FEATURE ARTICLE

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Lipidic biomass as a renewable chemical building block for polymeric materials

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Polymers are intrinsically connected to modern society and are found and used in a variety of technologies. Although polymers are valuable, concerns about synthetic polymers derived from non-renewable sources have emerged. Therefore, there is a need to develop new polymeric materials from renewable sources, especially those that are cost-effective, non-toxic, widely available, not derived from depleting sources and are designed to be biodegradable after disposal. In this regard, a perfect class of renewable resources are the lipids (not soluble in water), among which, we can find useful compounds such as triacylglycerols/triglycerides (vegetable oil), terpenes/terpenoids (essential oils), and abietic acid (rosin resin). These are liable to modification to new monomers that can be used in adhesives, 3D-printing, self-healing and so on. However, these materials still suffer from some limitations when compared to non-renewable polymers. Therefore, in this feature article, we will present a description/review of these renewable sources together with related polymeric materials and their mechanical/chemical/physical properties and applications.

1 Introduction

Indisputably, we are in a "polymeric age," as these materials can be found and applied in various fields, ranging from simple household utensils and furniture to biomaterials, coatings and technological applications.[1–6] However, the large-scale production of synthetic polymers has caused significant negative effects on

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Gabriel Iago dos Santos has been an undergraduate student at São Paulo State University (UNESP) since 2020. In 2021, he began his research on the synthesis of renewable polymeric materials and is currently working on the development of biomass-based photocurable monomers for 3D printing using green synthetic approaches, under the supervision of Prof. Gilbert Bannach.

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our ecosystem, including land and sea pollution due to low recycling rates and excessive waste dumping, depletion of finite sources (*e.g.* petroleum), and air contamination from the release of toxic gases during synthesis and processing.[7–10]

The annual production of polymeric materials exceeds 360 million tonnes, and by 2050, an increase of 30% is expected.[11] This data underscores society's dependence on polymers. Since polymer production is unavoidable, new approaches should be developed to meet our needs without vilifying these materials. Nevertheless, these approaches should focus on linking renewable compounds with sustainable methodologies, reuse/repair and environmental decomposition.[12,13] These efforts align with the circular economy, the principles of Green Chemistry and the United Nations Sustainable Development Goals (UNSDGs) 9 (Industry, innovation and infrastructure), 12 (Responsible consumption and production), and 13 (Climate action). In addition, researchers in the polymer field should focus on

novel materials that are fully renewable or contain significant amounts of renewable or biomass-derived compounds in their structure, to provide a higher percentage of bio-based content.[14–16]

In this context, it is crucial to use biomass as a primary compound for renewable polymers. Considering sustainable methodologies, the selection of biomass for technological and scientific proposes should consider the following considerations:[17]

1. It is better to select biomasses that are not edible to not compete with the food industry or market availability (*e.g.* castor oil, tung oil, and abietic acid), or use biomass from industrial waste (*e.g.* limonene from peels of citrus, grapeseed oil).

2. Biomasses with low or no investigation, which enable the research and investigation of the flora of a country or biomass from specific crops for technological and scientific purposes (*e.g.* tung oil and macaw palm oil).

Caroline Gaglieri obtained her chemical engineering degree in 2016 at Federal University of Alfenas (UNIFAL-MG). In 2022, she received her PhD in Science and Technology of Materials from São Paulo State University (UNESP), with a focus on the chemical modification of vegetable oils and their application in renewable polymer synthesis. She is currently a postdoctoral researcher at the same institution, focused on using rosin gum and its derivatives in photopolymerization (3D printing), carbonation reactions, and renewable vitrimers.
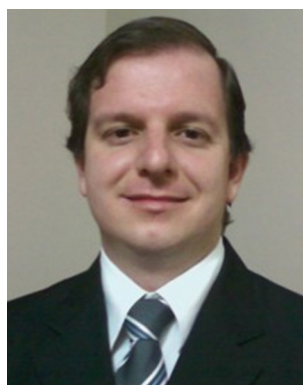
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Aniele de Moura obtained her chemistry degree in 2017 from São Paulo State University (UNESP). In 2023, she earned her PhD in Science and Technology of Materials from the same institution, focusing on using sustainable techniques to obtain functionalized curcumin derivatives to evaluate their biological and photophysical properties. She is currently a postdoctoral researcher at the Institute of Chemistry of São Carlos at the University of São Paulo (USP), with research interests in limonene-based polymers, 3D printing and vitrimers.

