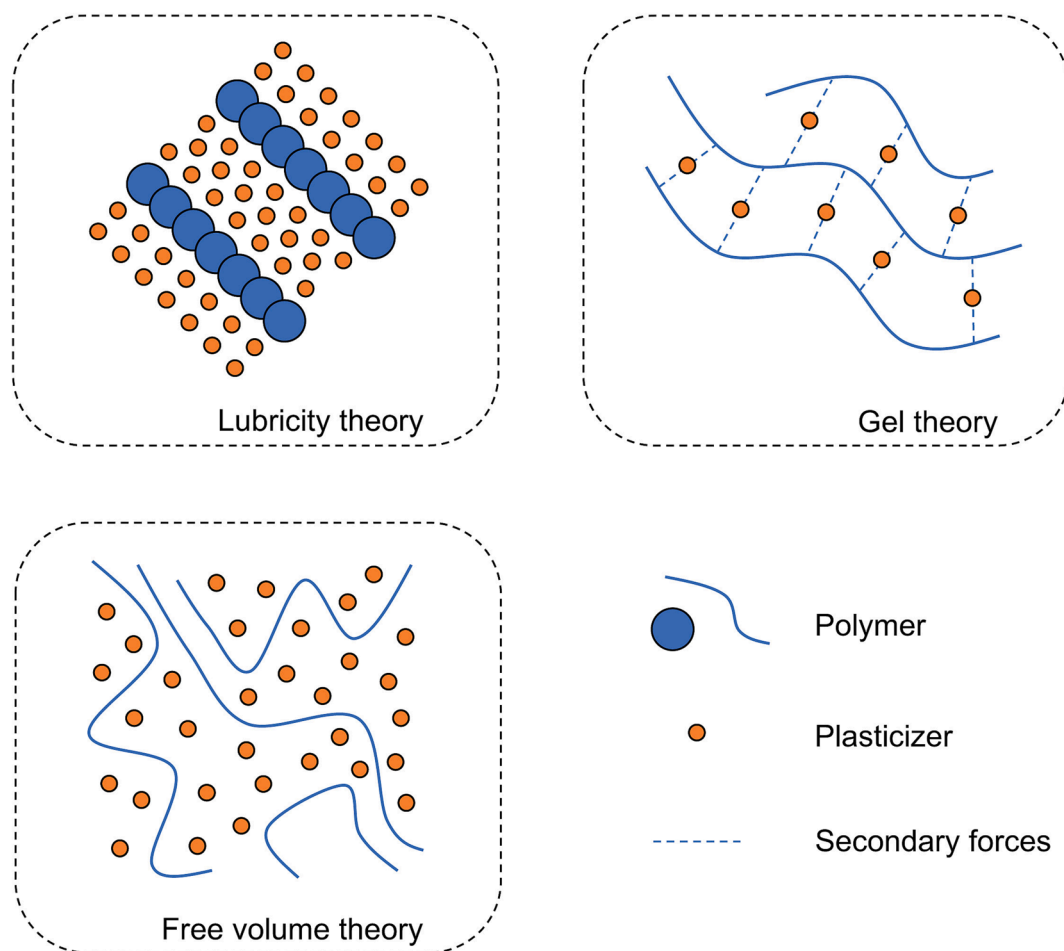


Fig. 3. Representation of plasticization theories. (Readapted from [99]).

asperities.

The gel theory was developed by Aiken [107]. It assumes that a 3D network exists in which polymer chains are tied by secondary forces (hydrogen bonds, Van der Waals interactions, ionic forces), and plasticizers can intercalate and break these interactions by establishing bonds with the polymer and masking the secondary bonds between the macromolecules. These bonds are not permanent and can be formed and broken as the plasticizer solvates and desolvates the polymer. Still, the increased space between polymer molecules reduces polymer–polymer interactions at sites where they could be re-established. At the same time, free molecules of the plasticizer behave as swelling agents, facilitating flexibility.

There are some common aspects between the lubricity and the gel theories. In the 1940s, Kirkpatrick [106] highlighted that every plasticizer should exert a solvent action, as predicted in the gel theory, and a simple lubrication mechanism, as described in the lubricity theory. A portion of the plasticizer molecule is bonded to a specific group in the polymer, expressing a solvating behavior, while the unbonded portions act as lubricants between the macromolecules. The presence of groups that enable mutual attraction between plasticizer and polymer, their reciprocal position for the attraction to occur effectively, and the shape of the plasticizer molecule are essential for the desired final properties to be obtained [108].

Subsequently to these two theories, the free volume theory was developed to interpret the effect of a plasticizer in decreasing the glass transition temperature of a polymer as well as to explain other properties as a function of temperature, such as viscosity, specific volume, and thermal expansion coefficients [103]. Free volume or free space can be defined as the difference between the volume observed at the absolute

zero temperature and the volume measured at a given temperature. In a polymer above the T_g , the energy acquired by the molecules generate motion, bending, or rotation. These Brownian motions of segments and molecules result in a larger free volume (i.e., space between the macromolecules), observed as the specific volume increases as the temperature rises.

In this regard, plasticization can be a way to increase the free volume. Free volume derives from three primary sources: the motion of the chain ends, the side chains, and the main chain. Therefore, the free volume of a polymer can be increased by: (i) increasing the number of end groups, i.e., lowering the molecular weight; (ii) increasing the number or length of side chains (internal plasticization); (iii) including in the main chain segments with low steric hindrance or low intermolecular attraction (low polarity and no H-bonding), e.g., the soft segments from polyols in many copolymers (internal plasticization); (iv) adding a compound with a low molecular weight, compatible with the polymer, which can increase the number of end groups and side chains and lower the molecular weight, acting as a spacer that only has weak interactions with the polymer (external plasticization); (v) raising the temperature [109].

Adding a plasticizer molecule increases the free volume per total volume due to a proportional increase in end groups. The free volume theory explains the lowering of the glass transition temperature with an increase in free space within the polymer. Other remarkable conclusions can be derived from the free volume theory: (i) plasticizers with lower T_g are more efficient in reducing the T_g of the plasticized system; (ii) for the same molecular weight, a branched plasticizer is more efficient than a linear one, because there is greater free volume associated with branches; (iii) increasing the molecular size of the plasticizer increases

the free volume introduced in the polymer; (iv) on a weight basis, the increase in total free volume could be more significant for small molecular-weight plasticizers.

However, this theory does not consider the importance of functional groups to achieve good compatibility. It can be concluded that a molecule is a suitable plasticizer when it is small, it generates greater free volume and establishes thermodynamic affinity with the polymer. After the free volume theory, no other significant conjectures have been developed; most aspects of plasticization are well explained by these three main theories.

3.3. Plasticizer-polymer interaction

It is nowadays established that good plasticization implies secondary bonds, also known as intermolecular forces, with the polymer. The attraction between plasticizer molecules and the polymer must be as strong as the interactions between molecules in the single components to generate an efficient polymer-plasticizer interaction. Polymer solvation by plasticizers is significantly linked to their chemical structure and polarity. Dissolution occurs when polymer and plasticizer have similar polarities, which is well described by the rule “like dissolves alike.” It means that the energy of interaction between heterogeneous molecules of solution components is as strong as the energy of interaction between homologous molecules [108]. In CA, for instance, polar groups in the polymer, such as acetyl and hydroxyl, can interact with polar groups of a plasticizer molecule (such as aromatic rings and ester bonds) and establish intermolecular forces such as Van der Waals and dipole–dipole interactions. These intermolecular bonds usually enable the plasticizer to solvate the amorphous part of the polymer but not the crystalline domains.

In CA, plasticizer-polymer interactions begin with the mixing step: the plasticizer first wets the polymer particles and then diffuses and solvates the amorphous domains of the polymer thanks to externally added heat (e.g., heating jacket on the mixer) or heat generated internally by the friction between macromolecules. Incompletely dry-mixed plasticized systems show regions where the plasticizer is not well dispersed and plasticizer concentration is higher due to possible self-association phenomena. In this situation, the plasticizer is likely to exudate during the lifetime of the finished product [106].

The need to identify suitable solvents and plasticizers compatible with polymers has led to the development of quantitative models of polymer–solvent compatibility. A useful parameter is the Hildebrand solubility parameter (δ), defined as the square root of the cohesive energy density (E/V), where E is the heat of vaporization and V is the molar volume. δ measures the attractive strength between molecules of the same material, i.e., dispersion (London) forces. Solvents that differ significantly in δ values (more than $2 \text{ MPa}^{1/2}$) are considered non-solvents for the polymer. In contrast, those with a δ value within $\pm 2 \text{ MPa}^{1/2}$ compared to that of the polymer are considered suitable solvents (Fig. 4A). The factor value of $2 \text{ MPa}^{1/2}$ was identified through empirical considerations. Values of δ can also be estimated by the method of Small [110], in which particular molecule groups give a specific contribution to the overall molar attraction. However, the extent to which two substances can form a homogeneous mixture depends not only on London forces.

The Hildebrand solubility parameter works well for non-polar hydrocarbon systems but not for polar solvents and solvents that exhibit hydrogen bonding [111]. For this reason, Hansen [112] proposed a change to this model by introducing a three-component parameter (Hansen parameter), taking into account not only dispersive forces (δ_D) but also dipole–dipole (δ_P) and hydrogen bonding (δ_H) interactions. Each contribution is empirically determined based on multiple experimental solubility observations [113]. A visual interpretation of the Hansen method (Fig. 4B) is represented by a three-dimensional sphere of solubility with a radius of $8 \text{ MPa}^{1/2}$ (this value is also determined based on empirical considerations), in which the coordinates of the center of

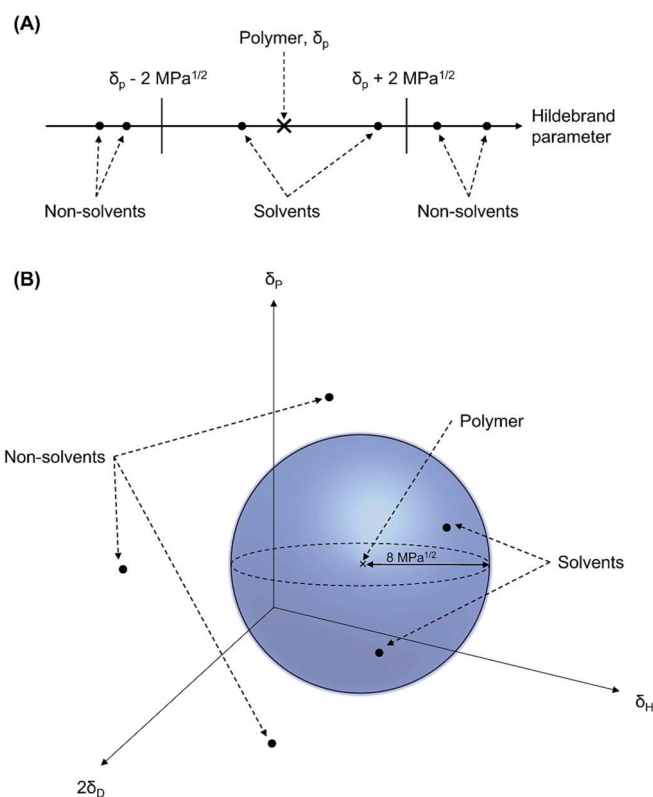


Fig. 4. Solubility criteria of (A) the Hildebrand solubility parameter (δ), where the solvent Hildebrand values are within $\pm 2 \text{ MPa}^{1/2}$ for the polymer Hildebrand value (δ_p), and the non-solvent Hildebrand values differ by more than $2 \text{ MPa}^{1/2}$. (B) Hansen solubility model, where the three axes represent the dispersion (δ_D), polar (δ_P), and hydrogen-bonding (δ_H) components, and solvents and non-solvents fall within or outside a sphere of radius $R = 8 \text{ MPa}^{1/2}$ centered on the polymer, respectively. (Re) adapted from [114]

the sphere correspond to the values of the components of the polymer solubility parameters [114]. The radius of this sphere can be used to identify the dissolving characteristics of polymers by different solvents. Each solvent is represented by a point in a three-dimensional space, with δ_D , δ_P , and δ_H as the axes. The point must fall inside the sphere (the solubility volume) for solvents.

In contrast, all non-solvents fall outside the solubility volume, which explains why two substances are mutually compatible when they have similar values of δ . In this regard, it is generally accepted that for good compatibility, the difference in solubility must be smaller than $3.7 \text{ (J/cm}^3)^{1/2}$ [99]. The polymer–solvent interaction is inversely proportional to the difference between the solubility parameters of polymer and solvent, i.e., the lower the difference, the stronger the polymer–solvent interaction [115]. These considerations, made initially for polymer–solvent system interaction, can be extended for a first rough evaluation of polymer-plasticizer compatibility when solubility data are available. Hansen’s method allows for screening the number of possible plasticizers for a specific polymer, which is advantageous in practical applications, even if polymers and plasticizers with the same solubility are not always compatible. As previously said, solubility depends on the presence of functional groups in the molecules of the solution components capable of mutual interaction. Plasticizer characteristics determine not only the compatibility but also the amount which can be added to the polymer while ensuring the thermodynamic stability of the mixture. Thermodynamic stability means the absence of plasticizer exudation at temperature changes, mechanical stresses, and pressure. The higher the compatibility is, the more the plasticized system is thermodynamically stable.

3.4. Practical approaches in using the theory of compatibility for plasticizer selection

Chemical similarity, “like dissolves alike”, is not always sufficient to determine the compatibility in a polymer-plasticizer system [108]. For instance, the interaction of polar polymers and plasticizers depends on the presence and arrangement of groups capable of donor–acceptor interaction. A polar plasticizer with a proton-acceptor character, such as an ester, is useful in polymers with average polarities [108], e.g., cellulose acetate. Apart from the chemistry of the selected plasticizer, other factors influence compatibility. For instance, branches in the main carbon-chain structure generally worsen compatibility with polymers due to steric hindrance [59,103,116]. The arrangement of polar groups is essential in the polymer-plasticizer interaction [117], especially if an internal hydrogen bonding would lead to plasticizer-plasticizer solid interactions. The molecular weight of a plasticizer influences entropy: lower molecular weight plasticizers have higher compatibility even if the chemical nature of plasticizers is not affected by a change in their molecular weight. Compatibility gains are counteracted by plasticizers’ increased volatility, which has many drawbacks we will discuss later. Also, plasticizers’ polarity changes with an increase in the molecule’s size in the homologous series.

As far as the alkyl chain length is concerned, the relative content of the polar group in the molecule increases as the alkyl chain length decreases [118]. The polar groups can form strong intermolecular interactions with CA and break the intertwining of CA chains. This can increase the free volume between polymer molecules and promote CA’s chain mobility, thereby reducing CA’s glass transition temperature. On the contrary, when the alkyl chains of the plasticizer are too long, plasticizer molecules do not interact with the polar groups of CA chains because of a shielding effect. This could lead to poor miscibility of the plasticizer with the polymer, even more when it is present at higher concentrations and phenomena such as oiliness, tackiness, and opacity due to incompatibility. As a general rule for cellulose acetate, it is found that low molecular weight esters with a C-2 terminal group are miscible, those with C-3 may be miscible under favorable circumstances, and those of C-4 are not miscible with CA [40,119,120]. This observation considerably limits the range of molecules used in CA as effective plasticizers.

4. Plasticization of cellulose acetate

In CA, many polar groups, including hydroxyl and acetyl, generate a strong intermolecular interaction. Consequently, CA chains are relatively compact, which results in little mobility and intrinsic rigidity, as confirmed by the material’s high T_g. Moreover, CA does not crystallize and exists in the amorphous form [121]. The processing temperature required to melt CA can approach or exceed its decomposition temperature, with possible thermal degradation of the polymer chains and inadequate mechanical properties for specific applications [65]. Low molecular weight plasticizers are added before or during the processing

to reduce the melt processing temperature. However, these low molecular weight plasticizers may have some drawbacks, such as volatility, high water solubility, and insufficient compatibility with CA. For these reasons, in addition to external plasticization, internal plasticization via introducing flexible substituents has been explored (Fig. 5).

In the following sections, plasticization strategies for CA will be analyzed thoroughly. In this regard, external plasticization has proven to be the most effective approach and is widely used in industry, even if it shows some limitations.

4.1. Internal plasticization

Chemical modification by covalent bonding is performed to plasticize cellulose acetate internally. Grafted substituents can break the H-bonds and promote the mobility of the matrix. Depending on the DS of CA, a variable number of hydroxyl groups can be available for the chemical reaction. New functionalities can be displayed using different species by modification in the melt state or a solvent. Bonding substituents have the primary purpose of plasticizing CA without external plasticizers, which tend to migrate [122–124]. Works in the literature mainly focus on the esterification derivatization of CA with DS between 2.1 and 2.5, i.e., CDA.

4.1.1. Grafting with cyclic esters, a mix of cyclic esters, and reactive grafting

The reaction of CA with cyclic esters such as L-lactide (LA) and ϵ -caprolactone (CL) is one of the approaches extensively studied in the literature (Fig. 6). Teramoto and Nishio [125], aiming to improve the thermal processability of industrially used cellulose ester and develop a material with biodegradation properties, prepared a series of copolymers by varying the molar substitution (MS) of lactyl units. CDA-grafted-poly(lactic acid)s (CDA-g-PLAs) were synthesized over a wide range of compositions in combination with different ways of graft polymerization: (i) polycondensation of lactic acid, (ii) ring-opening copolymerization of L-lactide in dimethyl sulfoxide, (iii) copolymerization similar to (ii) but in bulk and reacting with the residual hydroxyl groups [126]. Differential Scanning Calorimetry (DSC) measurements revealed that all the copolymers had a composition-dependent, single glass transition temperature (i.e., no phase separation occurred), which decreased from 202 °C (of pure CDA) to almost 60 °C, close to the T_g of PLA homopolymer, increasing the molar lactyl substitution (MS) to 8 (corresponding to 67 wt% in PLA content). For MS equal to 14 (79 wt% of PLA) or higher, the crystallization of PLA side chains could occur; it does not occur for MS \leq 8. Short PLA chains determined a plasticization of the system with a decrease in T_g, while longer PLA-grafted chains showed crystallization. Regarding CDA grafting, a fundamental parameter to consider is the DS: a low amount of residual hydroxyl groups can hinder co-polymerization with a high grafting density of PLA side chains.

The literature also reports the possibility of performing acetylation and derivatization with other substituents directly in the same reaction

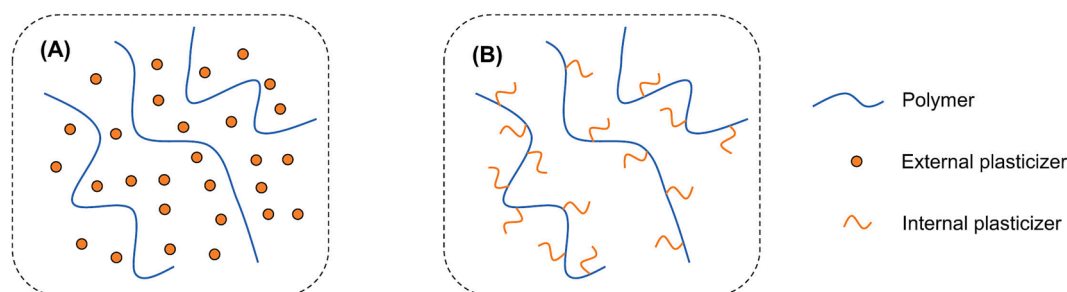


Fig. 5. External plasticization (A) with plasticizer molecules free to move within the polymer matrix. Internal plasticization (B) with grafted chains spacing the polymeric chains.

