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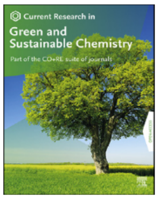

Vegetable oils as monomeric and polymeric materials: A graphical review

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ABSTRACT

Vegetable oils have been extensively researched, and many reviews have been published about them. However, most of them are focused on soybean and linseed oils and reactions, such as epoxidation, but do not take into account other potential sources or reactions that can provide high value products. Therefore, the present work aims to cover these overlooked topics illustrating different sources of vegetable oils including baru, macaw, andiroba, grape, passion fruits, neem, and so on. Furthermore, some chemical modifications and their resulting monomers are discussed, for instance, maleinization, epoxidation, acrylation, carbonatation, and click chemistry, and forth. Consequently, there are several ways to use vegetable oils to produce renewable polymers for use in technological fields, such as photopolymerisation and vitrimers. The latter has received great attention in recent research due to their recovering, reshaping, and welding properties.

1. Vegetable oils: definitions, sources, and classification

Vegetable oils (VOs) are ester derivatives of fatty acids and glycerol, these molecules are also known as triglycerides or triacylglycerols [1]. As the name suggests, VOs are extracted from plant seeds, and they function as the energetic source for the germination process. Some oils used by society are not triglycerides (Fig. 1a), but terpenes or terpenoids (essential oils). These are smaller volatile molecules also extracted from plants, which do not have the triacylglycerol structure; however, they are derived from isoprene [2].

VOs can be classified according to their source type, such as seed, grains, nuts, and palm (Fig. 1b). Castor, grapeseed, linseed, and safflower oils are examples of oils extracted from seeds, while two of the most consumed oils – soybean and corn – are extracted from grains. Some VOs are extracted from nuts, usually fruits raised on trees, and for this reason they are classified as nut oils, for instance, baru, macadamia, and Brazil nut oils. Furthermore, palm trees produce fruits such as macaw, palm, and buriti, resulting in oils from palm. Each oil has a percentage of unsaturation, resulting from the different fatty chains attached to the glycerol backbone. The iodine value (IV) is a parameter used to quantify the amount of unsaturation degree per 100 g of sample, which can be determined by titration or ^{1}H NMR; and according to the IV, the VOs can be classified as drying oils ($IV > 130$), semi-drying oils ($90 < IV < 130$), and non-drying oils ($IV < 90$) [3]. The IV of a VO can vary according to the extraction process, age of the plant, weather, and plant variety. However, a small variation is expected, allowing a VO exchange from non-drying to semi-drying or semi-drying to drying when its IV is near the previous limits. In addition, the small variation in fatty acid profile, the extraction method can also affect the percentage of other molecules found in the plant seed, such as antioxidants and terpenes/terpenoids [4]. The small fraction of components in oil, even after the purification process, can interfere in the odor and colour of VOs [5,6]. Therefore, different VOs can also present fluorescence in different wavelengths when exposed to UV light (Fig. 1-c).

2. Chemical modifications of vegetable oils

VOs are considered sustainable raw materials for biobased polymers, which are viable candidates to replace polymers derived from fossil sources, due to their low toxicity, affordable price, and versatility toward chemical modification. However, they present poor chemical reactivity to be used as resource in the polymer field. Therefore, one way to increase their reactivity is modifying the alkene groups (unsaturation) present in the fatty chain to produce renewable monomers, such as by maleinization, epoxidation, acrylation, carbonatation of epoxides, and so on (Fig. 2a) [7,8].

Maleinization can be carried out by different pathways such as an ene reaction or Diels-Alder addition. The ene reaction is a pericyclic reaction, in which one allylic hydrogen (ene) and one enophile are necessary [9]. VO acts as the ene, due to its allylic hydrogens, whereas maleic anhydride