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Éder Tadeu Gomes Cavalheiro

Gilbert Bannach graduated in Chemistry from Ponta Grossa State University in 2000 and obtained his PhD in Analytical Chemistry in 2006 from São Paulo State University. Since 2009, he has been working at the same institution as a professor of Analytical Chemistry in the Chemistry Department at the School of Science. His research aims to transform renewable chemicals (triglycerides, glycerol, terpenes, and carbohydrates) into new monomers and polymers, following the principles of Green Chemistry.

Gilbert Bannach

3. Renewable resources that do not need to be depleted to obtain the desirable biomass, and biomasses with low or non-toxicity, for health safety during polymer production.

Our research group has expertise in biomass modification for renewable monomers and polymers, exceptionally lipid compounds (not soluble in water), such as triacylglycerol (vegetable oils), liquid terpenes (limonene and myrcene) and *Pinus* resin (abietic acid). These compounds are extremely versatile since they have functional groups (*e.g.* alkene, carboxylic acid, ester, alcohol, aldehyde, and ketone) liable to modification.[18]

Vegetable oil is a versatile and relatively inexpensive chemical building block for monomers and polymers, which is extracted from the seeds of a variety of plants.[18] It is constituted by a glycerol backbone reacted with three fatty acid chains, providing an ester of glycerol (triacylglycerol or triglyceride). The fatty chain can present alkene groups (carbon double bonds, C=C, unsaturated) or not (saturated), the most common unsaturated chains are oleic ($C18:1^{cis}$), linoleic ($C18:2^{cis,cis}$), and α-linolenic ($C18:3^{cis,cis,cis}$); in these cases, the alkene groups are isolated, and the first alkene appears at C_9.

Some vegetable oils can present fatty chains containing conjugated alkenes – α-eleostearic $C18:3^{cis,trans,trans}$ (tung oil), or other functional groups such as hydroxyl – ricinoleic acid ($C18:1^{cis}$) found in castor oil – *Ricinus communis*, or epoxy groups found in vernolic acid (fatty chain containing one epoxy group and one unsaturation) – *Vernonia galamensis*.[18] Fig. 1 displays the chemical representation of triacylglycerol and some usual fatty chains.

The unsaturation content is determined by grams of I_2 per 100 grams of oil (iodine value – IV), this is related to the Wijs titration method, where IV can be converted into mols of alkene groups.[19–21] However, for a faster and cleaner determination, the ^{1}H-NMR can be used in this goal, assisting not only the iodine value determination but also the average quantity of alkenes (carbon double bonds) per triacylglycerol molecule, which is an important parameter for polymeric systems since vegetable oil is a mixture of triacylglycerols with different fatty chains, and to enhance the crosslinking of this material at least, two reactional points are necessary per triacylglycerol molecule.

The ^{1}H-NMR can also quantify the percentage of saturated, oleic, linoleic and α-linolenic chains in vegetable oil. These three factors – iodine value, average double bond and percentage of each fatty chain – can be used to predict the chemical structure and molecular mass.[19,22]

Three classes of vegetable oils are available depending on the iodine value:[18]