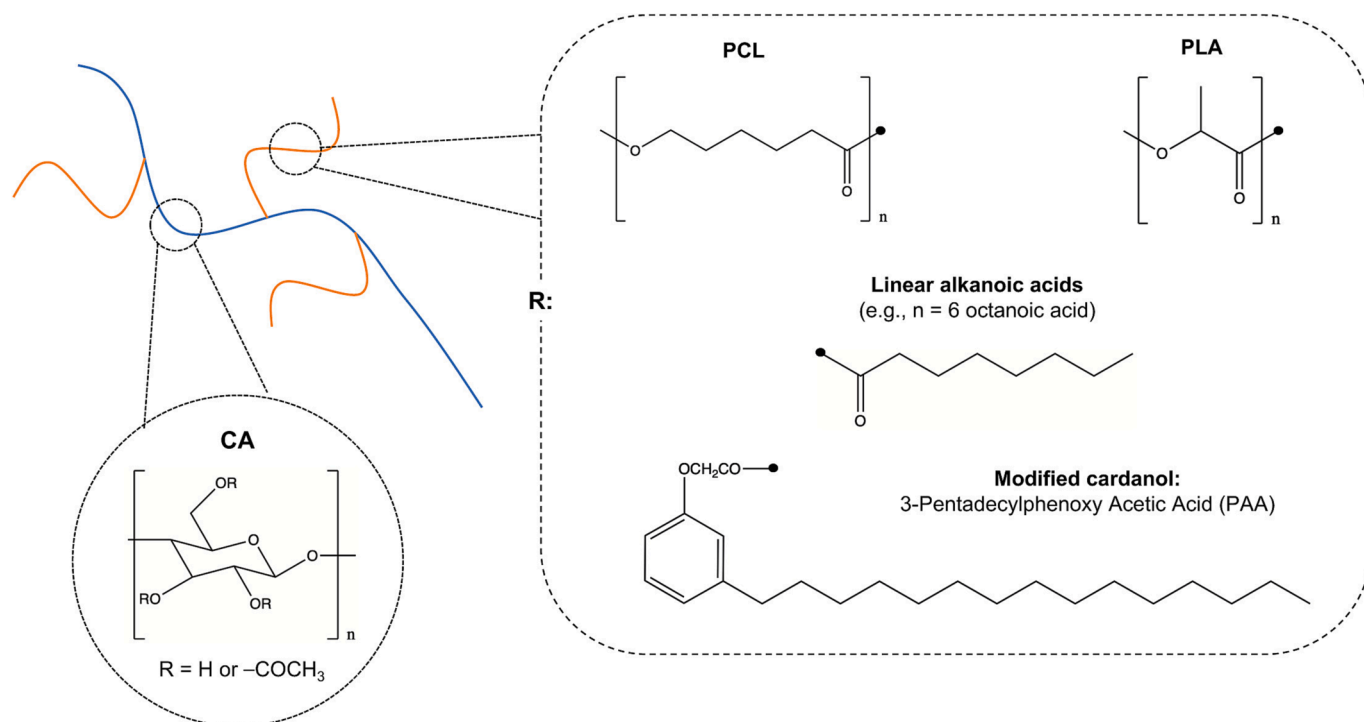


Fig. 6. Chemical structures of different substituents grafted on cellulose acetate (blue line). R is -H or -COCH₃ in the case of CA. Still, it could be a linear alkanolic acid, modified cardanol, polylactic acid (PLA) oligomers, or polycaprolactone (PCL). The black dot on the substituents indicates the linking site.

batch (i.e., one-pot process). Luan *et al.* [122] synthesized cellulose acetate-graft-poly (L-lactide) (CA-g-PLA) copolymers in a one-pot process in 1-allyl-3-methylimidazolium chloride (AmimCl). In this process, cellulose was first reacted with acetic anhydride, yielding CA. Ring-opening graft copolymerization of L-lactide was carried out from the residual hydroxyl groups of CA in the same solution using 4-dimethyl aminopyridine (DMAP) as the catalyst. The glass transition temperature was decreased by increasing the PLA content from 152 °C to 38 °C, for a PLA content of about 18 wt% and 76 wt%, respectively. In these studies, the grafting of PLA had an overall plasticizing effect.

The direct derivatization of cellulose with cyclic esters has also been reported. Yan *et al.* [123] grafted PLA directly on the underivatized cellulose backbone using DMAP as an organic catalyst and AmimCl as a solvent to obtain thermoplastic cellulose-g-PLA copolymers. Xu *et al.* [121] synthesized a series of CDA-g-PLA copolymers with tunable structures, and the resultant CDA-g-PLA copolymers were directly processed into transparent plastics by thermoplastic processing without any external plasticizers, or they were used as macromolecular plasticizers in CDA to improve mechanical strength, stability, and anti-migration properties of the materials. L-lactide grafting onto CA was performed by first dissolving CDA powder in N,N-dimethylformamide (DMF) and then adding L-lactide and DMAP as the catalyst. Different structures in the DS of PLA and DP of the grafted chains by varying the reaction conditions (i.e., reaction time and the molar ratio of LA to AGU) were obtained. The glass transition temperature of the copolymers, evaluated by DSC, was influenced by the DP but had no relation with the DS. Indeed, CDA-g-PLA, with a similar DS, showed a lower T_g value, which linearly decreased as the DP increased. CDA-g-PLA, with a similar DP, showed unchanged T_g even when the DS changed. For instance, CDA-g-PLA-12 and CA-g-PLA-13 with similar DP but different DS (0.53 and 0.29, respectively) displayed almost the same T_g values (164 °C and 163 °C).

Moreover, CDA-g-PLA copolymers exhibited thermal flowing behaviors at a temperature below that of the pristine CDA, and the specific melting temperature decreased as the weight fraction of PLA increased. As mentioned, these copolymers were also added in CDA as

macromolecular plasticizers. Compatibility between CDA and CDA-g-PLA copolymers used individually as plasticizers relied on the weight fraction of PLA of the specific CDA-g-PLA copolymer and were proven by the presence of a single T_g value by DSC analyses, good uniformity, and optical transparency. Phase separation occurred when the weight fraction of PLA in CDA-g-PLA was over 30 wt%. Regarding the mechanical properties, the storage modulus of the CDA/CDA-g-PLA system was higher than CDA plasticized with 30 wt% of triethyl citrate (TEC) at room temperature. From the authors' point of view, these results confirm the higher efficacy of external plasticization in reducing material stiffness.

Among cyclic esters for CA derivatives, CL is extensively reported. Szamel *et al.* [127,128] and Videki *et al.* [129] modified CA with a DS of 1.7 or 2.1 with CL (Fig. 6). The grafting of CL on CA was effective only at high temperatures and for long reaction times because milder conditions promoted only homopolymerization of CL, and no internal plasticization occurred. When reaction conditions allowed grafting, increasing time and temperature increased the length of the grafted chains.

Surprisingly, grafting was easier in CA with a higher DS despite the fewer OH groups. At the same time, reference samples were prepared without a catalyst to investigate the effect of external plasticization with monomeric CL. Increasing CL content by internal (grafted chains) or external plasticization proved efficient in lowering T_g. Comparing the DMTA (Dynamic Mechanical Thermal Analysis) spectra of CA plasticized externally with 40 wt% CL and CA with a gPCL content around 44 wt% (corresponding to an average length of about seven repeat units), the T_g values from tan δ resulted lower for CA-g-PCL (41 °C) than for externally plasticized CA (69 °C), a result which the slight difference in CL could not explain. Therefore, internal plasticization was more efficient than external plasticization with monomeric CL. Plasticization resulted in a decrease in stiffness and strength, while deformability increased only slightly.

Thermoplasticization of CA with a mix of cyclic esters, CL and LA, is also reported by Yoshioka *et al.* [130]. They plasticized CA by grafting CL and LA selectively by ROP in the melt state at 140 °C using stannous octanoate as the catalyst. The grafting reaction proceeded rapidly and

could be completed within 10–30 min by reactive processing in a twin extruder. LA was grafted more rapidly than CL onto CA. NMR spectroscopy of the grafted chains indicated the presence of block polymer portions and randomly polymerized parts. Mixed side chains confer high thermoplasticity, elasticity, and amorphous nature to grafted products. Aiming at expanding the possible range of cyclic esters, Teramoto *et al.* [131,132] grafted CA by ROP with different aliphatic lactones, (R,S)- β -butyrolactone (BL), δ -valerolactone (VL), and CL, in addition to previously synthesized CA-g-PLA on the residual hydroxyl groups of CA. CA-g-PHAs were evaluated to establish the relation between the molecular structure and the thermal behavior. Increasing the molecular weight of an acetylated AGU, which contains aliphatic polyester side chains of a given molar substitution, decreased T_g due to the side chains' plasticizing effect.

The bulk reactive extrusion process to produce grafted cyclic lactones simultaneously on the polysaccharide chain was produced by Warth *et al.* [133]. The advantages of this process are in situ formation of oligo- and poly-(ϵ -caprolactones) on CA as non-migrating plasticizers combined with in situ compatibilization. Shiraishi *et al.* [134] used the melt-processing reaction of CA with maleic anhydride (MAH) and glycerol (Gly). However, CA plasticized with MAH and Gly was unsatisfactory in elongation at break and elastic modulus. As external plasticizers, the subsequent addition of citrate esters, TEC, and acetyl triethyl citrate (ATEC) improved the physical properties of the materials. DSC analysis revealed a T_g decrease by 80–100 °C in plasticized CA with this procedure.

4.1.2. Cellulose acetate modification with cardanol

Iji *et al.* originally explored the derivatization of CDA with cardanol moieties [135]. Cardanol is a phenol derivative consisting of a hydrophobic long-side chain of 15 carbon atoms with unsaturated bonds (from 1 to 3) and phenol as a rigid aromatic part with a reactive hydroxyl group. Cardanol was first modified by changing the hydroxyl group to the acetic acid chloride group to make it more reactive (Fig. 6). Double bonds along the alkyl chain were saturated to prevent crosslinking between cardanol molecules. It is a viable secondary reaction that could occur during the esterification of hydroxyls on CDA chains.

The cardanol-bonded CDA had good thermo-plasticity without requiring an external plasticizer. It showed lower water absorption (1.2 % for 41 wt% cardanol) compared to pure CA (17 %) and TEC-plasticized CA (4.9 % for 41 wt% TEC). The lower water absorption of cardanol-bonded CA can be explained by the characteristic hydrophobicity of the grafted chains and the less available –OH groups on the backbone. CA bonded with 41 wt% cardanol exhibited a higher glass transition temperature (142 °C) than CA with 41 wt% TEC (80 °C), probably due to the rigid phenyl part's presence that impairs chain mobility.

Since the synthesis process by esterification using acid chlorides of cardanol requires high energy consumption and a large amount of solvents, in a more recent work, Tanaka *et al.* [136] used an isocyanate-modified cardanol, 3-pentadecylcyclohexyl (6-isocyanatohexyl) carbamate (PICC). They obtained a significant improvement in terms of productivity, making the separation process much easier. However, isocyanate-modified cardanol was unsatisfactory in plasticization due to the high interactions between the side grafts. For this reason, an upgrade was necessary to decrease the intermolecular forces. Incorporating a short aliphatic acyl group with lower polarity than the acetyl group was investigated to confer more plasticity to the material. While maintaining the DS of PICC, substituting acetyl groups with propionyl groups increased the melt flow rate (MFR) by about twenty times and decreased the bending strength. This was mainly attributed to the reduced intermolecular interactions of the PICC-bonded cellulose derivative because of the lower polarity of the propionyl group compared to the acetyl group.

From the authors' point of view, the attempt to modify cellulose with cardanol obtained from agricultural byproducts and claimed as

sustainable is a promising strategy; however, the synthesis process should be improved toward a green chemistry approach. Moreover, the final product often has unsatisfactory thermoplastic properties and may eventually require further modifications, limiting the benefits deriving from agricultural waste exploitation.

4.1.3. Grafting of fatty esters

Thermoplastic cellulose esters can be achieved by breaking the hydrogen bonding of cellulose with functional side chains acting as internal plasticizers (Fig. 6). The scientific literature is rich in studies on this topic. Among these works, Vaca-Garcia *et al.* [137] reported the esterification of cellulose with fatty acids (from n-octanoic to n-octadecanoic) and acetic anhydride, through which they obtained cellulose mixed triesters (CMT) with an average of 2.2 acetyl groups and 0.8 fatty substituents per AGU. These mixed esters were compared with cellulose simple fatty triesters (CST) synthesized using fatty acid chlorides. Dynamic Mechanical Analysis (DMA) in the bending mode showed remarkable differences between CMT and CST. Mixed esters were more rigid than homologous simple (i.e., no acetyl groups) esters and at the same temperature. The flexibility of the fatty chains and the space created between the cellulosic chains by long substituents led to a decrease in the mechanical performance compared with the mixed cellulose triesters. Indeed, the storage moduli E' for the CST were at least 25 times lower than the CMT's. A slight diminution of E' was observed when the side chains of CST were lengthened. On the contrary, no influence of the fatty chain length on E' for CMT was detected. The authors concluded that CMT's abundant short acetyl groups maintained superior rigidity. This fact, combined with the rise of the molecular weight of the polymer, accounted for the unexpected increase in T_g (from 144 °C for n-octanoic to 177 °C for n-octadecanoic) of the mixed esters at increasing size of the fatty substituent, with a similar DS.

Similarly, Crepy *et al.* [138] performed the esterification of cellulose by functionalizing the polymer backbone with aliphatic chains. When the fatty chain length exceeded 12 carbon atoms, a fraction of the alkyl chains crystallized into hexagonal packing with a side chain crystallization phenomenon revealed by the endothermic melting peak in the DSC thermograms. The second heating of DSC thermograms showed that T_g values increased as the chain length increased, from 75 °C for octanoate (C-8) to 114 °C for palmitate (C-16), due to the restriction of the backbone cooperative motion. In another study, the same authors [43] confirmed the crystallization phenomena of long alkyl chains (from C-10 to C-16). The plasticizing effect of alkyl chains on the glass transition of cellulose chains is affected by the DS rather than the fatty chain length.

Xiao *et al.* [139] investigated cellulose esters with aromatic substituents. They synthesized cellulose esters containing phosphorus, particularly cellulose diphenyl phosphate (C-Dp) and cellulose acetate diphenyl phosphate (CA-Dp) mixed esters. In the latter case, the co-presence of acetate and diphenyl substituents was obtained by adding diphenyl chlorophosphate (DCP) and acetyl chloride to substitute the residual hydroxyl groups. The total DS and partial DS of the cellulose mixed esters could be controlled by the ratio of DCP:AC:AGU. With the increase of DCP:AGU, the DS of diphenyl phosphate increased gradually. Still, the total DS values of cellulose mixed esters decreased because the steric effect of bulky diphenyl phosphate made the following acetylation step difficult. No thermal transition was evident in the DSC thermograms of CA-Dp samples. At the same time, for mixed esters, an increase in the DS of diphenyl phosphate substitute (DS_p) led to an important reduction in T_g. This could be explained by the almost complete substitution of the hydroxyl groups with the disruption of the hydrogen bonding network of cellulose and the expansion of the intermolecular distance generated by the bulky diphenyl phosphate groups, enhancing chain mobility with a reduction in the T_g. The lowest T_g value (97 °C) was reached for DS of diphenyl phosphate and acetyl groups, i.e., 1.19 and 1.53, respectively. Likewise, the T_f increased with DS_p, suggesting that the bulky diphenyl phosphate substituents played a remarkable role in the thermal melting of the synthesized cellulose esters.

Other researchers dealt with understanding the plasticization mechanisms of different substituents. Chen *et al.* [65] examined the role of the soft segments and bulky moieties in melt processable cellulose esters homogeneously synthesized in AmimCl by performing a complete substitution of the hydroxyl groups in a final acetylation step. The highest plasticization efficiency was observed with substituents consisting of soft segments between the bulky moiety and the cellulose chain compared to soft segments located at the end of the bulky groups directly attached to the cellulose chain. Besides, longer middle segments were more effective in decreasing the Tg. The presence of an oxygen atom or a double bond reduced the flexibility resulting in a higher Tg. The same decrease in molecular motion was observed when alkyl chains were located at the end of the substituent, away from the main chain. This behavior is probably due to additional interactions with the formation of regular structures, which was also reported in other studies [138,140,141]. Cellulose esters with common bulky moieties, such as phenyl and naphthyl groups, had Tg values similar to CA. Due to their high steric hindrance, bulkier substituents, such as adamantane and 4-*tert*-butyl phenyl groups, were shown to increase Tg. Therefore, ester groups with suitable volumes can promote the mobility of cellulose molecular chains, while oversized rigid ester groups will increase the Tg of cellulose esters. On the contrary, combining bulky terminal moieties and soft middle segments can improve the mobility of the cellulose chains. Phenyl propyl cellulose acetate ester (CpP-2.25-Ac-0.75) showed the lowest Tg at 80 °C. When the terminal phenyl group was replaced by a methyl group, resulting in a butyl chain, the corresponding ester's Tg increased to 127 °C. The terminal phenyl group effectively increases the molecular chains' mobility.

As mentioned above, cardanol is a phenol derivative with an aliphatic chain, in which the hydroxyl group can be functionalized to make it reactive toward CA. The aromatic ring will be very close to the main chain when a cardanol molecule is grafted on the CA backbone. In contrast, the aliphatic chain results in a simple pendant not directly bonded to the polymer. Based on these considerations, Iji *et al.* [142] compared the mechanical properties of cardanol-bonded CDA with stearic acid-bonded CDA to investigate the effects of the linear side chain and phenyl part of modified cardanol with the linear structure of bonded stearic acid (SA). SA has a linear structure like the cardanol alkyl chain but has no phenyl part. The maximum bending strength and the elastic modulus were higher in cardanol-bonded CDA than SA-bonded CDA with the same DS (0.50), with 80 MPa and 60 MPa for the bending strength, respectively, and 2.2 GPa and 1.9 GPa for the elastic modulus, respectively. The results revealed that the rigid phenyl part of cardanol caused a restriction of the movements of the CDA macromolecules

during the bending measurement. For the same reason, the impact strength of the cardanol-bonded CDA was lower than the SA-bonded CDA, 5.9 kJ/m² and 10.9 kJ/m², respectively.

An additional bonding of linear aliphatic and aromatic components on modified cardanol-bonded CDA was conducted to study the distinct effects of different substituents. Specifically, introducing an aromatic component, such as benzoic acid (BA), increased the elastic modulus and decreased the elongation as the proportion of BA was increased due to the rigidity of the phenyl part in BA (Fig. 7). On the contrary, additional bonding of linear alkanolic acids decreased the elastic modulus, and maximum strength of cardanol-bonded CDA as the proportions of these other components and their lengths were increased. Instead, additional bonding of the mixtures of BA and SA showed almost the same result as bonding SA alone because of the priority effect of the SA long alkyl chain.

Boulven *et al.* [64] investigated homogeneous CA acylation in dioxane and the relation between the structural characteristics of the acylating reagents and the final properties of the obtained cellulose mixed esters. CA with a DS of 2.45 was modified with a series of selected acylating reagents (acyl chlorides) featuring different chemical structures regarding chain length, with or without double bonds, ramification, bulky moieties, aromatic or cycloaliphatic. Esterification reaction with the OH groups of the AGU did not show to be regioselective, even when bulky acylating reagents were used. However, reactivity was dependent on the chemical structure of the used acylating reagent. Indeed, the reactivity of the fatty acyl chlorides decreased as the fatty chain length increased. Acylation, in addition to being affected by the solvent sensitivity of the acylating reagents, is influenced by the steric hindrance effect induced by the aliphatic groups that bear the acid chloride group and their polarity. An increase in the amount of the acylating reactant enhances the extent of substitution. DSC evaluated plasticization by different substituents in cellulose esters with the same DS in terms of Tg. Indeed, the grafting of aliphatic acyl moieties enabled to break hydrogen bonds while simultaneously increasing the free volume, leading to a reduction in Tg. Plasticization is strictly correlated to the DS and the chemical structure of the substituents: increasing the length of the fatty chain causes the Tg to decrease due to the higher degree of flexibility and greater free volume imparted when the size of the substituent lengthens [143]. However, high DS can promote the crystallization of acyl moieties. Moreover, possible double bonds on the substituent are detrimental to the overall ductility [144].