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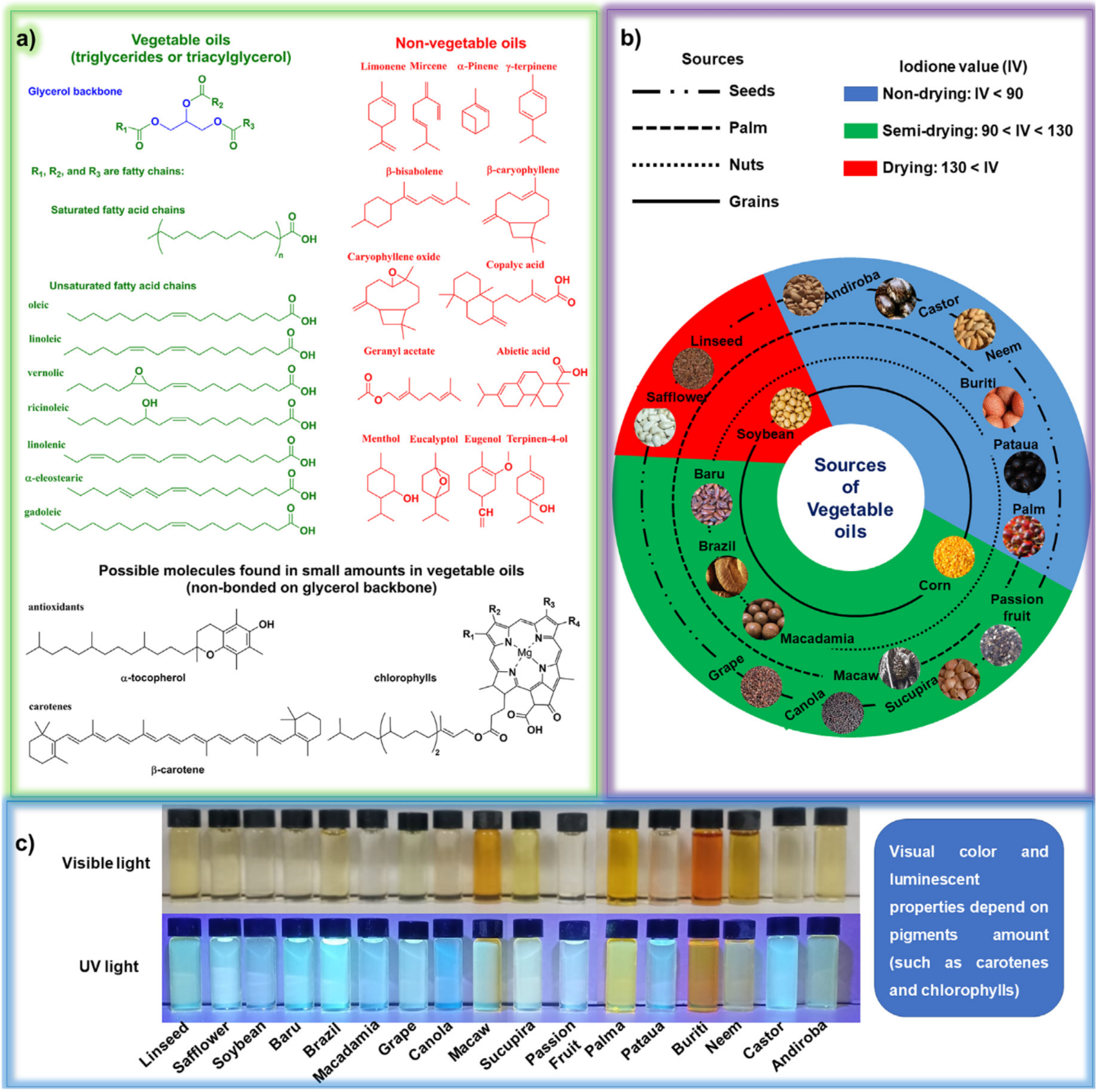

Fig. 1. *a)* representation of triacylglycerol structure, fatty acids, essential oils (non-triacylglycerol) and most common compounds found in vegetable oils. ***b)*** Classification of iodine value (IV), and plant sources to vegetable oils. ***c)*** vegetable oils from different sources under visible light and UV light.

is considered an enophile. The reaction starts exchanging the allylic hydrogen from the fatty acid to the anhydride ring, followed by the migration of the double bond of the anhydride to the fatty acid, then attaching it to the fatty acid chain. The Diels-Alder reaction can occur when the maleic anhydride is reacted with VO that contains α-eleostearic acid (a conjugated fatty acid), providing a cyclic six-membered adduct [10]. The maleinized VOs can be directly polymerized or can be used as precursor for the synthesis of an acrylated monomer (Fig. 2b).