I. The non-dry oil (IV < 90). A non-dry oil does not polymerize with exposure by oxygen in air or heat.

II. The Semi-dry oil (90 < IV < 130) can polymerize after a long time by oxygen or heating.

III. The dry oil (IV < 130) can easily self-polymerize by heating or in contact with oxygen to form a polymeric film in a few days.
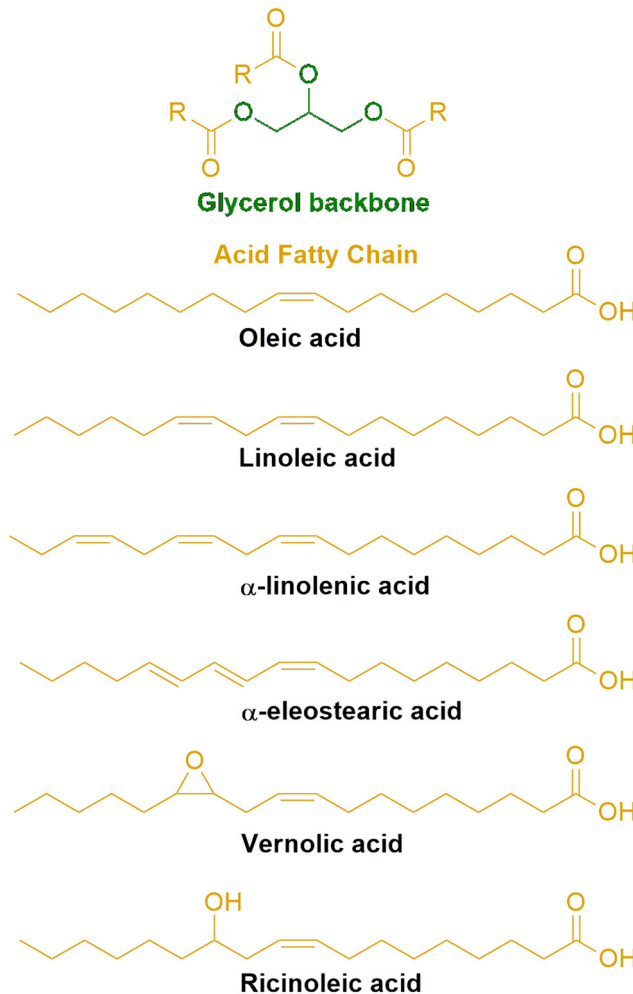

Fig. 1 Representation of a triacylglycerol, emphasizing the glycerol backbone and possible fatty chain substituents.

Therefore, researchers usually use those semi-dry and dry oils (*e.g.*, soybean oil, linseed oil, and tung oil) for polymers. Since non-dry oils have more saturated chains, they are not aimed at polymerization processes. Another point is the seasonality, which can interfere with the IV of vegetable oils. Hence, to overcome these problems, the use of an oil formulation between a non-dry oil and dry oil to obtain the desired IV for polymerization is recommended, and these formulations can assist the industrial process and are verified by the titration of ^{1}H-NMR.

Polymers derived from triacylglycerol generally are flexible, but not so resistant to fatigue, have good adhesion on different surfaces, present a shiny colour and luminescence under UV-light (due to aggregation-induced emission effect – AIE), and are suitable for hydrolysis in an alkaline medium.[17,22–27] Moreover, when vegetable oils are used for biodiesel production, which is a renewable fuel, glycerol is generated as a by-product; however, the glycerol is a useful compound for polymer industries and has been used in adhesives, 3D-printing/photo-polymerizable monomers, and crosslinkers.[28–36] This fact shows how the triacylglycerol molecule has potential power for renewable polymeric materials and industrial applications.
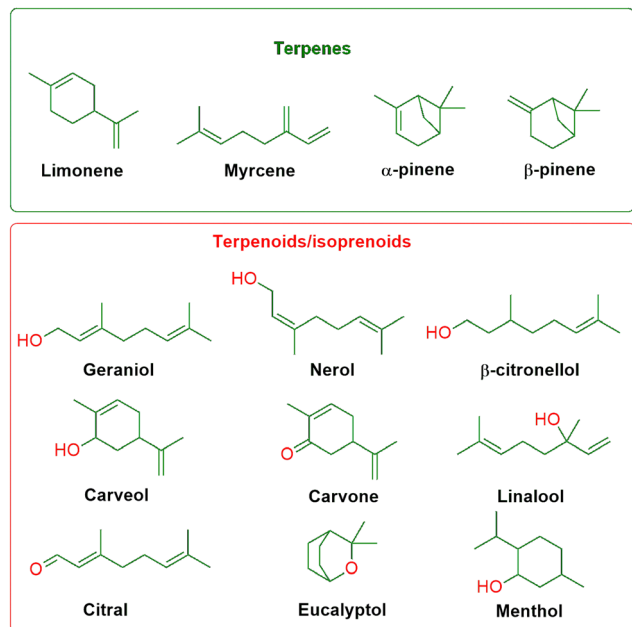
Fig. 2   Chemical structure of some terpenes and terpenoids.

Fig. 3   (a) Chemical structure of abietic acid and isomers, and (b) possible dimers.