Regarding the bulky moieties, longer segments between the aromatic ring and the cellulose backbone are more effective in increasing flexibility. In contrast, aromatic rings directly attached to the AGUs do not

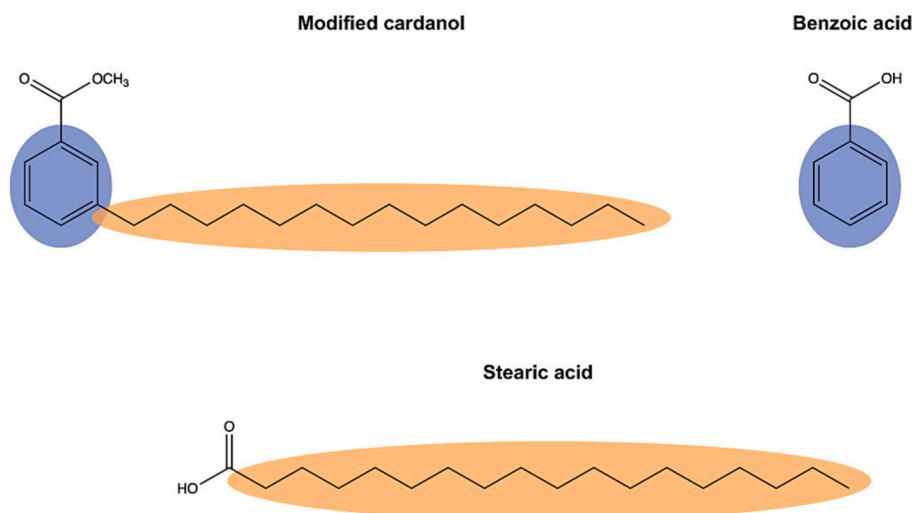


Fig. 7. Chemical structures of modified cardanol, benzoic acid (BA) and stearic acid (SA), highlighting in blue the benzene ring and in orange the aliphatic chain.

favor mobility gain. Adamantyl moieties cannot act as effective plasticizers to rigidify the CA derivative. On the contrary, the CDA derivative acylated with hydrocinnamoyl chloride seems to be the most promising acylated cellulose material. The reactivity of hydrocinnamoyl chloride was high enough to generate a completely substituted CDA derivative with a T_g value of 125 °C, due to the high degree of modification combined with the chemical structure of this substituent ($DS_{\text{acetyl}} = 2.45$; $DS_{\text{hydrocinnamoyl}} = 0.52$).

Overall, an acylating reagent consisting of a linear spacer segment attached to the cellulose chain with a terminal bulky aromatic group is the optimal structure for the internal plasticization of cellulose or cellulose acetate. Thermoplastic cellulose esters would resolve migration problems related to CA plasticized with external plasticizers. However, from a practical point of view, it is challenging to synthesize long-chain aliphatic esters because of the poor reactivity and steric effect of the long-chain fatty acyl chloride or long-chain fatty acid.

Regarding acyl moieties with bulky structures, special attention must be taken to prevent the appearance of a stiffening effect instead of plasticization. High reaction temperatures, long reaction times, basic catalysts, or special acylation reagents are often employed to increase the efficiency of internal plasticization. Moreover, the thermo-mechanical properties of cellulose esters obtained in this way are seldom satisfactory and do not pay back the costs and efforts of their synthesis. These considerations explain why external plasticization is still widely used at the industrial level.

4.2. External plasticization

External plasticization using low molecular weight plasticizers is the most widely applied approach in industrial applications. The glass transition temperatures and the mechanical properties (elastic modulus) of CA systems with different plasticizer contents are reported in Table 2. In the following section, we will review CA's most used families of plasticizers.

4.2.1. Phthalate esters

Phthalate esters, which are esters of *ortho*-phthalic acid, are the most popular plasticizers in plastics [145,146], constituting about 80 % of all plasticizers used worldwide [99]. Phthalates are obtained by the esterification of *o*-phthalic acid with alcohols. The effect of alcohol in plasticizers on physical, chemical, and mechanical properties has been widely investigated, mainly in polyvinyl chloride (PVC) [108,147]. In this regard, as the carbon content in the alcohol increases, the molecular weight of the plasticizer increases together with the boiling point. This, in turn, causes a decrease in the vapor pressure of the plasticizer, which is the most crucial feature for plasticizer retention [108].

Plasticizers showing similar chemical structures have similar interactions in the polymer, even with different molecular weights [108]. Among phthalates, dimethyl phthalate (DMP) and diethyl phthalate (DEP) are the most widely used [38,50,148–153]. In 1930, Walsh and Caprio discovered that shorter alkyl phthalates, such as DMP, DEP, and methyl ethyl phthalate (MEP), could be employed to obtain cellulose derivative plastics with excellent results. At that time, it was assumed that because of their relatively low boiling point (282 °C for DMP, 290 °C for DEP) these molecules would be too volatile to be used successfully since they would evaporate from the plastic. Instead, shorter alkyl phthalates were retained in the plastic even after prolonged exposure to elevated temperatures. This retentive power, able to overcome the tendency to evaporate due to lower boiling point, was surprising at that time [154].

Since then, DEP has been successfully employed in CA articles, despite a lack of knowledge of the plasticization mechanisms. More recently, Benazzouz et al. [38] studied the interactions responsible for the plasticizing effects of DMP in CA: DMP interacts with the polymer chains of CA via weak interactions of dipolar nature and not via stronger H-bonding. These dipole–dipole interactions, developed between acetyl

side groups of CA and the ester phthalate moieties of DMP, increase the overall mobility of CA chains, locally influencing the molecular mobility and water uptake tendency. Dipole-dipole interactions decrease the water uptake of CA films, at least for small water content, by hindering the access of water molecules to the acetyl side groups of CA. The same interactions are established with DEP due to the similarity of the molecular structures. The longer alkyl chains in DEP are more effective than DMP in spacing CA chains, creating higher free volume; moreover, DEP is slightly less volatile. The T_g shifts to lower temperatures as the amount of plasticizer is increased [155]. This decrease in T_g is due to the intercalation of plasticizer molecules between polymer chains, which increases the free volume and decreases the activation energy of CA chains' mobility. DEP is compatible with CA overall, but there is a miscibility threshold. By dielectric measurement of relaxation times, Bao et al. reported a phase separation effect for DEP concentration above 25 wt% [149]. Dibutyl phthalate (DBP), with butyl chains, is another low molecular weight phthalate used in CA, mainly for permeability studies related to transdermal applications [156,157]. It is worth noticing that in the eyewear industry, frames made of cellulose acetate plasticized with DEP cannot be used with polycarbonate lenses since phthalate has a strong affinity toward the latter, and migration to it takes place, with consequent loss of lens functionality.

4.2.2. Citrate esters

Citrate esters are well-known additives used in the plastic industry as the first choice for replacing dibenzoate and phthalates-based plasticizers. They are considered safe and non-toxic for many applications, such as food packaging, medical equipment, and toys [158]. Since they are derived from citric acid (2-hydroxy-1,2,3-propane tricarboxylic acid), a natural constituent and common metabolite of plants and animals [27] obtainable industrially through fermentation of organic waste [159,160] or fungal fermentation [161], citrates are deemed to be renewable molecules [162]. According to the literature, citrates such as acetyl triethyl citrate (ATEC) and triethyl citrate (TEC) were used successfully in CA [27,90,120,134,163–168].

Ghyia et al. melt-blended CA with TEC and ATEC to determine their effect on the biodegradation and plasticization of renewable resource derivatives such as CA. Beyond complete miscibility with CA, adding plasticizers reduced the glass transition temperature and Young's modulus, increasing the elongation at break and, more importantly, the biodegradation rate as the plasticizer content increased [27]. CA plasticized with ATEC was found to have superior tensile properties, compared with TEC, in CA components [134]. Other citrate esters reported as plasticizers in CA are tributyl citrate (TBC) and acetyl tributyl citrate (ATBC) [167,169]. When ATBC was used in CA, white and opaque films were obtained by casting. Further DSC analysis demonstrated the presence of a crystalline peak. This, however, did not occur when the films were prepared by melt processing [167].

4.2.3. Glycerol derivatives

Glycerol derivatives are triglycerides obtained by the reaction of glycerol with carboxylic acids, such as acetic, propionic, butanoic (butyric), isobutanoic (isobutyric), isopentanoic (isovaleric), and benzoic acids by direct low-temperature esterification and further purification. [170] Glycerol triacetate (GTA) (or triacetin) is the triglyceride obtained by acetylation of the three hydroxyl groups of glycerol [171], a well-performing plasticizer in CA, as well as tripropionin, obtained from glycerol and propionic acid [172].

Several studies analyzed the plasticizing efficiency of GTA in CA [44,120,173]. In one of these studies, GTA was reported to decrease the T_g of CA from 200 °C (pristine material) to 110–130 °C with 20 wt% of plasticizer [174]. Glycerol diacetate (GDA) (or diacetin), which has one less ester group than GTA and is more polar, was found to be more effective in reducing the T_g and stiffness of CA compared with GTA (Fig. 8) [39].

Phuong et al. [175] used GTA and GDA to plasticize CA and produce

Table 2

Plasticized CA systems. For processing, C = casting; IM = injection molding; CM = compression molding; E = extrusion; RP = reactive processing.

Plasticizer	DS	Content (w/w %)	Tg (°C)	Elastic Modulus (GPa)	Tg eval.	Processing	Application(s)	Ref (s)
Tricresyl phosphate (TCP)	2.96	0, 5, 10, 15	205, 184, 182, 180	–	tan δ	C	Optical films for LCD applications	[8]
Triphenyl Phosphate (TPP)	–	0, 6, 12, 15, 20	206.7, 184.8, 173.6, 171.8, 169.4	–	tan δ	C	Optical films for LCD applications	[189]
Biphenyl diphenyl phosphate (BDP)	–	–	206.7, 197.7, 185.9, 186.7, 174.5	–	–	–	–	–
Triethyl citrate (TEC)	2.45	20, 30, 40	130, 110, 86	4.1 \pm 0.1, 2.1 \pm 0.4, 0.8 \pm 0.3	tan δ	IM	Plasticized CA/clay hybrid nanocomposites	[163]
	2.5	0, 16.7, 23.1, 28.6, 33.4	190, 137, 121, 115, 112	–	DSC	IM	Biodegradable CA	[27]
	2.36	20	140	–	E''	IM	CA/poly(epichlorohydrin) blends and MMTO nanocomposites	[164]
	2.5	0, 10, 20	190, 153, 109	2.0 \pm 0.1, 1.53 \pm 0.08 (C) 1.86 \pm 0.2, 1.44 \pm 0.06 (CM)	DSC	C, CM	Degradation studies on CA	[167]
	2.1	29, 41	109, 80	–	DSC	IM	CA bonded with cardanol	[135]
	2.5	0, 15, 20, 25, 30, 35, 40	196.6, 142.4, 124, 115.6, 108.3, 100, 75.8	–	DSC	IM	Plasticized CA	[120]
	–	15, 20, 25, 30, 35, 40	149, 140, 129, 121, 115, 94	–	tan δ	–	–	–
	2.5	15	140	–	DSC	RP	Melt processing of CA with isocyanate	[210]
	2.4 – 2.5	25	99.6	–	DSC	CM	Plasticized CA with reactive plasticizer	[134]
Acetyl triethyl citrate (ATEC)	2.4 – 2.5	25	112.1	–	DSC	CM	Plasticized CA with reactive plasticizer	[134]
	2.5	0, 16.7, 23.1, 28.6, 33.4	138, 120, 116, 113	–	DSC	IM	Biodegradable CA	[27]
Glycerol Triacetate (GTA)	2.5	25	–	1.39 \pm 0.02	–	CM	Blending of CA with water soluble polymers	[211]
	2.5	20	110 – 130 (121)	1.75	DSC	E	Process of plasticized CA with different tools	[174]
	2.37	0, 5, 10, 20, 40	190, 173, 150, 135, 60	–	–	C	Water permeation in plasticized CA	[181]
	2.5	0, 10, 20	190, 151, 118	1.82 \pm 0.07, 1.55 \pm 0.11 (C) 2.15 \pm 0.16, 1.71 \pm 0.07 (CM)	DSC	C, CM	Degradation studies on CA	[167]
	2.63	0, 10, 20, 30	–	4.3, 3.9, 3.4, 1.9	–	IM	Nanocomposites of CA with clay	[212]
	2.5	0, 15, 20, 25, 30, 35, 40	196.6, 122.8, 130.7, 104.1, 102.4, 85.7, 84.7	–	DSC	IM	Plasticized CA	[120]
	2.5	15, 20, 25, 30, 35, 40	145, 133, 114, 99, 83, 71	–	tan δ	–	–	–
	2.5	15	133.5	–	DSC	RP	Melt processing of CA with isocyanate	[210]
	2.4	20, 30	–	3.1 \pm 0.1, 2.1 \pm 0.1	–	IM	Biodegradability of plasticized CA	[175]
	2.45	0, 10, 20, 30, 40	192, 142, 109, 82, 60	–	MDSC	C	CA/plasticizer systems	[173]
	2.08	0, 10, 20, 30, 40	212, 159, 118, 94, 62	–	tan δ	–	–	–
	–	0, 10, 20, 30	201, 156, 125, 101, 74	–	MDSC	–	–	–
	1.83	0, 10, 20, 30, 40	214, 167, 141, 122	–	tan δ	–	–	–
	1.83	0, 10, 20, 30, 40, 50	204, 147, 116, 89, 73	–	MDSC	–	–	–
	–	0, 10, 20, 30, 40, 50	220, 163, 129, 103, 74, 66	–	tan δ	–	–	–
	2.45	15, 20, 25, 30	142, 127, 115, 98	–	tan δ	IM	Injection molded CA	[44]
Glycerol diacetate (GDA)	2.4	30	–	1.9 \pm 0.1	–	IM	Biodegradability of plasticized CA	[175]
Dimethyl phthalate (DMP)	2.45	0, 10, 17, 22, 100	191 \pm 1, 126 \pm 5, 110 \pm 5, 97 \pm 5, –79 \pm 1	–	DSC	C	Interaction between DMP and CA	[38]
Diethyl phthalate (DEP)	2.4	0, 3, 9, 17, 29, 40, 50	199, 182, 160, 129, 110, 88, 77	–	tan δ	IM	Plasticized CA	[151]
	2.45	0, 15, 20, 25, 35, 45, 100	192, 118, 110, 101, 78, 57, –88	–	MDSC	C	Miscibility of CA/DEP systems	[149]
	2.45	0, 15, 20, 25, 35, 45	212, 120, 111, 101, 75, 55	–	E''	–	–	–
	2.45	0, 10, 20, 30, 40, 50	192, 141, 113, 84, 69, 65	–	MDSC	C	CA/plasticizer systems	[173]
	–	0, 5, 10, 15, 20, 25, 30, 35, 40, 45	212, 178, 150, 142, 129, 116, 111, 103, 81, 73	–	tan δ	–	–	–

(continued on next page)

Table 2 (continued)

Plasticizer	DS	Content (w/w %)	Tg (°C)	Elastic Modulus (GPa)	Tg eval.	Processing	Application(s)	Ref (s)		
Diocetyl phthalate (DOP)	2.08	0, 10, 20, 30, 40, 50	201, 160, 134, 132, 131, 134	2.8 ± 0.3, 1.4 ± 0.2	MDSC					
		0, 10, 20, 30, 40, 50	214, 170, 152, 141, 138, 137		tan δ					
	1.83	0, 10, 20, 30, 40, 50	204, 155, 125, 108, 100, 102		MDSC					
		0, 10, 20, 30, 40, 50	220, 168, 140, 125, 121, 120		tan δ					
	~2	13, 17, 20, 23, 28, 33	135, 125, 115, 112, 107, 103		–	–	–	CA plasticization	[213]	
	2.45	15, 20, 25, 30	143, 131, 123, 117		tan δ	IM	Injection molded CA	[110]		
	2.45	20, 30, 40	123, 94, 75		tan δ	CM	Comparison with IL	[204]		
	2.5	20, 30	115, 78		E''	IM	Biocomposites with curauá fibers	[214]		
	PEG8000	2.37	0, 5, 10, 20, 40		144, 111	1.71 ± 0.05, 1.75 ± 0.03 (C), 1.64 ± 0.08, 1.60 ± 0.07 (CM)	–	C	Water permeation in plasticized CA	[181]
					190, 184, 178, 166, 146					
PEG4000		0, 5, 10, 15, 20, 30	190, 179, 169, 161, 154, 142							
PEG600		0, 5, 10, 15, 20	190, 174, 161, 153, 145							
PEG200	2.5	0, 10, 20	190, 154, 156		DSC	C, CM	Degradation studies on CA	[167]		
PEG600	2.5	0, 10, 20, 30, 40, 50	198.1, 177.5, 166, 162.5, 152.8, 133.9, 206.7, 196.7, 174.2, 162.6, 130.2, 128.3	–	DSC	C (22 °C) C (40 °C)	Transdermal delivery	[12]		
α-GPA	2.5	8, 16	164, 142	2.38, 2.40	–	CM	Carbohydrate esters as plasticizers	[199]		
β-GPA			162, 142	2.44, 2.59						
α-GPP			165, 146	2.1, 2.2						
β-GPP			160, 142	2.17, 1.95						
α-GPB			166, 166	1.93, 1.71						
β-GPB			167, 133	1.98, 1.90						
BMIMCl			2.45	20, 30, 40	120, 84, 58				–	tan δ
BMIMBF ₄	~2	15	161		DMA	C	Ionic liquids as plasticizers for CA	[215]		
BMIMOTF	~2	15	163							
BMIMPF ₆	~2	15	176							

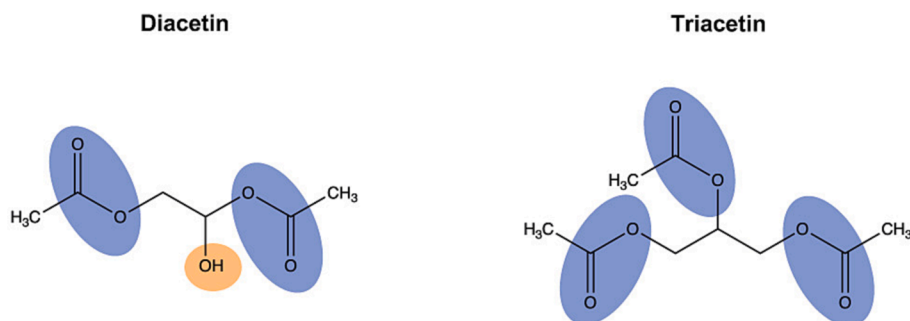


Fig. 8. Chemical structure of diacetin and triacetin. The higher polarity of diacetin is due to a hydroxyl group (orange) instead of an ester group (blue).

samples by melt processing. Both plasticizers provided a satisfactory plasticizing efficiency, such as DEP, due to their low viscosity and ease of diffusion into CA, which enables a large processing window and increases the material's flexibility. CA with 30 wt% GTA displayed a slightly higher elastic modulus than CA with 30 wt% GDA ($E = 2.1$ GPa and 1.9 GPa, respectively). The authors also identified 30 wt% as the maximum concentration required to process the material. Indeed, higher plasticizer contents (as 40 wt%) resulted in unacceptable low mechanical properties due to the complete solvation of the functional groups of CA and the separation of CA molecules, dramatically decreasing their interchain interactions.