Another VO modification is usually performed by epoxidation reaction, where the alkenes are transformed into epoxide groups in the presence of oxidizing agents such as hydrogen peroxide, peracids, or O_2 in the presence of catalysts. The epoxidized VO (EVO) is an important monomer and can be used in ring-opening or polycondensation polymerisation process to synthesize polyamide, polyether, polyester, and polysulfides [11]. In addition, epoxides can also be reacted with acrylic acid or CO_2 to form acrylated or carbonated monomers, respectively [12–14]. Acrylated VOs (AVOs) are usually used in photopolymerizable resins or plasticizers and stabilizers for PVC. In addition, AVOs can be used in click chemistry, in which thiols can be attached directly to carbon double bonds by thiol-ene reactions (Fig. 2-c).

The direct conversion of VOs to functionalized oils by one-step reaction is desirable in laboratories and industries, due to their economic and sustainable aspects, making the use of thiols an interesting option. Thiol compounds are similar to alcohols, containing a sulfur atom instead of an oxygen atom. The thiol-ene reaction proceeds in an equimolar ratio of thiol groups and double bonds, which is performed in the one-pot step, in a rapid way, resulting in a product with a high yield. This reaction often occurs by a photochemical process in the presence of photoinitiators under UV light. First, the photoinitiator generates radicals that attack the thiol, generating a thiyl radical ($R{-}S^\bullet$). The thiyl radical subsequently attacks the carbon double bond in an anti-Markovnikov reaction, attaching the sulfur atom to the carbon chain. If the thiol is reacted directly with unmodified VO, the reaction is not recognized as “click”, due to the less reactivity of the alkene, demanding a longer reaction time in a higher concentration of photoinitiator [15]. Several works have aimed to improve the reactivity of different VOs in thiol-ene reaction, changing the synthesis parameters and suggesting new synthesis strategies [15,16]. Furthermore, the thiol compound can react with epoxidized