Terpenes (essential oils) are also excellent chemical building blocks for renewable monomers and polymers. Terpenes are found in essential oils (odorous compounds widely used in perfumery, cosmetics and flavouring agent) from fruits, vegetables and flowers. Terpenes are hydrocarbons derived from isoprene and have the suffix "ene" due to alkene groups in their structure. Terpenes containing oxygen atoms and consequently their functional groups (alcohols, carbonyls, ethers, and epoxies) are known as terpenoids or isoprenoids.[18,37,38] In the terpene/terpenoid class, we can find, for instance, limonene, myrcene, geraniol, citral, linalool, β-citronellol, carveol, α-pinene, β-pinene, eucalyptol, nerol, menthol and carvone. All structures for each cited terpene compound are found in Fig. 2.

Limonene is very versatile, and our research group has initiated new photopolymerizable polymers from it. Limonene is generally extracted from orange peel, which is a waste in the juice industry. The limonene can be used not only as a chemical building block but also as a solvent and a varnish/adhesive remover.[39–41] In Brazil, we have the largest production of oranges in the entire world, producing a huge amount of peel wasting, and consequently, a resource for limonene.[42]

The limonene is a six-membered non-aromatic cycle compound with two substituents (methyl and isopropenyl) and two alkene groups. Some plants that present limonene also present carveol and carvone (limonene derivatives). Alkene groups in limonene are the principal part of the modification, which can be exploited to produce renewable monomers. Although terpenoids present versatility as monomers, some polymers made of them are powders or brittle films. This fact can be attributed to their structures with cycle members, which do not allow bond rotation and thus enhance rigidity. Furthermore, limonene polymerization is not easy to occur in its neat form; however, this characteristic can be improved by using a formulation
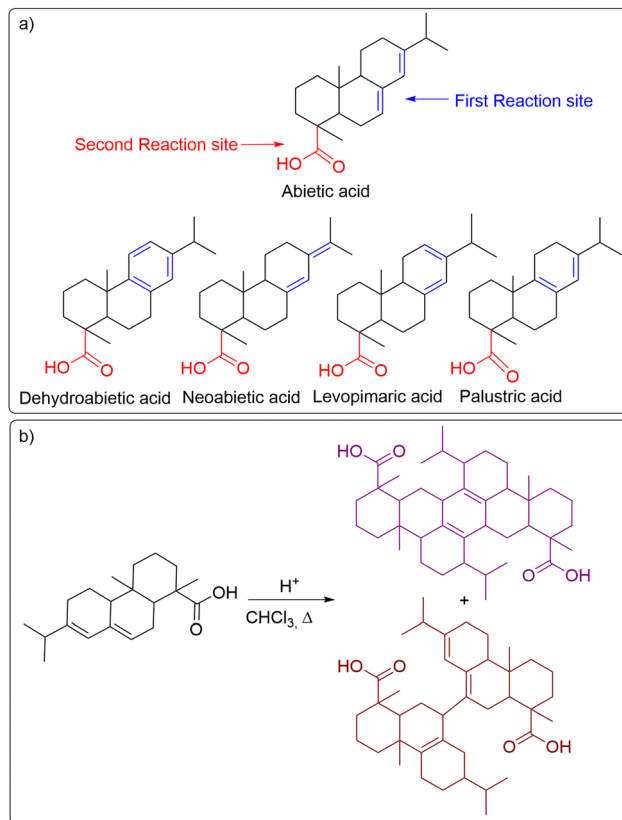
containing different monomers for copolymers and not forming only homopolymers.[43–45]

Abietic acid is the third renewable chemical building block that our group is exploring. This compound is also a terpenoid that is a residue from turpentine (essential oil containing the terpene α-pinene) distillation from coniferous trees (Pinus). This residue is a yellow resin called rosin and is constituted by abietic acid and other derivative isomers (*e.g.* dehydroabietic acid, neoabietic acid, levopimaric acid, and palustric acid). All structures for each cited rosin acid derivative are found in Fig. 3(a).[46,47]

Its structure contains three condensed six-membered rings (non-aromatic) with three substituents (two methyl and one isopropyl) and a conjugated diene, giving this compound a rigid structure. The diene is the second main group liable to modification, for instance, it can be epoxidized, and further acrylated or carbonated for new monomers, react with some dienophiles by pericyclic reactions, or react with other abietic acid structures under an acidic medium to synthesize a dimer derivative; two possible structures are displayed in Fig. 3(b).[48,49]

Abietic acid also contains a carboxylic acid in this structure that can be reacted with alcohols and amines to produce esters and amides, respectively. It also reacts with isocyanate to produce urethanes or with epoxides to form esters. The carboxylic acid is also able to be reacted with some inorganic salts to form metallic complexes. In our laboratory, these

reactions have been executed to form new monomers and catalysts (metallic complexes) for carbonation reactions.