4.2.4. Polyethylene glycols (PEGs) and Polypropylene glycols (PPGs)

Polyethylene glycols (PEGs) with low molecular weight, such as

PEG200 and PEG400, are considered environmentally friendly, safe, inexpensive, recyclable, and water-soluble plasticizers [176]. They are widely employed due to their biodegradability, biocompatibility, and non-toxicity properties. They are soluble in acetone and form a single-phase solution with CA having a DS greater than 2.1 [5]. Unfortunately, they have been found to increase hygroscopicity when blended in CA. The high content of higher MW PEG (PEG600) used as a plasticizer in CA films also increased the film's moisture content and water solubility. PEG plasticizers indeed act as water-holding agents [177].

Rosa *et al.* [178] reported that blending CA with PEG400 or PEG1500 decreased the Tg but enhanced the tensile strength: the authors pointed out the effect of the interactions between the free hydroxyl groups of PEG and the chains of CA as an explanation of the enhanced resistance of CA. Polypropylene glycols (PPGs), with a repetitive unit of three carbon

atoms between ether oxygen atoms, have been reported as CA plasticizers in film applications. A range of 16–20 wt% in PPG content resulted in acceptable physical properties in elastic modulus and tensile strength [179].

4.2.5. Comparison between different plasticizers

To date, several studies that directly compare the efficiency of different plasticizers have been reported in the literature. Quintana *et al.* plasticized CA with PEG 200, GTA, tripropionin, and TEC at 10 and 20 wt%, obtaining a decrease in the elastic modulus and stress at the break while increasing ductility. Interestingly, when CA was mixed with ATBC, the films obtained by casting were white and opaque, and DSC analysis demonstrated the presence of a crystalline melting peak [167]. Opaque films usually reveal scarce compatibility between the plasticizer and the polymer [180]: butyl chains increase apolarity of the plasticizer molecule and decrease the affinity with CA. On the contrary, shorter alkyl chains with two or three carbon atoms (as in triacetin and tripropionin, respectively) did not show poor compatibility, and the films were utterly transparent.

Zepnik *et al.* evaluated the elongational flow properties of externally plasticized CA with TEC [165]. The higher the plasticizer content, the stronger the dilution effect and the lower the viscosity. Disentanglement of CA chains is favored at higher plasticizer content under extensional flow, yielding lower melt strength and higher melt extensibility [165]. These observations confirm that plasticizers increase polymers' flexibility at room temperature and can be used as processing aids.

Erdmann *et al.* [120] studied CA plasticized with TEC and GTA from 15 to 40 wt%. By analyzing the Tg decrease as a function of plasticizer content, they stated the higher effectiveness of GTA. They attributed this slight difference in the glass transition temperature decrease to the interactions between the plasticizer and CA in hydrogen bonding and dipole–dipole interactions. TEC contains a free hydroxyl group and can therefore interact with the hydroxyl groups of CA, unlike GTA. The latter, instead, behaves more as a shielding plasticizer, reducing the intermolecular forces between the CA chains, increasing the free volume, and resulting in lower Tg.

Charvet *et al.* observed a more substantial decrease of Tg with GTA than DEP [44], due to a different plasticization mechanism. As both plasticizers can plasticize CDA through dipolar interactions between the ester groups, the significant difference probably comes from the aromatic ring of DEP molecules, which can induce steric effects [173]. Guo *et al.* reported a higher effectiveness of GTA compared to PEG8000, PEG4000, and PEG600: GTA, whose molecular weight is lower, had a better plasticizing efficiency in reducing the glass transition temperature, while the Tg of CA films plasticized with PEG increased as PEG molecular weight increased [181].

4.2.6. Phosphates

Cellulose esters have excellent transparency and have been used for decades because of their optical properties in many applications, such as polarizer protective films in liquid crystal displays (LCD). The most common plasticizer used in these applications is tricresyl phosphate (TCP) [7,182,183]. The addition of TCP increases the orientation birefringence of CA and CAP. In the case of CA, which has a negative birefringence with wavelength dispersion, adding TCP changes the sign of birefringence to positive. The usual plasticizer concentration is 5 wt%.

TCP is an aryl ester of phosphoric acid consisting of a strongly polar core due to the presence of a phosphorus atom with three cresol groups attached to it. It is a bulky molecule that stiffens chain movements and decreases compatibility at higher concentrations. In addition, it was found that TCP does not interact with CTA. Still, pulse-induced ring-down compression ATR-DirLDL step-scan time-resolved spectroscopy (TRS)/2D-IR studies revealed molecular interactions between propionyl groups of CAP and methyl- and phenyl rings of TCP [183].

Manaf *et al.* analyzed the relation between the peak temperature of tan δ and TCP weight content for CAP-TCP and CTA-TCP blends. For the

CAP-TCP blends, the peak temperature of tan δ decreases almost linearly as the TCP content increases. In contrast, it drops sharply when the TCP content is low, showing a minimal decrease beyond 5 wt% for the CTA-TCP blends. CTA has limited miscibility with TCP, which results in forming a sea-island structure in which almost no molecular interactions occur. Instead, CAP has good TCP miscibility, thus showing the molecular interaction previously described [8,183]. A possible explanation could be CAP apolarity being higher than that of CA.

Aryl phosphates can be used as flame retardants with low volatility and good extraction resistance, even if they decrease low-temperature flexibility. Triphenyl phosphate (TPP), with phenols groups instead of cresols, has been used in cellulose acetate [148] for animation cells [184], photographic films [29], optical films [185], conductive composite [186], flame retardant in moldings [187]. However, the proportion used as a plasticizer in CA is limited due to its weak plasticizing efficiency and poor compatibility, which results in brittleness and exudation.

The plasticizer was reported to bleed out for a content of 28 wt% [119]. In general, it has been used solely to take advantage of its fire retarding properties [188]. Kim *et al.* plasticized cellulose acetate with TPP, biphenyl diphenyl phosphate (BDP), and a mixture. As evidenced by the decrease in Tg, plasticizing efficiency was higher for TPP, probably because of the greater size of BDP, with an extra benzene ring, restricted chain motion, and reduced free volume. However, BDP had higher thermal stability because of its higher boiling point [189].

Alkyl phosphates are suitable low-temperature plasticizers but are less effective as flame-retardant additives [108]. Triethyl phosphate was reported in CA molding compositions [190]. Tributyl phosphate was blended with CA in CO₂ separation membrane application [191], preparing extremely tough and flexible films, even at -18°C , to be used as interlayers to manufacture safety glass [192].

4.2.7. Trimellitates

Trimellitate esters are like phthalic acid esters, except they have a third ester functionality on the aromatic ring. They are considered plasticizers with excellent permanence due to reduced volatility loss and migration rate into other materials [147]. Short-chain esters of trimellitic acids, such as trimethyl trimellitate (TMTM), triethyl trimellitate (TETM), and tributyl trimellitate (TBTM), are known plasticizers for CA. In particular, TMTM proved good plasticizing efficiency and a low migration rate toward polycarbonate used for eyewear lenses [2]. The reduced migration of trimellitates toward polycarbonate, compared to DEP, is most likely due to the presence of a third ester moiety on the aromatic ring at position 4 that increases the steric hindrance of the plasticizer molecule and therefore lowers the diffusion coefficient of the plasticizer both in the acetate matrix and in polycarbonate.

4.2.8. Sulfonamides

Other external plasticizers, such as sulfonamides, are suitable for CA, sometimes with partial compatibility, as reported in the literature [193–198]. The sulfonamide group, with atoms such as sulfur and nitrogen, is polar, which makes the molecule compatible with cellulose esters. At the same time, the benzene ring, as mentioned previously, has entropic effects [99].

4.2.9. Sugars esters

The use of carbohydrates esters, such as α , β -glucose pentaacetate (GPA), α , β -glucose pentapropionate (GPP), α , β -glucose pentabutryrate (GPB) as plasticizers in CA with low volatility and good compatibility has been reported in some patents. CA plasticized with GPA or GPP had higher elastic modulus and stress at break than CA plasticized with TEC blended at the same concentrations [199]. As for GPA, the film properties of the formulations were essentially the same at an equal concentration for both anomers. The Tg was composition-dependent, while the films maintained optical transparency and thermal stability. In the case of CA formulations with α -GPP, the films were optically

transparent, but those containing 16 wt% became opaque after prolonged storage. With β -glucose propionate (β -GPP), instead, the films remained transparent. β -GPP was more efficient than α -GPP in reducing the T_g, the stress at break, and the elastic modulus of the formulations. In the case of CA/GPB (glucose pentabutyrate), the longer ester chain diminished the miscibility of both anomers with CA, and the films appeared opaque. Still, the β -anomer had higher compatibility with the CA. Interestingly, this patent has reported for the first time the influence of the anomeric configuration of a plasticizer in determining the miscibility in CA [199].

Besides being nonvolatile, other sugar derivatives such as sucrose octaacetate, mannitol hexaacetate, and sorbitol hexaacetate have been reported as plasticizers forming a rigid gel structure with CA [200]. Having a pyranose or furanose unit as the structural core provides a certain rigidity to the plasticizer molecule, which is less effective in reducing the material's stiffness, at least at room temperature. Moreover, fatty acid esters of sucrose, such as sucrose octaacetate, when incorporated into cellulose esters at a normal plasticizer concentration of 10–50 %, caused the cast film to be brittle and opaque due to crystallization of the sucrose octaacetate. Also, fatty acid esters of sucrose have high water solubility and poor hydrolysis resistance. It has been found that sucrose or glucose mixed esters prepared to contain at least 20 % isobutyryl or propionyl based on the acyl content (the remaining part being acetyl or propionyl) do not crystallize or affect film transparency, as it is resistant to both heat and hydrolysis at the same time. These sugar esters, soluble in organic solvents, are suitable plasticizers for cellulose esters due to their non-crystallizing property and stability to heat and hydrolysis [201].

4.2.10. Ionic liquids

Ionic liquids are another class of plasticizers used in CA [50,202]. In most cases, they are organic salts consisting of a large organic cation and an organic or inorganic anion and have interesting properties such as negligible vapor pressure, non-flammability, ionic conduction, and thermal and electrochemical stability [203]. CA plasticized by 1-butyl-3-methylimidazolium chloride (BMIMCl) was shown to have properties similar to those of CA plasticized with DEP. Electrostatic interactions and hydrogen bonding between BMIMCl and CA made an efficient plasticized system. Moreover, the ionic liquid demonstrated higher performance in the destruction of the crystalline structure of CA than in CA plasticized with DEP [204]. This behavior could be explained by the smaller size and higher polarity of the ionic liquid and by dissociation of BMIMCl, which raises the diffusion rate of ions, increasing the solvating power toward the polymer chains. Other ionic solvent cellulose ester plasticizers reported in the literature include AmimCl [205] and other ionic liquids based on methylimidazolium and methyl pyridinium cores with allyl-, ethyl-, or butyl-side chains [206]. Despite being considered environmentally friendly chemicals, ionic liquids have recently been indicated as a cause for concern because of their documented toxicity [207,208]. Moreover, compared to organic solvents and commercially available plasticizers, the current costs of ionic liquids hinder their potential industrial application [209].

5. Limitations of plasticized cellulose acetate

5.1. Plasticized cellulose durability

Cellulose-based materials usually degrade due to chemical and biological hydrolysis [216]. CA's most significant deterioration process is the hydrolysis of acetate groups, the first degradation step. CA spontaneously undergoes hydrolysis, which is enhanced by high temperatures and relative humidity [217]. Deacetylation causes a decrease in the DS. Release of acetic acid, also known as 'vinegar syndrome', with the beginning of an autocatalytic process, lowers the pH and accelerates the aging process [30]. Moreover, the released acid can cause chain scission due to the catalysis of hydrolysis of C-O bonds in the polymer backbone,

further decreasing mechanical properties [218]. Hydrolysis is favored by water absorption, which is the starting point of CA degradation, followed by deacetylation and chain scission [219].

External plasticization, while necessary for processability and good material properties, is one of the leading causes of CA deterioration because of the migration and evaporation of plasticizers. Secondary reactions of plasticizers with water and other chemicals in the surroundings can also occur. For example, triphenyl phosphate reacts with water to form phenol and diphenyl phosphate, and the subsequent reaction of phenol with acetic acid forms phenyl acetate and water [148]. The plasticizers and the reaction products can be released into the environment due to said deterioration; CA items become prone to cracking, warping, discoloration, exudation, shrinkage, and powdering as they age [50]. As far as the tendency of plasticizers to separate or exude from the polymer matrix is concerned, the most well-known case in the eyewear industry is the migration of DEP from CA to polycarbonate, used to manufacture lenses. This phenomenon causes the polycarbonate to become opaque with the outbreak of cracks (Fig. 9).

Possible strategies to reduce this phenomenon are available in literature and patents. We report herein strategies mainly based on combining plasticizers or blending CA with other polymers.

WO2017/109043A1 patent reports a composition comprising CA, starch acetate, and a monomeric plasticizer. CA is at least half the composition by weight, while the plasticizer content is at most 18 % of the total weight. Such compositions are claimed to prevent the phenomenon of exudation of plasticizers while maintaining the processability in terms of appropriate viscosity ranges and increasing the maximal use temperature. The latter is the lowest temperature at which the storage modulus E' is higher than 1 GPa. For the ternary blends of the invention, this is greater than 100 °C [220].

In other compositions, using camphor as a plasticizer in CA formulations prevented the exudation of the monomeric plasticizers that were incorporated to increase the material's toughness. This composition increased the rigidity of the molded material compared to materials obtained using toughening but exuding plasticizers [188].

In another invention, CA compositions, including one citric acid ester and at least a second plasticizer selected from the organic phosphates, glycerol esters, or trimellitates, showed negligible migration toward the polycarbonate [2]. In another invention, incorporating a synthetic resin based on formaldehyde was claimed to reduce the tendency of plasticizers to exude from the CA-based material [154].

It should, however, be noted that these methodologies, such as blending with other polymers, are not always applicable and convenient. Despite satisfactory results in migration, by reducing the amount of plasticizer or combining different plasticizers, the final plasticizing effect on the mechanical properties is often lower, with increased rigidity of the final products. Moreover, it is worth noticing that camphor and synthetic resins based on formaldehyde raise concerns due to their toxicity for humans [221–224].

5.2. Biodegradability of cellulose acetate and plasticizer effect on biodegradability

Cellulose and cellulose derivatives biodegrade by the action of bacteria and fungi because of their ability to synthesize cellulolytic enzymes (e.g., endoglucanases, cellobiohydrolases, and β -D-glucosidases) [72]. The literature claims that CA is a biodegradable bioplastic [27,176,225]. Nevertheless, the biodegradation rate is affected by the DS and the conditions of the selected degradation environment [216]. The biodegradation rate of CA is known to decrease as the DS increases [226]. The CA's molar mass, crystallinity, and physical form also affect its degradability [227]. Also, environmental factors play a key role in the degradation of materials in combination with the polymer features: temperature, humidity, pH, sunlight, and availability of oxygen, nutrients, and microorganisms can favor the degradation rate of cellulose derivatives such as CA [216,228].

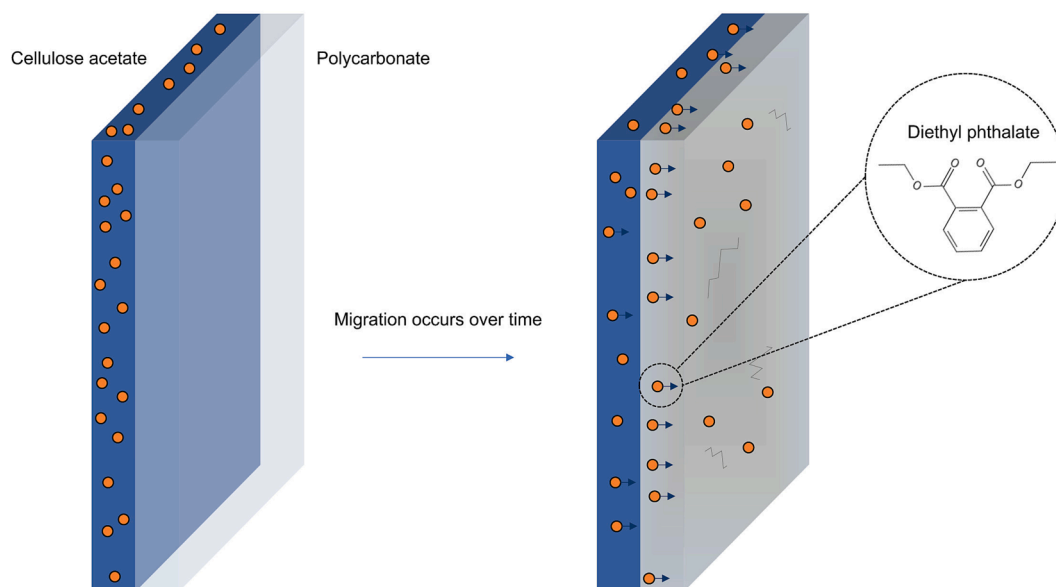


Fig. 9. Representative image of a CA sample plasticized with DEP in contact with a polycarbonate plate. Over time the plasticizer will tend to migrate from CA into polycarbonate, causing the material to become opaque and crack.

Hydrolysis of acetate groups is the first step required for degradation. However, it is slow in ambient conditions, which is a plus for applications intended for long-term use but is a drawback for disposable items. Strong acids (e.g., hydrochloric acid, *ortho*-phosphoric acid, sulfuric acid) or bases (e.g., sodium hydroxide) can catalyze deacetylation [229,230] through enzymes (e.g., acetyl esterase) or UV light irradiation. In the cases where the DS is too high for esterase, biodegradation is initiated by non-biological mechanisms under ambient conditions. The decrease in DS allows biological systems to attack better CA, especially when DS reaches ~ 1.5 – 1.8 . As deacetylation progresses or reaches completion, the cellulose backbone chain scission can occur. The degradation leads to the shortening of the chain length and decreasing the mechanical properties, which usually results in embrittlement of the material [231]. Chain scission of the cellulosic skeleton is generally achieved with enzymes, e.g., cellobiohydrolases, cellobiases, or strong acids [232]. Combining enzymes capable of deacetylation and chain scission can promote CA degradability.

Literature reports other strategies to increase the biodegradability of CA. Chemical functionalization of the CA backbone by reaction of the OH groups with certain biodegradable polyesters could be a useful approach to enhance the degradation rate compared to merely acetylated materials [216]. Several studies have already demonstrated the feasibility of grafting on the CA chain via ring-opening polymerization (ROP) [132,233].

As plasticizers, additives influence the material's degradability due to their hydrophilicity/hydrophobicity behavior. Since water is the primary cause of deacetylation, incorporating hydrophilic plasticizers or blend components could foster material degradation. In this regard, Quintana *et al.* [167] exposed CA plasticized with different molecules to accelerated weathering and evaluated the effect of plasticization on the degradation rate of CA. The plasticization of CA triggered an increase in weight loss significantly higher than that of the pristine CA. The hydrophilicity of CA as a function of the type and concentration of the plasticizer was estimated via contact angle measurements. Only the CA/PEG blend showed higher hydrophilicity than CA, but degradation was shown to be higher with plasticizers known to be more hydrophobic.

The degradation properties may be improved by blending CA with a water-soluble component, such as a biodegradable polymer, making the composition water dispersible. Upon exposure to water, the water-soluble component may dissolve, and plasticized CA may be broken up into small pieces and dispersed. Sensitivity to water, however, limits

the use of these blends for most conventional polymer applications [5]. In practice, most applications use cellulose acetate with DS 2.2–2.4, which is less prone to water absorption and, consequently, to biodegradation at ambient conditions. For these reasons, plasticized acetate, still used in niche sectors such as eyewear and jewelry, cannot be considered a biodegradable material.