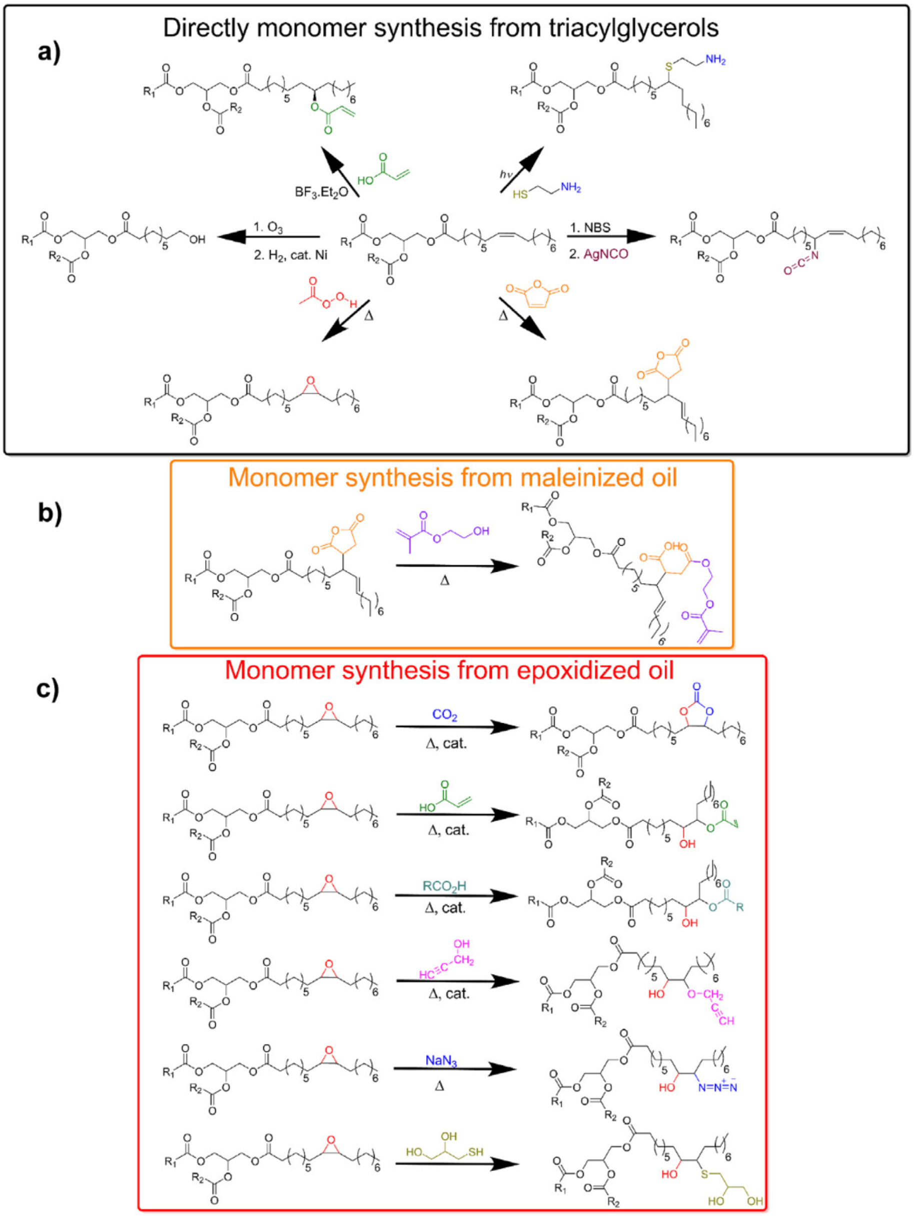

Fig. 2. *a)* Examples of direct modifications on triacylglycerol structure to provide monomers. ***b)*** Acrylated monomer from maleinized triacylglycerol ***c)*** Examples of monomers from epoxidized triacylglycerol.

VOs in the presence of alkaline catalysts or photo-generated base initiators. A second type of click chemistry considers a reaction between azide groups and alkynes to produce units of triazole rings [17]. EVO can be reacted with sodium azide (Fig. 2b) to form a triacylglycerol with azide pendants (TAP). Therefore, the TAP can be reacted with different polyalkynes, such as triacylglycerol with alkyne pendants, producing renewable polymers.

Carbonated VOs have been used in to obtain non-isocyanate polyurethanes, avoiding the use of highly toxic isocyanates, which is common in industrial processes, since polyurethanes are synthesized by the reaction of polyols and di-isocyanates [13,14]. This reaction highlights the atom economy, in which the epoxide group reacts with carbon dioxide to produce cyclic carbonates without by-products [13]. The reaction occurs in the presence of a catalyst, high pressure CO_2, and mild temperatures. Thereafter, the carbonated VO can be reacted with polyfunctional amine compounds to synthesize polyhydroxyurethanes, which are greener than conventional polyurethanes from isocyanates [14]. Moreover, using carbonated monomers to produce high value products is one (carbon capture and utilization – CCU) of the two solutions available for CO_2 present in atmosphere. CCU considers CO_2 as a resource instead of waste as it is considered in the second available solution (carbon capture and storage, CCS) [18].

3. Vitrimers: a new class of biopolymeric materials

Thermoset biobased polymers have a 3D crosslinked network, which provides good thermal and mechanical properties, chemical stability, insolubility, and swelling properties. The crosslink occurs by covalent bonds, which normally do not permit a reshaping property or recycling after synthesis [19]. However, new biobased polymers have been researched that provide both good stability for the crosslinked network and reprocessability. Therefore, new polymers with Covalent Adaptable Network (CAN) – Vitrimers have been synthesized (Fig. 3) [19,20]. Although most vitrimers derived from VOs are resulted from associative CANs (they do not depend on temperature); there are also dissociative CANs that present vitrimers properties. However, they depend on

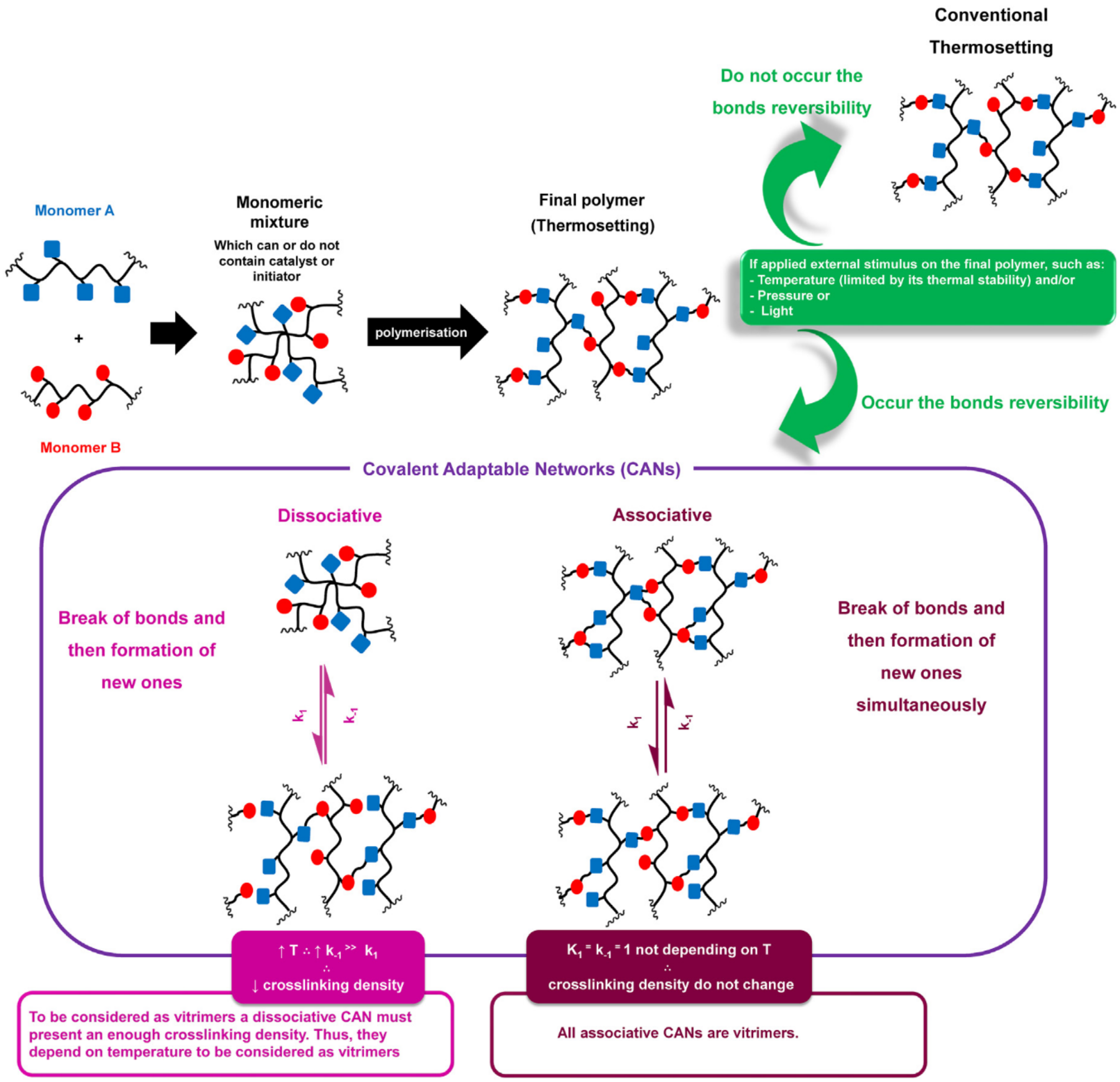

Fig. 3. Representative scheme of syntheses of conventional thermosetting polymers and Covalent Adaptable Networks (CANs).

temperature to be considered as vitrimers since the rate of new bond formation must be higher than the rate of bond breaking (Fig. 3) [19–21].

The term vitrimers was firstly reported by Leibler et al. in 2011, which are crosslinked polymers that can be welded (self-healed) or reshaped under a physical process, such as pressure and heat/light [20]. Vitrimers present covalent bonds that can be rapidly shifted during the heating process to provide new covalent bonds and restructure, the cleavage and generation of these covalent bonds are in equilibrium at any temperature. Vitrimers presents two main thermal events, the first event is a glass transition (T_g) that normally occurs at subambient temperatures. The second event is associated with the topology-freezing transition temperature (T_V). Above $T_{V,}$ the polymer turns from a viscoelastic solid into a viscoelastic liquid, occurring a rapid bond exchange and permitting structure recovery [19–21].