6. Conclusions

6.1. Guidelines for designing a plasticizer molecule for CA

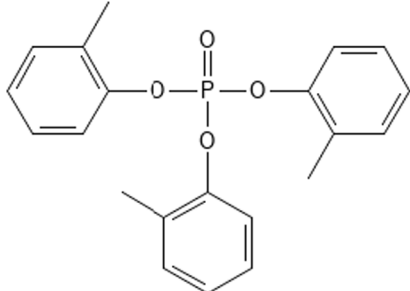
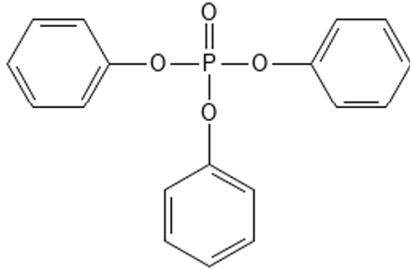
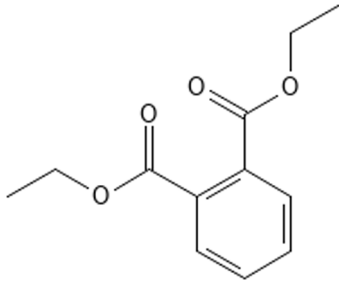
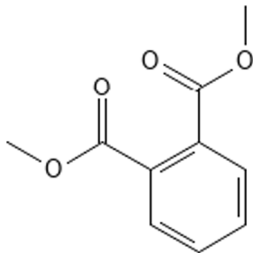
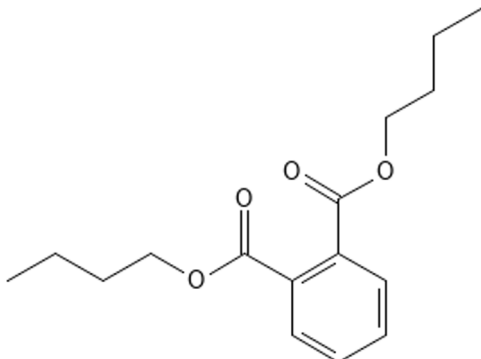
A comparative analysis between the most widely used plasticizers allows us to highlight the molecule's structural characteristics to be effective in CA plasticizing. Table 3 summarizes the chemical structure, molecular weight, physical state at room temperature, boiling point, and the presence of specific functional groups (ester groups, benzene rings, alkyl chains, acetyls) of these molecules.

The molecular weight of CA plasticizers ranges from 178 g mol^{-1} (diacetin) to 378 g mol^{-1} (tricresyl phosphate), with an average value of $\sim 260 \text{ g mol}^{-1}$. It should be noted that high molecular weight plasticizers showed limited compatibility in CA [182,183]. Nevertheless, a high molecular weight plasticizer is usually preferred to preserve the dimensional stability of the final product and keep the original thermomechanical properties unaltered, thanks to reduced plasticizer loss over time. Conversely, limited compatibility is usually observed for molecules with a high molecular weight and bulky structures [59,105,234]. For instance, phosphates, which show limited compatibility in CA, possess a rigid and bulky structure with three benzene rings that restrict the motion of CA chains. In addition, it might be expected that short aliphatic chains (instead of aromatic rings) would be more flexible. In this regard, molecules with one benzene ring, such as phthalates, have good plasticizing properties in many polymers and not only in CA [108,235]. Additionally, aromatic groups behave as compatibilizer units with various plastics [99].

It is worth mentioning that plasticizers compatible with CA, even at high concentrations (20–30 wt%), do not have generally more than two carbon atoms per alkyl chain. Indeed, acetate groups, as in citrates and glycerol derivatives, have two carbon atoms. The presence of acetate groups seems important for the chemical affinity with CA, considering that citrates and glycerol derivatives do not have any benzene ring as compatibilizers. Instead, plasticizers with three to four carbon atoms

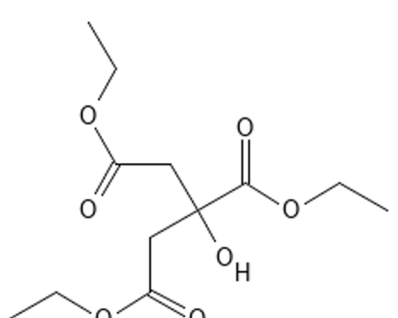
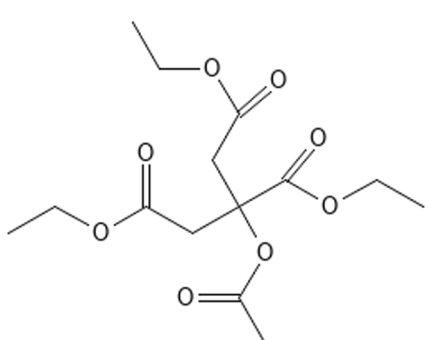
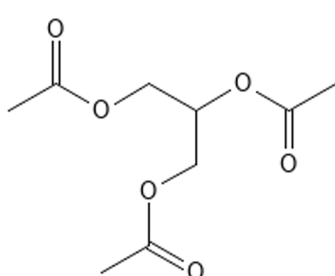
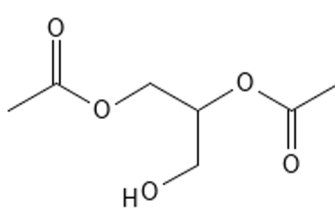
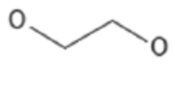
Table 3

List of the most used plasticizers in CA. In addition to molecular weight, physical state, and boiling point, the main purpose is to highlight the presence of different functional groups and their number, as well as the number of oxygen atoms.

Plasticizer	Molecular structure	Molecular weight (g/mol)	Physical state	Boiling point (°C)	Ester groups	Oxygen atoms	Benzene rings	Acetyl groups	Alkyl chains (C atoms each)
Tricresyl phosphate (TCP)		368.4	Solid	410	–	4	3	–	–
Triphenyl phosphate (TPP)		326.3	Solid	412	–	4	3	–	–
Diethyl phthalate (DEP)		222.2	Liquid	298	2	4	1	–	2 (2)
Dimethyl phthalate (DMP)		194.2	Liquid	284	2	4	1	–	2 (1)
Dibutyl phthalate (DBP)		278.3	Liquid	340	2	4	1	–	2 (4)

(continued on next page)

Table 3 (continued)

Plasticizer	Molecular structure	Molecular weight (g/mol)	Physical state	Boiling point (°C)	Ester groups	Oxygen atoms	Benzene rings	Acetyl groups	Alkyl chains (C atoms each)
Triethyl citrate (TEC)		276.3	Liquid	294	3	7	–	–	3 (2)
Acetyl triethyl citrate (ATEC)		318.3	Liquid	327	4	8	–	1	4 (2)
Glycerol triacetate (GTA)		218.2	Liquid	259	3	6	–	3	3 (2)
Glycerol diacetate (GDA)		178.2	Liquid	280	2	5	–	2	2 (2)
PEG200 n = 4		200	Liquid	~200	–	5	–	–	–

side chains show limited compatibility, as for DBP [40] or ATBC [167]. Unfortunately, molecules with shorter chains diffuse faster and have the drawback of being more volatile.

It is very important to point out that all plasticizers in Table 3 are esters (except for PEG200) with at least four oxygen atoms, which are polar and able to interact with CA by specific interactions such as hydrogen, electrostatic, or van der Waals bonds [50]. Overall, ester groups act as cohesive blocks. Designing a new molecule for CA, therefore, requires considering that ester groups are necessary for compatibility and plasticizing efficiency, but the carbon atoms in the

alkyl moieties must not be more than two or three; otherwise, the polarity of the plasticizer would decrease accordingly, and its maximum concentration in the plasticized system would have to be reduced to prevent incompatibility effects. A combination of flexible elements and polar groups to promote compatibility with the polymer is almost necessary [236]. For this reason, acetyls and ethyl moieties are reasonable spacers to be used to design a plasticizer molecule that is effective for CA.

Another key feature to ensure good compatibility with the polymer is the number of branches: branched chains could reduce the plasticizing

effectiveness, and, if the branches are close to the polar group, plasticization is even less efficient [99]. At the same time, numerous polar groups could establish a strong network with CA, which eventually would limit the movement of the polymer chains due to the excessive number of links created, as revealed by atomistic simulations with starch plasticized systems [237]. However, compatibility is based on intermolecular attractions due to the polar groups [117]. Indeed, plasticization occurs because of the ability of plasticizer molecules to create secondary bonds with polymer and to replace chain interactions by plasticizer-polymer bonds [238].

Based on these considerations, plasticizers with low molecular weight and a few polar groups provide higher flexibility and plasticization. On a weight basis, it is important to emphasize that the higher plasticization efficiency obtained with lower molecular weight plasticizers may be related to the higher number of plasticizer molecules (i.e., a higher number of moles per total mass). With the role of solvating groups in mind, a higher number of plasticizer molecules means higher solvation capacity, a major reduction in interchain linkages within the polymer, and greater mobility of the plasticized system [117].

In the available literature, plasticizing efficiency is always referred to as the weight percentage of the plasticizer on the total mass. Similarly, comparisons between different plasticizers are based on the same approach [103]. From these authors' point of view, plasticizing efficiency should be evaluated based on the molar concentrations, namely the number of molecules, to prevent misleading conclusions or wrong ranking of different plasticizer molecules. So far, both in the industry and research, it has been more practical to formulate plasticized systems based on weight fractions [149,165,210]. A different approach based on molar concentrations may be more suitable if the aim is to study and correlate the plasticizing efficiency to molecular structure and functional groups.

In summary, a plasticizer molecule tailored for CA should have these structural characteristics:

- Low molecular weight compound, with a MW in the 200–400 g/mol range (better lower than 350 g/mol) with a core structure comprised of a benzene ring or a short carbon core with three or four carbon atoms.
- Be an ester or other groups containing oxygen atoms (ether, aldehyde, ketone, and hydroxyl groups). Polar groups must not be more than two or three, with four or five oxygen atoms in total, to create enough interactions with the polar groups of CA without stiffening the matrix.
- Have a core structure accompanied by two or three short alkyl chains, acting as spacers, with two or three carbon atoms spaced out from the central core by the polar groups that are essential to ensure compatibility with cellulose acetate.

Based on state-of-the-art plasticizers used in CA, these empirical rules can potentially be integrated with new developments in the sector. It is necessary to underline that the design of a new plasticizer is strictly related to the application of the final material and its additional requirements (e.g., safety, thermal stability, etc.). For this reason, a comprehensive assessment is needed to evaluate the plasticizer's behavior in processing conditions and during use, as well as toxicity to human health and effects on environmental pollution.

6.2. Future perspectives

This work provided an extensive overview of the published literature about plasticizers for cellulose acetate, with the final purpose of finding a common thread in choosing or designing new molecules for CA. In this regard, effective internal plasticization of CA can be obtained with acylating reagents consisting of a terminal bulky moiety spaced from CA chains by a linear chain: they have been found to efficiently separate macromolecular chains without generating detrimental stiffening

interactions [64,65]. Concerning external plasticization, it turned out that a plasticizer, to be successful in CA, should be a low molecular weight ester able to interpose the polymer chains, with short apolar alkyl chains and some polar groups able to interact with the polymer. Moreover, the presence of a benzene ring would positively affect the plasticization efficiency. Unfortunately, small molecular weight compounds have a high rate of diffusion, which ensures greater plasticizing efficiency, but a lower permanence in the plasticized system. Choosing a plasticizer with concurrent efficiency and permanence represents a trade-off among different plasticizer properties.

Future developments in CA formulations should primarily aim to design new plasticizers with optimized plasticizing efficiency and migration properties. In this regard, innovation must be driven by a thorough understanding of the role of the molecular structures of plasticizers. Keeping in mind the need to prevent plasticizer migration, the addition of the desired functional groups through grafting of oligomers with different chemistry could provide efficient plasticization and give CA new properties without the drawbacks and limitations of external plasticization [121,129,239]. Moreover, the chemical bonding of cellulose or CA by acylation with acyl moieties that have different chemical structures (fatty chains with different lengths, ramified, bulky, aliphatic, or aromatic rings disposed more or less near the polymer backbone) can enhance the overall mobility of the macromolecular chains [64,141]. Anyway, the plasticizing efficiency of different substituents can vary because of their structural features, and it is strictly correlated to the molecules' mobility within the polymer matrix.

At this point, considering that external plasticization is the most widely used approach in the industrial field, in addition to being, in general, more effective than internal plasticization [41,240], it is of utmost importance to guide the research toward the development of more performing plasticizers than those already used to date. The design of new effective molecules for plasticizing CA must of course take as a starting point the chemical structures and the building blocks of plasticizers that have worked well until today but is also pivotal that it aims at developing new formulations.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [Luigi De Nardo reports financial support was provided by Luxottica Group SpA. Alessandro Bonifacio, Etienne Piantanida, Luigi De Nardo reports a relationship with Luxottica Group SpA that includes: employment, funding grants, non-financial support, and travel reimbursement].

Data availability

No data was used for the research described in the article.

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References

- [1] A. Montalto, S. Graziosi, M. Bordegoni, L. Di Landro, M.J.L. van Tooren, An approach to design reconfigurable manufacturing tools to manage product variability: the mass customisation of eyewear, *J Intell Manuf.* 31 (2020) 87–102, <https://doi.org/10.1007/s10845-018-1436-5>.