Vegetable oil is one of the most promising resources for new vitrimers. Epoxidized vegetable oil (EVO) can react with cyclic anhydrides or diacids to form crosslinked structures with free OH groups, so the polymer can be reshaped or welded at $T_{V,}$ due to a transesterification reaction between the ester groups and free OH groups, which was the first reported in the literature for vitrimers. In 2021, Di Mauro, Tran, and Mija reported a thermoset terpolymer by reacting epoxidized linseed oil with maleic or phthalic anhydrides and dipropylene glycol, in which the recovery process occurs by a transesterification reaction between free OH groups and ester groups present in the cross-linking sites [22].

More recently, EVO was reacted with disulfide derivatives (amines or carboxylic acids) to provide new vitrimers that are welded under heat and pressure [23]. This type of disulfide exchange can also be achieved by reacting VOs with elemental sulfur to form crosslinked poly-sulfide networks. In 2021 Shan et al. reacted an EVO (soybean) with 2,2'dithiodibenzoic acid and dimer acid to produce crosslinked polymers. These polymers showed self-healing ability and were tested as strain sensors [24].

In 2022, Li and co-workers reacted EVO with a borate derivative to synthesize a crosslinked polymer with diboronic ester units, which can exchange themselves under pressure and heat, providing the polymer recovering [25]. This biobased polymer can be applied as coating and adhesives for materials such as glass, steel, plastic, and wood. Zhao et al. in 2020 synthesized a vitrimer from epoxidized soybean oil and a vanillin-derived Schiff base (synthesized by the reaction between vanillin and different diamines); the recovering process is based on the exchanging of the imine units at 120.0 °C [26]. Furthermore, Cortés-Guzmán et al. showed that the vanillin can be reacted with methacrylic anhydride or acryloyl chloride to produce a vanillin acrylate derivative. Thereafter, this derivative can be reacted with diamines to form a diimine-diacrylate derivative (final monomer). The respective final monomer was used in 3D printing and presented a weldable ability due to imine exchange [27].

Vegetable oil vitrimers using crosslinking units that are susceptible to Diels-Alder reaction have also been described in the literature [19]. Lorero and co-workers reported a weldable polymer bismaleimide, DGEBA and furfurylamine (renewable compound). The welding process occurs by a retro Diels-Alder reaction when polymer is heated (90–180 °C) and cooled (<60 °C). The polymer presented thermal forming and shape recovering, and thermochemical recycling in DMSO and DMF [28].

The EVO can also be reacted with pressurized CO_2 in the presence of catalysts to form cyclic carbonates. The carbonated vegetable oil (CVO) can easily react with diamine compounds to provide a cross-linked polymer structure with hydroxyurethane linkages [14]. The recovering process can be achieved by the bond exchange between urethane and alcohol groups linked on the polymer structure (transcarbomoylation reaction). Studies on polyhydroxyurethanes from CVO have expanded, providing new vitrimers materials with easy recovery [19,20]. To summarize, Fig. 4 illustrates the most used groups as well as the resulted reactions found in vitrimers; hence inserting them on VOs structures can provide renewable polymers with vitrimer's properties.

Here, a brief summary was described evidencing the application of modified VOs as monomers to synthesize biobased vitrimers, proving their versatility as a renewable resource in the polymer field.

4. Future perspectives

The VOs are renewable sources produced by different plants, in which many of them are not commercialized by the food industry, such as macaw, baru, sucupira, buriti, and neem oils. Moreover, there are others considered as by-products by the beverage industry, for instance, passion fruit, orange, and grapeseed oil. As consequence, several options of renewable sources could be used in polymeric materials (and in coating and painting fields) instead of soybean, corn, sunflower, canola, and linseed oils, usually also destinated for the food industry.