- [2] D.O. Mazzucchelli, Material based on cellulose acetate with plasticisers and manufactured article produced therewith, US2013/0169921A1, 2013.
- [3] P. Ruestemeyer, 5.2 CA filter tow for cigarette filters, *Macromol. Symp.* 208 (2004) 267–292, <https://doi.org/10.1002/masy.200450411>.
- [4] Q. Zhang, C. Fang, Y. Cheng, J. Chen, Z. Huang, H. Han, Construction and properties of cellulose diacetate film derived from waste cigarette filters, *Cellul. 27* (2020) 8899–8907, <https://doi.org/10.1007/s10570-020-03393-2>.
- [5] Y. Lemmouchi, R. Quintana, L. Bonnaud, P. Dubois, O. Persenaire, *Cell. Acetate Composit.* US8851084B2 (2014).
- [6] A. De Fenzo, M. Giordano, L. Sansone, A clean process for obtaining high-quality cellulose acetate from cigarette butts, *Materials* 13 (2020) 4710, <https://doi.org/10.3390/ma13214710>.
- [7] M. Yamaguchi, K. Okada, M.E.A. Manaf, Y. Shiroyama, T. Iwasaki, K. Okamoto, Extraordinary wavelength dispersion of orientation birefringence for cellulose esters, *Macromolecules* 42 (2009) 9034–9040, <https://doi.org/10.1021/ma901676j>.
- [8] M.E. Abd Manaf, M. Tsuji, Y. Shiroyama, M. Yamaguchi, Wavelength dispersion of orientation birefringence for cellulose esters containing tricresyl phosphate, *Macromolecules* 44 (10) (2011) 3942–3949.
- [9] H. Yamanaka, Y. Teramoto, Y. Nishio, Orientation and birefringence compensation of trunk and graft chains in drawn films of cellulose acetate- graft-PMMA synthesized by ATRP, *Macromolecules* 46 (2013) 3074–3083, <https://doi.org/10.1021/ma400155f>.
- [10] T. Wu, X. Han, X. Min, M. An, J. Zhao, W. Yu, L. Li, Regulation of orientation birefringence for cellulose acetate film: The role of crystallization and orientation, *Carbohydrate Polym.* 296 (2022), 119915, <https://doi.org/10.1016/j.carbpol.2022.119915>.
- [11] J. Ganster, H.-P. Fink, Cellulose and cellulose acetate, in: S. Kabasci (Ed.), *Bio-Based Plastics*, John Wiley & Sons Ltd, Chichester, UK, 2013, pp. 35–62, <https://doi.org/10.1002/9781118676646.ch3>.
- [12] F.-J. Wang, Y.-Y. Yang, X.-Z. Zhang, X. Zhu, T. Chung, S. Mochhala, Cellulose acetate membranes for transdermal delivery of scopolamine base, *Mater. Sci. Eng.: C* 20 (2012) 93–100, [https://doi.org/10.1016/S0928-4931\(02\)00018-8](https://doi.org/10.1016/S0928-4931(02)00018-8).
- [13] M.A. Wsoo, S. Shahir, S.P. Mohd Bohari, N.H.M. Nayan, S.I.A. Razak, A review on the properties of electrospun cellulose acetate and its application in drug delivery systems: A new perspective, *Carbohydrate Res.* 491 (2020), 107978, <https://doi.org/10.1016/j.carres.2020.107978>.
- [14] S. Absar, M. Khan, K. Edwards, J. Neumann, Investigation of synthesis and processing of cellulose, cellulose acetate and poly(ethylene oxide) nanofibers incorporating anti-cancer/tumor drug cis-diammineplatinum (II) dichloride using electrospinning techniques, *J. Polym. Eng.* 35 (2015) 867–878, <https://doi.org/10.1515/polyeng-2015-0057>.
- [15] M. Gouda, A. Hebeish, A. Aljafari, Synthesis and characterization of novel drug delivery system based on cellulose acetate electrospun nanofiber mats, *J. Ind. Text.* 43 (2014) 319–329, <https://doi.org/10.1177/1528083713495250>.
- [16] P. Taepaiboon, U. Rungsardthong, P. Supaphol, Vitamin-loaded electrospun cellulose acetate nanofiber mats as transdermal and dermal therapeutic agents of vitamin A acid and vitamin E, *Eur. J. Pharm. Biopharm.* 67 (2007) 387–397, <https://doi.org/10.1016/j.ejpb.2007.03.018>.
- [17] K. Khoshnevisan, H. Maleki, H. Samadian, S. Shahsavari, M.H. Sarrafzadeh, B. Larijani, F.A. Dorkoosh, V. Haghpanah, M.R. Khorramzadeh, Cellulose acetate electrospun nanofibers for drug delivery systems: Applications and recent advances, *Carbohydr. Polym.* 198 (2018) 131–141, <https://doi.org/10.1016/j.carbpol.2018.06.072>.
- [18] J. Fan, S. Zhang, F. Li, Y. Yang, M. Du, Recent advances in cellulose-based membranes for their sensing applications, *Cellul. 27* (2020) 9157–9179, <https://doi.org/10.1007/s10570-020-03445-7>.
- [19] N.S. Abdel Rahman, Y.E. Greish, S.T. Mahmoud, N.N. Qamhieh, H.F. El-Maghraby, D. Zeze, Fabrication and characterization of cellulose acetate-based nanofibers and nanofilms for H₂S gas sensing application, *Carbohydr. Polym.* 258 (2021), 117643, <https://doi.org/10.1016/j.carbpol.2021.117643>.
- [20] C.d.S. Meireles, G.R. Filho, M. Fernandes Ferreira, D.A. Cerqueira, R.M. N. Assunção, E.A.M. Ribeiro, P. Poletto, M. Zeni, Characterization of asymmetric membranes of cellulose acetate from biomass: Newspaper and mango seed, *Carbohydr. Polym.* 80 (3) (2010) 954–961.
- [21] V. Vatanpour, M.E. Pasaoglu, H. Barzegar, O.O. Teber, R. Kaya, M. Bastug, A. Khataee, I. Koyuncu, Cellulose acetate in fabrication of polymeric membranes: A review, *Chemosphere* 295 (2022), 133914, <https://doi.org/10.1016/j.chemosphere.2022.133914>.
- [22] T. Arakawa, K. Tomoto, H. Niita, K. Toma, S. Takeuchi, T. Sekita, S. Minakuchi, K. Mitsubayashi, A wearable cellulose acetate-coated mouthguard biosensor for in vivo salivary glucose measurement, *Anal. Chem.* 92 (2020) 12201–12207, <https://doi.org/10.1021/acs.analchem.0c01201>.
- [23] C.M. Kee, A. Idris, Permeability performance of different molecular weight cellulose acetate hemodialysis membrane, *Sep. Purif. Technol.* 75 (2010) 102–113, <https://doi.org/10.1016/j.seppur.2010.08.013>.
- [24] S.H. Hong, Y. Cho, S.W. Kang, Highly porous and thermally stable cellulose acetate to utilize hydrated glycerin, *J. Ind. Eng. Chem.* 91 (2020) 79–84, <https://doi.org/10.1016/j.jiec.2020.07.019>.
- [25] S.H. Kim, S.W. Kang, Thermally stable and highly porous separator based on cellulose acetate by glycolic acid, *Polymer* 242 (2022), 124592, <https://doi.org/10.1016/j.polymer.2022.124592>.
- [26] S. Byun, S.W. Kang, Porous channels in cellulose acetate by compressed nitrogen with lactic acid, *Cellulose* 30 (2023) 6163–6171, <https://doi.org/10.1007/s10570-023-05279-5>.
- [27] V.P. Ghiya, V. Dave, R.A. Gross, S.P. McCarthy, Biodegradability of cellulose acetate plasticized with citrate esters, *J. Macromol. Sci. A* 33 (1996) 627–638, <https://doi.org/10.1080/10601329608010883>.
- [28] R. Breuer, Y. Zhang, R. Erdmann, O.E. Vernaez Hernandez, S. Kabasci, M. Kostka, N. Reinhardt, M. Facklam, C. Hopmann, Development and processing of flame retardant cellulose acetate compounds for foaming applications, *J. Appl. Polym. Sci.* 137 (2020) 48863, <https://doi.org/10.1002/app.48863>.
- [29] E.E. Arrington, R.J. Kehl, Process for making a cellulose triacetate photographic film base, US5529737A, 1996.
- [30] M. Edge, N.S. Allen, T.S. Jewitt, C.V. Horie, Fundamental aspects of the degradation of cellulose triacetate base cinematograph film, *Polym. Degrad. Stab.* 25 (1989) 345–362, [https://doi.org/10.1016/S0141-3910\(89\)81016-X](https://doi.org/10.1016/S0141-3910(89)81016-X).
- [31] Z. Jia, Y. Li, Y. Qi, Y. Zhou, D. Hu, X. Chao, H. Xing, J. Li, Study on microbubble of cellulose acetate microfilm of the Republic of China (AD 1912–1949) collected in the second historical archives of China, *Herit. Sci.* 8 (2020) 29, <https://doi.org/10.1186/s40494-020-00374-3>.
- [32] S. Ahmadian-Fard-Fini, D. Ghanbari, O. Amiri, M. Salavati-Niasari, Electrospinning of cellulose acetate nanofibers/Fe/carbon dot as photoluminescence sensor for mercury (II) and lead (II) ions, *Carbohydr. Polym.* 229 (2020), 115428, <https://doi.org/10.1016/j.carbpol.2019.115428>.
- [33] A. Petropoulou, S. Kralj, X. Karagiorgis, I. Savva, E. Loizides, M. Panagi, T. Krasiachristoforou, C. Riziotis, Multifunctional gas and pH fluorescent sensors based on cellulose acetate electrospun fibers decorated with rhodamine B-functionalised core-shell ferrous nanoparticles, *Sci Rep.* 10 (2020) 367, <https://doi.org/10.1038/s41598-019-57291-0>.
- [34] X. Meng, J. Yang, Z. Liu, W. Lu, Y. Sun, Y. Dai, Non-contact, fibrous cellulose acetate/aluminum flexible electronic-sensor for humidity detecting, *Compos. Commun.* 20 (2020), 100347, <https://doi.org/10.1016/j.coco.2020.04.013>.
- [35] M.T.S. Chani, K.S. Karimov, S.B. Khan, A.M. Asiri, Fabrication and investigation of cellulose acetate-copper oxide nano-composite based humidity sensors, *Sens. Actuators, A* 246 (2016) 58–65, <https://doi.org/10.1016/j.sna.2016.05.016>.
- [36] H. Su, H. Li, H. Lin, X. Shi, Y. Du, Y. Luo, H. Deng, Highly sensitive formaldehyde sensors based on CuO/ZnO composite nanofibrous mats using porous cellulose acetate fibers as templates, *Int. J. Biol. Macromol.* 206 (2022) 653–660, <https://doi.org/10.1016/j.ijbiomac.2022.02.167>.
- [37] A.A. Hoffmann, S.L.P. Dias, J.R. Rodrigues, F.A. Pavan, E.V. Benvenuto, E. C. Lima, Methylene blue immobilized on cellulose acetate with titanium dioxide: an application as sensor for ascorbic acid, *J. Braz. Chem. Soc.* 19 (2008) 943–949, <https://doi.org/10.1590/S0103-50532008000500020>.
- [38] A. Benazzouz, E. Dudognon, N.T. Correia, V. Molinier, J.-M. Aubry, M. Descamps, Interactions underpinning the plasticization of a polymer matrix: a dynamic and structural analysis of DMP-plasticized cellulose acetate, *Cellul. 24* (2017) 487–503, <https://doi.org/10.1007/s10570-016-1148-y>.
- [39] S. Hu, X. Liu, M. Zhang, Y. Wei, R. Qi, Y. Zhu, S. Chen, Interfacial effects of plasticizers on the properties of cellulose diacetate materials, *Cellul. 29* (14) (2022) 7849–7861.
- [40] C.R. Fordyce, I.W.A. Meyer, Plasticizers for cellulose acetate and cellulose acetate butyrate, *Ind. Eng. Chem.* 32 (1940) 1053–1060, <https://doi.org/10.1021/ie50368a009>.
- [41] M. Klähn, R. Krishnan, J.M. Phang, F.C.H. Lim, A.M. van Herk, S. Jana, Effect of external and internal plasticization on the glass transition temperature of (Meth) acrylate polymers studied with molecular dynamics simulations and calorimetry, *Polymer* 179 (2019), 121635, <https://doi.org/10.1016/j.polymer.2019.121635>.
- [42] C.J. Malm, C.R. Fordyce, H.A. Tanner, Properties of cellulose esters of acetic, propionic, and butyric acids, *Ind. Eng. Chem.* 34 (1942) 430–435, <https://doi.org/10.1021/ie50388a010>.
- [43] L. Duchatel-Crépey, N. Joly, P. Martin, A. Marin, J.-F. Tahon, J.-M. Lefebvre, V. Gaucher, Substitution degree and fatty chain length influence on structure and properties of fatty acid cellulose esters, *Carbohydr. Polym.* 234 (2020), 115912, <https://doi.org/10.1016/j.carbpol.2020.115912>.
- [44] A. Charvet, C. Vergelati, D.R. Long, Mechanical and ultimate properties of injection molded cellulose acetate/plasticizer materials, *Carbohydr. Polym.* 204 (2019) 182–189, <https://doi.org/10.1016/j.carbpol.2018.10.013>.
- [45] A.K. Mohanty, A. Wibowo, M. Misra, L.T. Drzal, Effect of process engineering on the performance of natural fiber reinforced cellulose acetate biocomposites, *Compos. A Appl. Sci. Manuf.* 35 (2004) 363–370, <https://doi.org/10.1016/j.compositesa.2003.09.015>.
- [46] A. Ach, Journal of macromolecular science, part A: Pure and applied chemistry, *J. Macromol. Sci. Part A* 52 (1993), <https://doi.org/10.1080/10601325.2015.984542>.
- [47] A.K. Mohanty, A. Wibowo, M. Misra, L.T. Drzal, Development of renewable resource-based cellulose acetate bioplastic: Effect of process engineering on the performance of cellulosic plastics, *Polym. Eng. Sci.* 43 (2003) 1151–1161, <https://doi.org/10.1002/pen.10097>.
- [48] F.J. Rodríguez, R.L. Abarca, J.E. Bruna, P.E. Moya, M.J. Galotto, A. Guarda, M. Padula, Effect of organoclay and preparation method on properties of antimicrobial cellulose acetate films, *Polym. Compos.* 40 (2019) 2311–2319, <https://doi.org/10.1002/pc.25041>.
- [49] R.C. Law, 5. Applications of cellulose acetate 5.1 Cellulose acetate in textile application, *Macromol. Symp.* 208 (2004) 255–266, <https://doi.org/10.1002/masy.200450410>.
- [50] T. Mekonnen, P. Mussone, H. Khalil, D. Bressler, Progress in bio-based plastics and plasticizing modifications, *J. Mater. Chem. A* 1 (2013) 13379, <https://doi.org/10.1039/c3ta12555f>.

- [51] D. Littlejohn, R.A. Pethrick, A. Quye, J.M. Ballany, Investigation of the degradation of cellulose acetate museum artefacts, *Polym. Degrad. Stab.* 98 (1) (2013) 416–424.
- [52] R. Quintana, O. Penseña, L. Bonnaud, P. Dubois, Recent advances in (reactive) melt processing of cellulose acetate and related biodegradable bio-compositions, *Polym. Chem.* 3 (2012) 591–595, <https://doi.org/10.1039/C1PY00421B>.
- [53] W. Xuan, K. Odelius, M. Hakkarainen, Tailoring oligomeric plasticizers for polylactide through structural control, *ACS Omega* 7 (2022) 14305–14316, <https://doi.org/10.1021/acsomega.2c01160>.
- [54] W. Xuan, M. Hakkarainen, K. Odelius, Levulinic Acid as a versatile building block for plasticizer design, *ACS Sustainable Chem. Eng.* (2019), <https://doi.org/10.1021/acssuschemeng.9b02439>.
- [55] H.C. Erythropel, S. Shipley, A. Börmann, J.A. Nicell, M. Maric, R.L. Leask, Designing green plasticizers: Influence of molecule geometry and alkyl chain length on the plasticizing effectiveness of diester plasticizers in PVC blends, *Polymer* 89 (2016) 18–27, <https://doi.org/10.1016/j.polymer.2016.02.031>.
- [56] H.C. Erythropel, M. Maric, D.G. Cooper, Designing green plasticizers: Influence of molecular geometry on biodegradation and plasticization properties, *Chemosphere* 86 (2012) 759–766, <https://doi.org/10.1016/j.chemosphere.2011.10.054>.
- [57] H.C. Erythropel, Evaluation of maleate, fumarate, and succinate diesters as potential green plasticizers, *McGill University*, 2016.
- [58] C. Gao, Y. Wang, Y. Gao, R. Wang, H. Wang, Y. Wu, Y. Liu, Structure design, performance simulation and plasticizing properties of bio-based copolyesters plasticizer on PVC, *J. Polym. Environ.* 30 (11) (2022) 4651–4661.
- [59] J. Czogała, E. Pankalla, R. Turczyn, recent attempts in the design of efficient PVC plasticizers with reduced migration, *Materials* 14 (2021) 844, <https://doi.org/10.3390/ma14040844>.
- [60] W. Xuan, K. Odelius, M. Hakkarainen, Dual-functioning antibacterial eugenol-derived plasticizers for polylactide, *Biomolecules* 10 (2020) 1077, <https://doi.org/10.3390/biom10071077>.
- [61] R. Sothornvit, J.M. Krochta, Plasticizers in edible films and coatings, in: innovations in Food Packaging, Elsevier, 2005, pp. 403–433, <https://doi.org/10.1016/B978-012311632-1/50055-3>.
- [62] R. Navarro, M. Pérez Perrino, M. Gómez Tardajos, H. Reinecke, Phthalate plasticizers covalently bound to PVC: Plasticization with suppressed migration, *Macromolecules* 43 (2010) 2377–2381, <https://doi.org/10.1021/ma902740t>.
- [63] Y. Hu, J. Zhou, Y. Ma, Y. u. Bei, F. Hu, Z. Kou, Y. Zhou, P. Jia, Branched plasticizers derived from eugenol via green polymerization for low/non-migration and externally/internally plasticized polyvinyl chloride materials, *Arab. J. Chem.* 15 (12) (2022) 104331.
- [64] M. Boulven, G. Quintard, A. Cottaz, C. Joly, A. Charlot, E. Fleury, Homogeneous acylation of Cellulose diacetate: Towards bioplastics with tuneable thermal and water transport properties, *Carbohydr. Polym.* 206 (2019) 674–684, <https://doi.org/10.1016/j.carbpol.2018.11.030>.
- [65] Z. Chen, J. Zhang, P. Xiao, W. Tian, J. Zhang, Novel thermoplastic cellulose esters containing bulky moieties and soft segments, *ACS Sustainable Chem. Eng.* 6 (2018) 4931–4939, <https://doi.org/10.1021/acssuschemeng.7b04466>.
- [66] A.M. Stephen, G.O. Phillips, P.A. Williams (Eds.), *Food Polysaccharides and Their Applications*, 2nd ed, CRC/Taylor & Francis, Boca Raton, FL, 2006.
- [67] I.M. Saxena, R.M. Brown, Cellulose biosynthesis: Current views and evolving concepts, *Ann. Bot.* 96 (2005) 9–21, <https://doi.org/10.1093/aob/mci155>.
- [68] H. El-Saied, A.H. Basta, R.H. Gobran, Research progress in friendly environmental technology for the production of cellulose products (bacterial cellulose and its application), *Polym.-Plast. Technol. Eng.* 43 (2004) 797–820, <https://doi.org/10.1081/PPT-120038065>.
- [69] L. Urbina, M.A. Corcuera, N. Gabilondo, A. Eceiza, A. Retegi, A review of bacterial cellulose: sustainable production from agricultural waste and applications in various fields, *Cellulose* 28 (2021) 8229–8253, <https://doi.org/10.1007/s10570-021-04020-4>.
- [70] Z. Hussain, W. Sajjad, T. Khan, F. Wahid, Production of bacterial cellulose from industrial wastes: a review, *Cellulose* 26 (2019) 2895–2911, <https://doi.org/10.1007/s10570-019-02307-1>.
- [71] B. Debnath, D. Haldar, M.K. Purkait, A critical review on the techniques used for the synthesis and applications of crystalline cellulose derived from agricultural wastes and forest residues, *Carbohydr. Polym.* 273 (2021), 118537, <https://doi.org/10.1016/j.carbpol.2021.118537>.
- [72] L. Bonetti, L. De Nardo, S. Farè, Thermo-responsive methylcellulose hydrogels: from design to applications as smart biomaterials, *Tissue Eng. B Rev.* 27 (2021) 486–513, <https://doi.org/10.1089/ten.teb.2020.0202>.
- [73] Y. Zhou, X. Zhang, J. Zhang, Y. Cheng, J. Wu, J. Yu, J. Zhang, Molecular weight characterization of cellulose using ionic liquids, *Polym. Test.* 93 (2021), 106985, <https://doi.org/10.1016/j.polymertesting.2020.106985>.
- [74] P. Strunk, Characterization of cellulose pulps and the influence of their properties on the process and production of viscose and cellulose ethers, Department of Chemistry, Umeå University, Umeå, 2012.
- [75] V. Köpcke, Improvement on cellulose accessibility and reactivity of different wood pulps. *Fiber- Och Polymerteknologi, Fibre and Polymer Technology, Kungliga Tekniska högskolan, Stockholm*, 2008.
- [76] P. Nasatto, F. Pignon, J. Silveira, M. Duarte, M. Nosedá, M. Rinaudo, Methylcellulose, a cellulose derivative with original physical properties and extended applications, *Polymers* 7 (2015) 777–803, <https://doi.org/10.3390/polym7050777>.
- [77] T. Heinze, Cellulose: Structure and Properties, in: O.J. Rojas (Ed.), *Cellulose Chemistry and Properties: Fibers, NanoCelluloses and Advanced Materials*, Springer International Publishing, Cham, 2015, pp. 1–52, https://doi.org/10.1007/12_2015_319.
- [78] X. Qiu, S. Hu, “Smart” materials based on cellulose: A review of the preparations, properties, and applications, *Materials* 6 (2013) 738–781, <https://doi.org/10.3390/ma6030738>.
- [79] T. Heinze, O.A. Elseoud, A. Koschella, Cellulose Esters, in: *Cellulose Derivatives*, Springer International Publishing, Cham, 2018, pp. 293–427, doi: 10.1007/978-3-319-73168-1_5.
- [80] H. An, W. Feng, M.E. Donelson, T.J. Pecorini, Cellulose ester and polymeric aliphatic polyester compositions and articles, US2020/0399445A1, 2020.
- [81] A.C. Puleo, D.R. Paul, S.S. Kelley, The effect of degree of acetylation on gas sorption and transport behavior in cellulose acetate, *J. Membr. Sci.* 47 (1989) 301–332, [https://doi.org/10.1016/S0376-7388\(00\)83083-5](https://doi.org/10.1016/S0376-7388(00)83083-5).
- [82] T.J. Heinze, W.G. Glasser (Eds.), *Cellulose Derivatives: Modification, Characterization, and Nanostructures*, American Chemical Society, Washington, DC, 1998, <https://doi.org/10.1021/bk-1998-0688>.
- [83] T. Heinze, T.F. Liebert, K.S. Pfeiffer, M.A. Hussain, Unconventional cellulose esters: synthesis, characterization and structure–property relations, *Cellul.* 10 (2003) 283–296, <https://doi.org/10.1023/A:1025117327970>.
- [84] T. Heinze, T. Liebert, 4.2 Chemical characteristics of cellulose acetate, *Macromol. Symp.* 208 (2004) 167–238, <https://doi.org/10.1002/masy.200450408>.
- [85] Kirk, Othmer, *Encyclopedia of Chemical Technology*, 5th ed., 2004.
- [86] H. Nawaz, R. Casarano, O.A. El Seoud, First report on the kinetics of the uncatalyzed esterification of cellulose under homogeneous reaction conditions: a rationale for the effect of carboxylic acid anhydride chain-length on the degree of biopolymer substitution, *Cellulose* 19 (2012) 199–207, <https://doi.org/10.1007/s10570-011-9622-z>.
- [87] T. Kakko, A.W.T. King, I. Kilpeläinen, Homogenous esterification of cellulose pulp in [DBNH][OAc], *Cellulose* 24 (2017) 5341–5354, <https://doi.org/10.1007/s10570-017-1521-5>.
- [88] S. Fischer, K. Thümmmler, B. Volkert, K. Hettrich, I. Schmidt, K. Fischer, Properties and applications of cellulose acetate, *Macromol. Symp.* 262 (2008) 89–96, <https://doi.org/10.1002/masy.200850210>.
- [89] S. Yoshioka, T. Nakamura, S. Shimamoto, T. Kishimoto, Cellulose acetate and method for producing cellulose acetate, JP 6453851 B, 2022.
- [90] A.W. Cindradewi, R. Bandi, C.-W. Park, J.-S. Park, E.-A. Lee, J.-K. Kim, G.-J. Kwon, S.-Y. Han, S.-H. Lee, Preparation and characterization of cellulose acetate film reinforced with cellulose nanofibril, *Polymers* 13 (2021) 2990, <https://doi.org/10.3390/polym13172990>.
- [91] M. Gilbert, *Cellulose Plastics*, in: *Brydson’s Plastics Materials*, Elsevier, 2017, pp. 617–630, <https://doi.org/10.1016/B978-0-323-35824-8.00022-0>.
- [92] O. Jögundula, V. Eta, M. Hedenström, O. Sundman, T. Salmi, J.-P. Mikkola, Ionic liquid mediated technology for synthesis of cellulose acetates using different co-solvents, *Carbohydr. Polym.* 135 (2016) 341–348, <https://doi.org/10.1016/j.carbpol.2015.08.092>.
- [93] Y. Yang, H. Xie, E. Liu, Acylation of cellulose in reversible ionic liquids, *Green Chem.* 16 (2014) 3018–3023, <https://doi.org/10.1039/C4GC00199K>.
- [94] L.C. McCormick, P.A. Callais, Derivatization of cellulose in lithium chloride and N,N-dimethylacetamide solutions, *Polymer* 28 (1987) 2317–2323, [https://doi.org/10.1016/0032-3861\(87\)90393-4](https://doi.org/10.1016/0032-3861(87)90393-4).
- [95] C. Zhang, R. Liu, J. Xiang, H. Kang, Z. Liu, Y. Huang, Dissolution mechanism of cellulose in N,N -Dimethylacetamide/lithium chloride: Revisiting through molecular interactions, *J. Phys. Chem. B.* 118 (2014) 9507–9514, <https://doi.org/10.1021/jp506013c>.
- [96] T.F. Liebert, T.J. Heinze, K.J. Edgar (Eds.), *Cellulose Solvents: For Analysis, Shaping and Chemical Modification*, American Chemical Society, Washington, DC, 2010 doi: 10.1021/bk-2010-1033.
- [97] S. Sen, J.D. Martin, D.S. Argyropoulos, Review of cellulose non-derivatizing solvent interactions with emphasis on activity in inorganic molten salt hydrates, *ACS Sustainable Chem. Eng.* 1 (2013) 858–870, <https://doi.org/10.1021/sc400085a>.
- [98] C. Achetl, T. Heinze, Homogeneous acetylation of cellulose in the new solvent triethyloctylammonium chloride in combination with organic liquids, *Macromol. Chem. Phys.* 217 (2016) 2041–2048, <https://doi.org/10.1002/macp.201600217>.
- [99] M. Bocqué, C. Voirin, V. Lapinte, S. Caillol, J.-J. Robin, Petro-based and bio-based plasticizers: Chemical structures to plasticizing properties, *J. Polym. Sci. Part A: Polym. Chem.* 54 (2016) 11–33, <https://doi.org/10.1002/pola.27917>.
- [100] L.H. Sperling (Ed.), *Introduction to Physical Polymer Science*, Wiley, 2005.
- [101] M. Rahman, C. Brazel, The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges, *Prog. Polym. Sci.* 29 (2004) 1223–1248, <https://doi.org/10.1016/j.progpolymsci.2004.10.001>.
- [102] G. Mathews, PVC. Production, properties and uses, CRC Press, 1997.
- [103] E.H. Immergut, H.F. Mark, Principles of plasticization, in: *Plasticization and Plasticizer Processes*, American Chemical Society, 1965, p. 26.
- [104] Y. Ma, S. Liao, Q. Li, Q. Guan, P. Jia, Y. Zhou, Physical and chemical modifications of poly(vinyl chloride) materials to prevent plasticizer migration - Still on the run, *React. Funct. Polym.* 147 (2020), 104458, <https://doi.org/10.1016/j.reactfunctpolym.2019.104458>.
- [105] L.G. Krauskopf, Plasticizer structure/performance relationships, *J. Vinyl Addit. Technol.* 15 (1993) 140–147, <https://doi.org/10.1002/vnl.730150306>.
- [106] P.H. Daniels, A brief overview of theories of PVC plasticization and methods used to evaluate PVC-plasticizer interaction, *J. Vinyl Addit Technol.* 15 (2009) 219–223, <https://doi.org/10.1002/vnl.20211>.
- [107] W. Aiken, T. Alfrey, A. Janssen, H. Mark, Creep behavior of plasticized vinylite VYNW, *J. Polym. Sci.* 2 (1947) 178–198, <https://doi.org/10.1002/pol.1947.120020206>.

- [108] G. Wypych (Ed.), Handbook of Plasticizers, 3rd edition, ChemTec Publishing, Toronto, 2017.
- [109] E. Langer, K. Bortel, S. Waskiewicz, M. Lenartowicz-Klik, in: Plasticizers Derived From Post-Consumer PET, Elsevier, 2020, pp. 101–126.
- [110] A. Mills, A. Lepre, L. Wild, Effect of plasticizer-polymer compatibility on the response characteristics of optical thin CO₂ and O₂ sensing films, *Anal. Chim. Acta* 362 (2-3) (1998) 193–202.
- [111] A. Tripathi, G.N. Parsons, S.A. Khan, O.J. Rojas, Synthesis of organic aerogels with tailorable morphology and strength by controlled solvent swelling following Hansen solubility, *Sci. Rep.* 8 (2018) 2106, <https://doi.org/10.1038/s41598-018-19720-4>.
- [112] F. Gharagheizi, A. Eslamimanesh, A.H. Mohammadi, D. Richon, Group contribution-based method for determination of solubility parameter of nonelectrolyte organic compounds, *Ind. Eng. Chem. Res.* 50 (2011) 10344–10349, <https://doi.org/10.1021/ie201002e>.
- [113] M. Belmares, M. Blanco, W.A. Goddard, R.B. Ross, G. Caldwell, S.-H. Chou, J. Pham, P.M. Olofson, C. Thomas, Hildebrand and Hansen solubility parameters from molecular dynamics with applications to electronic nose polymer sensors, *J. Comput. Chem.* 25 (2004) 1814–1826, <https://doi.org/10.1002/jcc.20098>.
- [114] S. Venkatram, C. Kim, A. Chandrasekaran, R. Ramprasad, Critical assessment of the Hildebrand and Hansen solubility parameters for polymers, *J. Chem. Inf. Model.* 59 (2019) 4188–4194, <https://doi.org/10.1021/acs.jcim.9b00656>.
- [115] K.A. Geburu, C. Das, Effects of solubility parameter differences among PEG, PVP and CA on the preparation of ultrafiltration membranes: Impacts of solvents and additives on morphology, permeability and fouling performances, *Chin. J. Chem. Eng.* 25 (2017) 911–923, <https://doi.org/10.1016/j.cjche.2016.11.017>.
- [116] M.W. Halloran, J.A. Nicell, R.L. Leask, M. Marić, Small molecule plasticizers for improved migration resistance: Investigation of branching and leaching behaviour in PVC blends, *Mater. Today Commun.* 29 (2021), 102874, <https://doi.org/10.1016/j.mtcomm.2021.102874>.
- [117] P.B. Stickney, L.E. Cheyney, Plasticizers for rubbers and resins, *J. Polym. Sci.* 3 (1948) 231–245, <https://doi.org/10.1002/pol.1948.120030210>.
- [118] H. Zhu, J. Yang, M. Wu, Q. Wu, J. Liu, J. Zhang, Biobased plasticizers from tartaric acid: synthesis and effect of alkyl chain length on the properties of poly(vinyl chloride), *ACS Omega* 6 (2021) 13161–13169, <https://doi.org/10.1021/acsomega.1c01006>.
- [119] W.E. Gloor, C.B. Gilbert, Plasticizers for cellulose organic ester plastics, *Ind. Eng. Chem. Res.* 33 (1994) 597–601, <https://doi.org/10.1021/ie50377a011>.
- [120] R. Erdmann, S. Kabasci, H.-P. Heim, Thermal properties of plasticized cellulose acetate and its β-relaxation phenomenon, *Polymers* 13 (2021) 1356, <https://doi.org/10.3390/polym13091356>.
- [121] R.-M. Xu, T.-T. Yang, E. Vidović, R.-N. Jia, J.-M. Zhang, Q.-Y. Mi, J. Zhang, Cellulose acetate thermoplastics with high modulus, dimensional stability and anti-migration properties by using CA-g-PLA as macromolecular plasticizer, *Chin J Polym Sci.* 38 (2020) 1141–1148, <https://doi.org/10.1007/s10118-020-2470-2>.
- [122] Y. Luan, J. Wu, M. Zhan, J. Zhang, J. Zhang, J. He, “One pot” homogeneous synthesis of thermoplastic cellulose acetate-graft-poly(L-lactide) copolymers from unmodified cellulose, *Cellulose* 20 (2013) 327–337, <https://doi.org/10.1007/s10570-012-9818-x>.
- [123] C. Yan, J. Zhang, Y. Lv, J. Yu, J. Wu, J. Zhang, J. He, Thermoplastic cellulose-graft-poly(L-lactide) copolymers homogeneously synthesized in an ionic liquid with 4-dimethylaminopyridine catalyst, *Biomacromolecules* 10 (2009) 2013–2018, <https://doi.org/10.1021/bm900447u>.
- [124] A.P. Mathew, K. Oksman, M. Sain, Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC), *J. Appl. Polym. Sci.* 97 (2005) 2014–2025, <https://doi.org/10.1002/app.21779>.
- [125] Y. Teramoto, Y. Nishio, Biodegradable cellulose diacetate-graft-poly(L-lactide)s: enzymatic hydrolysis behavior and surface morphological characterization, *Biomacromolecules* 5 (2004) 407–414, <https://doi.org/10.1021/bm034453i>.
- [126] Y. Teramoto, Y. Nishio, Cellulose diacetate-graft-poly(lactic acid)s: synthesis of wide-ranging compositions and their thermal and mechanical properties, *Polymer* 44 (2003) 2701–2709, [https://doi.org/10.1016/S0032-3861\(03\)00190-3](https://doi.org/10.1016/S0032-3861(03)00190-3).
- [127] G.y. Számel, S. Klébert, I. Sajó, B. Pukánszky, Thermal analysis of cellulose acetate modified with caprolactone, *J. Therm. Anal. Calorim.* 91 (3) (2008) 715–722.
- [128] G. Számel, A. Domján, S. Klébert, B. Pukánszky, Molecular structure and properties of cellulose acetate chemically modified with caprolactone, *Eur. Polym. J.* 44 (2008) 357–365, <https://doi.org/10.1016/j.eurpolymj.2007.11.006>.
- [129] B. Vidéki, S. Klébert, B. Pukánszky, External and internal plasticization of cellulose acetate with caprolactone: Structure and properties, *J. Polym. Sci. B Polym. Phys.* 45 (2007) 873–883, <https://doi.org/10.1002/polb.21121>.
- [130] M. Yoshioka, Nahoko Hagiwara, N. Shiraishi, Thermoplasticization of cellulose acetates by grafting of cyclic esters, *Thermoplast. Cellulose Acetates Graft. Cyclic Esters* 6 (1999) 193–212.
- [131] Y. Teramoto, S. Ama, T. Higeshiro, Y. Nishio, Cellulose acetate-graft-poly(hydroxyalkanoate)s: Synthesis and dependence of the thermal properties on copolymer composition, *Macromol. Chem. Phys.* 205 (2004) 1904–1915, <https://doi.org/10.1002/macp.200400160>.
- [132] Y. Teramoto, M. Yoshioka, N. Shiraishi, Y. Nishio, Plasticization of cellulose diacetate by graft copolymerization of ε-caprolactone and lactic acid, *J. Appl. Polym. Sci.* 84 (2002) 2621–2628, <https://doi.org/10.1002/app.10430>.
- [133] H. Warth, R. Mulhaupt, J. Schatzle, Thermoplastic cellulose acetate and cellulose acetate compounds prepared by reactive processing, *J. Appl. Polym. Sci.* 64 (1997) 231–242, [https://doi.org/10.1002/\(SICI\)1097-4628\(19970411\)64:2<231::AID-APP4>3.0.CO;2-S](https://doi.org/10.1002/(SICI)1097-4628(19970411)64:2<231::AID-APP4>3.0.CO;2-S).
- [134] S.-H. Lee, N. Shiraishi, Plasticization of cellulose diacetate by reaction with maleic anhydride, glycerol, and citrate esters during melt processing, *J. Appl. Polym. Sci.* 81 (2001) 243–250, <https://doi.org/10.1002/app.1435>.
- [135] M. Iji, S. Moon, S. Tanaka, Hydrophobic, mechanical and thermal characteristics of thermoplastic cellulose diacetate bonded with cardanol from cashew nutshell, *Polym. J.* 43 (2011) 738–741, <https://doi.org/10.1038/pj.2011.57>.
- [136] S. Tanaka, H. Honzawa, M. Iji, Development of cardanol-bonded cellulose thermoplastics: High productivity achieved by using isocyanate-modified cardanol, *J. Appl. Polym. Sci.* 130 (2013) 1578–1587, <https://doi.org/10.1002/app.39313>.
- [137] C. Vaca-Garcia, S. Thiebaut, M.E. Borredon, G. Gozzelino, Cellulose esterification with fatty acids and acetic anhydride in lithium chloride/N,N-dimethylacetamide medium, *J. Amer. Oil Chem. Soc.* 75 (1998) 315–319, <https://doi.org/10.1007/s11746-998-0047-2>.
- [138] L. Crépy, V. Miri, N. Joly, P. Martin, J.-M. Lefebvre, Effect of side chain length on structure and thermomechanical properties of fully substituted cellulose fatty esters, *Carbohydr. Polym.* 83 (2011) 1812–1820, <https://doi.org/10.1016/j.carbpol.2010.10.045>.
- [139] P. Xiao, J. Zhang, Y. Feng, J. Wu, J. He, J. Zhang, Synthesis, characterization and properties of novel cellulose derivatives containing phosphorus: cellulose diphenyl phosphate and its mixed esters, *Cellulose* 21 (2014) 2369–2378, <https://doi.org/10.1007/s10570-014-0256-9>.
- [140] S. Tanaka, T. Iwata, M. Iji, Long/short chain mixed cellulose esters: effects of long acyl chain structures on mechanical and thermal properties, *ACS Sustainable Chem. Eng.* 5 (2017) 1485–1493, <https://doi.org/10.1021/acssuschemeng.6b02066>.
- [141] J. Chen, J. Zhang, Y. Feng, J. He, J. Zhang, Effect of molecular structure on the gas permeability of cellulose aliphataate esters, *Chin. J. Polym. Sci.* 32 (2014) 1–8, <https://doi.org/10.1007/s10118-014-1384-2>.
- [142] M. Iji, K. Toyama, S. Tanaka, Mechanical and other characteristics of cellulose ester bonded with modified cardanol from cashew nut shells and additional aliphatic and aromatic components, *Cellulose* 20 (2013) 559–569, <https://doi.org/10.1007/s10570-012-9832-z>.
- [143] C. Vaca-Garcia, G. Gozzelino, W.G. Glasser, M.E. Borredon, Dynamic mechanical thermal analysis transitions of partially and fully substituted cellulose fatty esters, *J. Polym. Sci. B Polym. Phys.* 41 (2003) 281–288, <https://doi.org/10.1002/polb.10378>.
- [144] L. Crépy, L. Chaveriat, J. Banoub, P. Martin, N. Joly, Synthesis of cellulose fatty esters as plastics-influence of the degree of substitution and the fatty chain length on mechanical properties, *ChemSusChem* 2 (2009) 165–170, <https://doi.org/10.1002/cssc.200800171>.
- [145] R. Jamarani, H. Erythropel, J. Nicell, R. Leask, M. Marić, How green is your plasticizer? *Polymers* 10 (2018) 834, <https://doi.org/10.3390/polym10080834>.
- [146] R. Nagorka, W. Birmili, J. Schulze, J. Koschorreck, Diverging trends of plasticizers (phthalates and non-phthalates) in indoor and freshwater environments—why? *Environ. Sci. Eur.* 34 (2022) 46, <https://doi.org/10.1186/s12302-022-00620-4>.
- [147] A.D. Godwin, Plasticizers, in: Applied Polymer Science: 21st Century, 2000, pp. 157–175.
- [148] M. Schilling, M. Bouchard, H. Khanjian, T. Learner, A. Phenix, R. Rivenc, Application of chemical and thermal analysis methods for studying cellulose ester plastics, *Acc. Chem. Res.* 43 (2010) 888–896, <https://doi.org/10.1021/ar1000132>.
- [149] C.Y. Bao, D.R. Long, C. Vergelati, Miscibility and dynamical properties of cellulose acetate/plasticizer systems, *Carbohydr. Polym.* 116 (2015) 95–102, <https://doi.org/10.1016/j.carbpol.2014.07.078>.
- [150] S. Da Ros, A. Gili, K. Curran, Equilibrium distribution of diethyl phthalate plasticizer in cellulose acetate-based materials: Modelling and parameter estimation of temperature and composition effects, *Sci. Total Environ.* 850 (2022), 157700, <https://doi.org/10.1016/j.scitotenv.2022.157700>.
- [151] M. Scandola, G. Ceccorulli, Viscoelastic properties of cellulose derivatives: 2 Effect of diethylphthalate on the dynamic mechanical relaxations of cellulose acetate, *Polymer* 26 (1985) 1958–1962, [https://doi.org/10.1016/0032-3861\(85\)90174-0](https://doi.org/10.1016/0032-3861(85)90174-0).
- [152] V.J. McBrierty, C.M. Keely, F.M. Coyle, Hydration and plasticization effects in cellulose acetate: Molecular motion and relaxation, *Faraday Discuss.* 103 (1996) 255–268, <https://doi.org/10.1039/FD9960300255>.
- [153] C.M. Keely, X. Zhang, V.J. McBrierty, Hydration and plasticization effects in cellulose acetate: a solid-state NMR study, *J. Mol. Struct.* 355 (1995) 33–46, [https://doi.org/10.1016/0022-2860\(95\)08865-S](https://doi.org/10.1016/0022-2860(95)08865-S).
- [154] J.F. Walsh, A.F. Caprio, Plastic material containing derivatives of cellulose, US1930069, 1933.
- [155] G. Ceccorulli, M. Pizzoli, M. Scandola, Effect of a low-molecular-weight plasticizer on the thermal and viscoelastic properties of miscible blends of bacterial poly(3-hydroxybutyrate) with cellulose acetate butyrate, *Biomacromolecules* 26 (1993) 6722–6726, <https://doi.org/10.1021/ma00077a005>.
- [156] P.R. Rao, P.V. Diwan, Permeability studies of cellulose acetate free films for transdermal use: Influence of plasticizers, *Pharm. Acta Helv.* 72 (1997) 47–51, [https://doi.org/10.1016/S0031-6865\(96\)00060-X](https://doi.org/10.1016/S0031-6865(96)00060-X).
- [157] S.J. Doyle, R.A. Pethrick, Dielectric relaxation studies of heterogeneously substituted cellulose acetate and its plasticization by dibutyl phthalate, *Polym. Int.* 27 (1992) 321–331, <https://doi.org/10.1002/pi.4990270407>.
- [158] A. Alhanish, M. Abu Ghalia, Developments of biobased plasticizers for compostable polymers in the green packaging applications: A review, *Biotechnol. Prog.* 37 (6) (2021).