Concerns about the environment and cost reduction have resulted in greener processes through the modification of VOs. As a result, VO derivatives have increased in some fields, such as photopolymerisation and vitrimers, providing new outcomes in 3D printing, robotic, and biomaterials. Hence, VOs have great potential to be on the frontiers of research to provide technologies demanded by humanity.

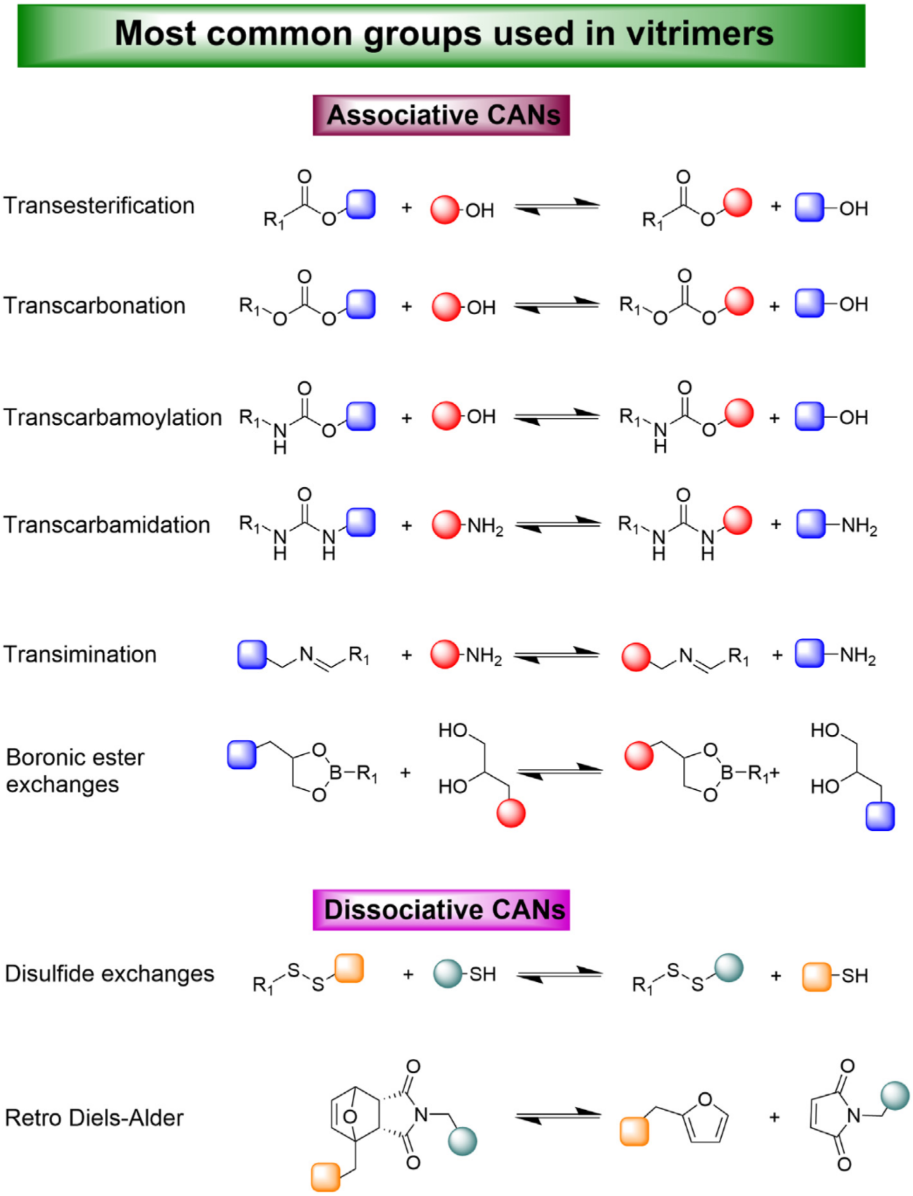

Fig. 4. Most common chemical groups observed in polymeric vitrimers.

CRediT authorship contribution statement

Caroline Gaglieri: Conceptualization, Data curation, Formal analysis, Investigation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Rafael T. Alarcon:** Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Aniele de Moura:** Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Gilbert Bannach:** Conceptualization, Funding acquisition, Project administration, Resources, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

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

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