- [159] K.Y. Nandiwale, S.P. Borikar, V.V. Bokade, Synthesis of non-toxic triethyl citrate plasticizer by esterification of renewable citric acid using modified zeolite, *Clean Soil Air Water*. 43 (2015) 787–966, <https://doi.org/10.1002/clen.201400189>.
- [160] O. Sawant, S. Mahale, V. Ramchandran, G. Nagaraj, A. Bankar, Fungal citric acid production using waste materials: a mini-review, *J. Microb. Biotech. Food Sci.* 8 (2018) 821–828, <https://doi.org/10.15414/jmbfs.2018.8.2.821-828>.
- [161] H.S. Grewal, K.L. Kalra, Fungal production of citric acid, *Biotechnol. Adv.* 13 (1995) 209–234, [https://doi.org/10.1016/0734-9750\(95\)00002-8](https://doi.org/10.1016/0734-9750(95)00002-8).
- [162] S. Howard, Processes for making renewable source-based citrate esters and acylated citrate esters, WO2012/027038 A2, 2012.
- [163] H.-M. Park, M. Misra, L.T. Drzal, A.K. Mohanty, “Green” nanocomposites from cellulose acetate bioplastic and clay: Effect of eco-friendly triethyl citrate plasticizer, *Biomacromolecules* 5 (2004) 2281–2288, <https://doi.org/10.1021/bm049690f>.
- [164] J.A. de Lima, C.A. Pinotti, M.I. Felisberti, M.do C. Gonçalves, Blends and clay nanocomposites of cellulose acetate and poly(epichlorohydrin), *Compos. Part B: Eng.* 43 (2012) 2375–2381, <https://doi.org/10.1016/j.compositesb.2011.11.073>.
- [165] S. Zepnik, S. Kabasci, R. Kopytzky, H.-J. Radusch, T. Wodke, Extensional flow properties of externally plasticized cellulose acetate: Influence of plasticizer content, *Polymers* 5 (2013) 873–889, <https://doi.org/10.3390/polym5030873>.
- [166] S.C. Teixeira, R.R.A. Silva, T.V. de Oliveira, P.C. Stringheta, M.R.M.R. Pinto, N.de F.F. Soares, Glycerol and triethyl citrate plasticizer effects on molecular, thermal, mechanical, and barrier properties of cellulose acetate films, *Food Biosci.* 42 (2021), <https://doi.org/10.1016/j.fbio.2021.101202>.
- [167] R. Quintana, O. Persenaire, Y. Lemmouchi, J. Sampson, S. Martin, L. Bonnaud, P. Dubois, Enhancement of cellulose acetate degradation under accelerated weathering by plasticization with eco-friendly plasticizers, *Polym. Degrad. Stab.* 98 (2013) 1556–1562, <https://doi.org/10.1016/j.polydegradstab.2013.06.032>.
- [168] J.S. Choi, S.T. Lim, H.J. Choi, S.M. Hong, A.K. Mohanty, L.T. Drzal, M. Misra, A.C. Wibowo, Rheological, thermal, and morphological characteristics of plasticized cellulose acetate composite with natural fibers, *Macromol. Symp.* 224 (2005) 297–308, <https://doi.org/10.1002/masy.200550626>.
- [169] C. Pang, R.A. Shanks, F. Daver, Bio-composites based on cellulose acetate and kenaf fibers: Processing and properties, in: Nuremberg, Germany, 2014, pp. 350–353, doi: 10.1063/1.4873798.
- [170] O.Y. Suárez Palacios, P.C. Narváez Rincón, J.-P. Corriou, M. Camargo Pardo, C. Fouteix, Low-molecular-weight glycerol esters as plasticizers for poly(vinyl chloride), *J. Vinyl Addit. Technol.* 20 (2014) 65–71, <https://doi.org/10.1002/vnl.21351>.
- [171] X. Liao, Y. Zhu, S.-G. Wang, Y. Li, Producing triacetyl glycerol with glycerol by two steps: Esterification and acetylation, *Fuel Process. Technol.* 90 (2009) 6.
- [172] D. Hull, Process for the manufacture of tripropionin, US2005371, 1935.
- [173] Cong Yu Bao, Cellulose acetate / plasticizer systems: structure, morphology and dynamics, Université Claude Bernard - Lyon I, 2015.
- [174] T. Cousin, C. Berto, T. Budtova, J. Kurek, P. Navard, Influence of the scale and type of processing tool on plasticization of cellulose acetate: Influence of the scale and type of processing tool on plasticization of cellulose acetate, *Polym. Eng. Sci.* 57 (5) (2017) 563–569.
- [175] V.T. Phuong, S. Versteche, P. Cinelli, I. Anguillesi, M.-B. Coltelli, A. Lazzeri, Cellulose acetate blends - Effect of plasticizers on properties and biodegradability, *J. Renew. Mater.* 2 (2014) 35–41, <https://doi.org/10.7569/JRM.2013.634136>.
- [176] C.M. Buchanan, D. Dorschel, R.M. Gardner, R.J. Komarek, A.J. Matosky, A. W. White, M.D. Wood, The influence of degree of substitution on blend miscibility and biodegradation of cellulose acetate blends, *J. Environ. Polym. Degr.* 4 (1996) 179–195, <https://doi.org/10.1007/BF02067452>.
- [177] S. Nigam, A.K. Das, M.K. Patidar, Synthesis, characterization and biodegradation of bioplastic films produced from Parthenium hysterophorus by incorporating a plasticizer (PEG600), *Environ. Challenges.* 5 (2021), 100280, <https://doi.org/10.1016/j.envc.2021.100280>.
- [178] D.S. Rosa, C.G.F. Guedes, F. Casarin, F.C. Bragança, The effect of the Mw of PEG in PCL/CA blends, *Polym. Test.* 24 (2005) 542–548, <https://doi.org/10.1016/j.polymertesting.2005.02.002>.
- [179] J.M. Mayer, G.R. Ellison, Cellulose acetate and starch based biodegradable injection molded plastics compositions and methods of manufacture, US5288318A, 1994.
- [180] S.-Y. Lin, C.-J. Lee, Y.-Y. Lin, The effect of plasticizers on compatibility, mechanical properties, and adhesion strength of drug-free Eudragit E films, *Pharm. Res.* 8 (1991), <https://doi.org/10.1023/a:1015850301214>.
- [181] J.-H. Guo, Effects of plasticizers on water permeation and mechanical properties of cellulose acetate: Antiplasticization in slightly plasticized polymer film, *Drug Dev. Ind. Pharm.* 19 (1993) 1541–1555, <https://doi.org/10.3109/03639049309069325>.
- [182] M.E. Abd Manaf, M. Tsuji, Y. Shiroyama, M. Yamaguchi, Wavelength dispersion of orientation birefringence for cellulose esters containing tricresyl phosphate, *Macromolecules* 44 (2011) 3942–3949, <https://doi.org/10.1021/ma200317g>.
- [183] Y. Nishikawa, H. Ito, I. Noda, Analysis of molecular interaction using a pulse-induced ring-down compression ATR-DIRLD step-scan time resolved spectroscopy/2D-IR, *J. Mol. Struct.* 1156 (2018) 9, <https://doi.org/10.1016/j.molstruc.2017.12.025>.
- [184] M.T. Ghachet, M. Schilling, K. McCormick, J. Mazurek, E. Richardson, H. Khanjian, T. Learner, Assessment of the composition and condition of animation cels made from cellulose acetate, *Polym. Degrad. Stab.* 107 (2014) 223–230.
- [185] E.W. Erdhuisen, Method of producing optical films on triphenylphosphate-containing cellulose triacetate substrate, EP1010996A1, 2000.
- [186] A. Pron, Y.-F. Nicolau, M. Nechtschein, F. Genoud, Composition for producing a conductive composite material containing a polyaniline, and resulting composite material, WO1998005040A1, 1998.
- [187] M. Ormsby, Analysis of laminated documents using solid-phase microextraction, *J. Am. Inst. Conserv.* 44 (2005) 13–26, <https://doi.org/10.1179/019713605806082400>.
- [188] M. Macht, D. Fletcher, Cellulose acetate molding compositions, US2109593, 1936.
- [189] H. Tae Kim, M. Hee Kim, B. Kim, C. Min Koo, K. Kahb Koo, S. Man Hong, Effect of plasticization on physical and optical properties of triacetyl cellulose films for LCD application, *Mol. Cryst. Liq. Cryst.* 512 (1) (2009) 188/[2034]–198/[2044].
- [190] B.T. Lamborn, Method of producing a thermoplastic cellulose acetate composition, US2591077, 1952.
- [191] K. Shankar, P. Kandasamy, Carbon dioxide separation using α -alumina ceramic tube supported cellulose triacetate-tributyl phosphate composite membrane, *Greenhouse Gas. Sci. Technol.* 9 (2019) 287–305, <https://doi.org/10.1002/gbg.1845>.
- [192] E.A. Rodman, Plasticized cellulose acetate compositions, US2231818, 1941.
- [193] J. Berger, M. Reist, J.M. Mayer, O. Felt, N.A. Peppas, R. Gurny, Structure and interactions in covalently and ionically crosslinked chitosan hydrogels for biomedical applications, *Eur. J. Pharm. Biopharm.* 57 (2004) 19–34, [https://doi.org/10.1016/S0939-6411\(03\)00161-9](https://doi.org/10.1016/S0939-6411(03)00161-9).
- [194] A.Y.W. Young, G. Audira, F. Saputra, H.C. Alos, C.A. Aventura, Y.-H. Lai, R. D. Vasquez, C.-D. Hsiao, C.-H. Hung, Toxicity assessment of an anti-cancer drug of p-toluene sulfonamide in Zebrafish larvae based on cardiovascular and locomotion activities, *Biomolecules* 12 (2022) 1103, <https://doi.org/10.3390/biom12081103>.
- [195] X. Zhang, W. Bisset, M. Combs, Cellulose acetate film forming compositions, WO2017/100159A2, 2017.
- [196] T.S. Carswell, Sulfamide derivatives as plasticizers for acetyl cellulose, *Ind. Eng. Chem.* 21 (1929) 1176–1178, <https://doi.org/10.1021/ie50240a006>.
- [197] J. Mazurek, A. Laganà, V. Dion, S. Etyemez, C. Carta, M.R. Schilling, Investigation of cellulose nitrate and cellulose acetate plastics in museum collections using ion chromatography and size exclusion chromatography, *J. Cult. Herit.* 35 (2019) 263–270, <https://doi.org/10.1016/j.culher.2018.05.011>.
- [198] S.T. Cox, M.G. Mitchell, P.J. Kennedy, G.F. Massie, F.W. Williams, High pressure laminates made with paper containing cellulose acetate, US5928777, 1999.
- [199] C.M. Buchanan, N.L. Buchanan, K.J. Edgar, J.L. Lambert, Carbohydrate esters and polyol esters as plasticizers for polymers, compositions and articles including such plasticizers and methods of using the same, US7276546B2, 2007.
- [200] W.E. Gloor, Molding material, US2328269, 1940.
- [201] G. Touey, D. Herman, Mixed esters of glucose and sucrose, US2931802, 1960.
- [202] K. Aghmih, A. Boukhriss, M. El Bouchti, M. Ait Chaoui, S. Majid, S. Gmouh, Introduction of ionic liquids as highly efficient plasticizers and flame retardants of cellulose triacetate films, *J. Polym. Environ.* 30 (2022) 2905–2918, <https://doi.org/10.1007/s10924-022-02407-3>.
- [203] W. Ning, Z. Xingxiang, L. Haihui, H. Benqiao, 1-Allyl-3-methylimidazolium chloride plasticized-corn starch as solid biopolymer electrolytes, *Carbohydr. Polym.* 76 (2009) 482–484, <https://doi.org/10.1016/j.carbpol.2008.11.005>.
- [204] A. Bendaoud, Y. Chalame, Plasticizing effect of ionic liquid on cellulose acetate obtained by melt processing, *Carbohydr. Polym.* 108 (2014) 75–82, <https://doi.org/10.1016/j.carbpol.2014.03.023>.
- [205] S. Ramesh, R. Shanti, E. Morris, Plasticizing effect of 1-allyl-3-methylimidazolium chloride in cellulose acetate based polymer electrolytes, *Carbohydr. Polym.* 87 (2012) 2624–2629, <https://doi.org/10.1016/j.carbpol.2011.11.037>.
- [206] A. Pinkert, K.N. Marsh, S. Pang, M.P. Staiger, Ionic liquids and their interaction with cellulose, *Chem. Rev.* 109 (2009) 6712–6728, <https://doi.org/10.1021/cr9001947>.
- [207] T.P. Thuy Pham, C.-W. Cho, Y.-S. Yun, Environmental fate and toxicity of ionic liquids: A review, *Water Res.* 44 (2010) 352–372, <https://doi.org/10.1016/j.watres.2009.09.030>.
- [208] V. Thamke, P. Singh, S. Pal, M. Chaudhary, K. Kumari, I. Bahadur, R.S. Varma, Current toxicological insights of ionic liquids on various environmental living forms, *J. Environ. Chem. Eng.* 10 (2) (2022) 107303.
- [209] A.J. Greer, J. Jacquemin, C. Hardacre, Industrial applications of ionic liquids, *Molecules* 25 (2020) 5207, <https://doi.org/10.3390/molecules25215207>.
- [210] R. Erdmann, S. Kabasci, J. Kurek, S. Zepnik, Study of reactive melt processing behavior of externally plasticized cellulose acetate in presence of isocyanate, *Materials* 7 (2014) 7752–7769, <https://doi.org/10.3390/ma7127752>.
- [211] R. Quintana, O. Persenaire, Y. Lemmouchi, L. Bonnaud, P. Dubois, Compatibilization of co-plasticized cellulose acetate/water soluble polymers blends by reactive extrusion, *Polym. Degrad. Stab.* 126 (2016) 31–38, <https://doi.org/10.1016/j.polydegradstab.2015.12.023>.
- [212] M. Hassan-Nejad, J. Ganster, A. Bohn, M. Pinnow, Bert Volkert, Bio-based nanocomposites of cellulose acetate and nano-clay with superior mechanical properties, *Macromol. Symp.* 280 (2009) 123–129, <https://doi.org/10.1002/masy.200950614>.
- [213] O.A. Fridman, A.V. Sorokina, Criteria of efficiency of cellulose acetate plasticization, *Polym. Sci. Ser. B.* 48 (2006) 233–236, <https://doi.org/10.1134/S1566009406090028>.
- [214] M.C. Gutiérrez, M.-A. De Paoli, M.I. Felisberti, Cellulose acetate and short curauá fibers biocomposites prepared by large scale processing: Reinforcing and thermal insulating properties, *Ind. Crop. Prod.* 52 (2014) 363–372, <https://doi.org/10.1016/j.indcrop.2013.10.054>.

- [215] N. Liu, J.W. Zhang, H.P. Wang, Plasticization of cellulose diacetate by ionic liquid, *AMR* 936 (2014) 1002–1006, <https://doi.org/10.4028/www.scientific.net/AMR.936.1002>.
- [216] N. Yadav, M. Hakkarainen, Degradable or not? Cellulose acetate as a model for complicated interplay between structure, environment and degradation, *Chemosphere* 265 (2021), 128731, <https://doi.org/10.1016/j.chemosphere.2020.128731>.
- [217] I. del Gaudio, E. Hunter-Sellars, I.P. Parkin, D. Williams, S. Da Ros, K. Curran, Water sorption and diffusion in cellulose acetate: The effect of plasticisers, *Carbohydr. Polym.* 267 (2021), 118185, <https://doi.org/10.1016/j.carbpol.2021.118185>.
- [218] J.M. Cardamone, M.T. Baker (Eds.), *Historic Textiles, Papers, and Polymers in Museums*, American Chemical Society, Washington, DC, 2000, <https://doi.org/10.1021/bk-2001-0779>.
- [219] N.S. Allen, M. Edge, J.H. Appleyard, T.S. Jewitt, C.V. Horie, D. Francis, Degradation of historic cellulose triacetate cinematographic film: The vinegar syndrome, *Polym. Degrad. Stab.* 19 (1987) 379–387, [https://doi.org/10.1016/0141-3910\(87\)90038-3](https://doi.org/10.1016/0141-3910(87)90038-3).
- [220] A. Argoud, O. Andres, C. Vergelati, *New plasticized compositions comprising cellulose acetate*, WO2017/109043A1 (2017).
- [221] K. Solomons, J.W.C. Cochrane, Formaldehyde toxicity. Part 2 - Review of acute and chronic effects on health, 66 (1984).
- [222] O.T. Somade, Camphor toxicity: A review of recent findings, *Proc. Natl. Acad. Sci., India, Sect. B Biol. Sci.* (2022), <https://doi.org/10.1007/s40011-022-01437-0>.
- [223] N.S. Dosoky, W.N. Setzer, Maternal reproductive toxicity of some essential oils and their constituents, *IJMS* 22 (2021) 2380, <https://doi.org/10.3390/ijms22052380>.
- [224] P.R. Sarika, P. Nancarrow, A. Khansaheb, T. Ibrahim, Bio-based alternatives to phenol and formaldehyde for the production of resins, *Polymers* 12 (2020) 2237, <https://doi.org/10.3390/polym12102237>.
- [225] R.J. Komarek, R.M. Gardner, C.M. Buchanan, S. Gedon, Biodegradation of radiolabeled cellulose acetate and cellulose propionate, *J. Appl. Polym. Sci.* 50 (1993) 1739–1746, <https://doi.org/10.1002/app.1993.070501009>.
- [226] K.J. Edgar, C.M. Buchanan, J.S. Debenham, P.A. Rundquist, B.D. Seiler, M. C. Shelton, D. Tindall, Advances in cellulose ester performance and application, *Prog. Polym. Sci.* 26 (2001) 1605–1688, [https://doi.org/10.1016/S0079-6700\(01\)00027-2](https://doi.org/10.1016/S0079-6700(01)00027-2).
- [227] C. Abrusci, D. Marquina, A. Santos, A. Del Amo, T. Corrales, F. Catalina, Biodeterioration of cinematographic cellulose triacetate by *Sphingomonas paucimobilis* using indirect impedance and chemiluminescence techniques, *Int. Biodeter. Biodegr.* 63 (2009) 759–764, <https://doi.org/10.1016/j.ibiod.2009.02.012>.
- [228] B. Laycock, M. Nikolić, J.M. Colwell, E. Gauthier, P. Halley, S. Bottle, G. George, Lifetime prediction of biodegradable polymers, *Prog. Polym. Sci.* 71 (2017) 144–189, <https://doi.org/10.1016/j.progpolymsci.2017.02.004>.
- [229] K. Hosono, A. Kanazawa, H. Mori, T. Endo, Photodegradation of cellulose acetate film in the presence of benzophenone as a photosensitizer, *J. Appl. Polym. Sci.* 105 (2007) 3235–3239, <https://doi.org/10.1002/app.26386>.
- [230] Y. Yamashita, T. Endo, Deterioration behavior of cellulose acetate films in acidic or basic aqueous solutions, *J. Appl. Polym. Sci.* 91 (2004) 3354–3361, <https://doi.org/10.1002/app.13547>.
- [231] A. Göpferich, *Mechanisms of polymer degradation and erosion*, *Biomater.: Silver Jubilee Compendium* 17 (2) (1996) 103–114.
- [232] A.A. Klyosov, Trends in biochemistry and enzymology of cellulose degradation, *Biochemistry* 29 (1990) 10577–10585, <https://doi.org/10.1021/bi00499a001>.
- [233] B. Vidéki, S. Klébert, B. Pukánszky, Grafting of caprolacton to cellulose acetate by reactive processing, *Eur. Polym. J.* 41 (2005) 1699–1707, <https://doi.org/10.1016/j.eurpolymj.2005.03.002>.
- [234] T.D. Stark, H. Choi, P.W. Diebel, Plasticizer molecular weight and plasticizer retention in PVC geomembranes, 12 (2015) 99–110, doi: 10.1680/gein.2005.12.2.99.
- [235] P.R. Graham, Phthalate ester plasticizers - why and how they are used, *Environ. Health Perspect.* 3 (1973) 3–12, <https://doi.org/10.1289/ehp.73033>.
- [236] R.F. Boyer, The compatibility, efficiency and permanence of plasticizers, *J. Appl. Phy.* 20 (1949) 540–552, <https://doi.org/10.1063/1.1698423>.
- [237] H.D. Özeren, M. Guivier, R.T. Olsson, F. Nilsson, M.S. Hedenqvist, Ranking plasticizers for polymers with atomistic simulations: PVT, mechanical properties, and the role of hydrogen bonding in thermoplastic starch, *ACS Appl. Polym. Mater.* 2 (2020) 2016–2026, <https://doi.org/10.1021/acsapm.0c00191>.
- [238] M. Esmaeili, G. Pircheraghi, R. Bagheri, Optimizing the mechanical and physical properties of thermoplastic starch via tuning the molecular microstructure through co-plasticization by sorbitol and glycerol: Optimizing the properties of thermoplastic starch, *Polym. Int.* 66 (2017) 809–819, <https://doi.org/10.1002/pi.5319>.
- [239] S. Zhao, J. Li, L. Wu, M. Hua, C. Jiang, Y. Pan, L. Yao, S. Xu, J. Ge, G. Pan, Synthesis and characterization of cellulose diacetate-graft-poly lactide via solvent-free melt ring-opening graft copolymerization, *Polymers* 15 (2022) 143, <https://doi.org/10.3390/polym15010143>.
- [240] J. Yuan, B. Cheng, A strategy for nonmigrating highly plasticized PVC, *Sci Rep.* 7 (2017) 9277, <https://doi.org/10.1038/s41598-017-10159-7>.