The rosin resin can be applied as a varnishing/coating in wood surfaces, and polymeric materials synthesised by abietic acid are generally lustrous and rigid but do not present good mechanical resistance.

In addition, these lipids can be saponifiable (*i.e.* react with aqueous alkaline solution) or not, depending on their structures. Therefore, terpenes/terpenoids are classified as non-saponifiable lipids, whereas triacylglycerol and abietic acid can react easily with sodium or potassium hydroxide solutions. The triacylglycerol reacts with an alkaline solution by an ester hydrolyses process producing the acid salt and glycerol (alcohol), while abietic acid reacts with an alkaline solution by a neutralization reaction producing the salt and water.[50] Saponifiable lipids can form saponifiable polymeric materials that can be easily degraded in an alkaline environment assisting their biodegradability.[17,18]

The shared group in triacylglycerols, limonene and abietic acid is alkene, which is perfect for modification.[18] This group can react with elemental sulphur at a temperature above 170 °C to produce cross-linked polymers (vulcanization process)[51] or react with thiol compounds in the presence of a photoinitiator under UV-light to then undergo a thiol–ene reaction.[52–54]

Furthermore, these alkenes can react with maleic anhydride or itaconic anhydride by an Alder–Ene reaction, and the product is triacylglycerol, limonene containing anhydride. In the case of abietic acid, this anhydride derivative is formed by the Diels–Alder reaction (formation of a cyclic compound). These anhydride derivatives easily react with alcohols/epoxides and amines to synthesise polyesters and polyamines/polyimides, respectively.[17,23–25] Recently, we have demonstrated that the Alder–Ene reaction is well performed under microwave radiation, without using solvent catalysts, and with reduced time (12× less) and energy (6× less). Furthermore, the anhydride can be incorporated into renewable structures by a radical addition reaction.[55,56]

We have reported an easy methodology to transform the carbon double into epoxide groups using a greener Prilezhaev reaction, which occurs under mild conditions and uses hydrogen peroxide and acetic acid to form peracetic acid in the presence of a heterogeneous polymeric acid catalyst (Amberlite™ IR120). This methodology does not use organic solvents during the reaction and is entirely complete in 3 hours with a conversion of $\geq 99.9\%$ and without parallel reactions (opening of epoxide rings).[57,58] The epoxidation process in triacylglycerols also occurs using metallic oxides (*e.g.* TiO_2 and Nb_2O_5) in the presence of hydrogen peroxide and in the absence of an organic acid and solvents; however, for good conversion, the reaction should be maintained for 24 hours. At first glance, epoxidation by metallic oxides seems to be greener by not using organic solvents and generating less waste but it consumes more energy due to a higher reaction time.[59]

Epoxidized derivatives can be used as monomers to form polyesters, polyamines and polyethers by reacting with carboxylic acids, amines or alcohols, respectively. Furthermore, this derivative can be further reacted with acrylic or methacrylic acids to produce renewable photopolymerizable monomers that can be applied to 3D-printing,[60–62] or either react with CO_2 in the presence of metallic catalysts and ammonium salts (tetrabutyl ammonium bromide) to obtain five-membered ring cyclic carbonate monomers.[22] The cyclic carbonate is usually reacted with polyamines to synthesise poly-hydroxyurethanes, and this reaction is aligned with carbon dioxide utilization (CDU) methodology and presents an atom efficiency of 100%.[63,64] Moreover, the epoxidized monomer reacts with sodium azide in order to obtain organic azide, which is generally used in click chemistry reactions with an alkyne (a second monomer).[65,66]

The mentioned reactions are displayed in Fig. 4, using a triacylglycerol structure as a representative (containing only one oleic chain).

Using these renewable compounds is a gold way to a sustainable world, but this gold way is not so shiny yet. Although the production of bio-based polymers has been encouraged and
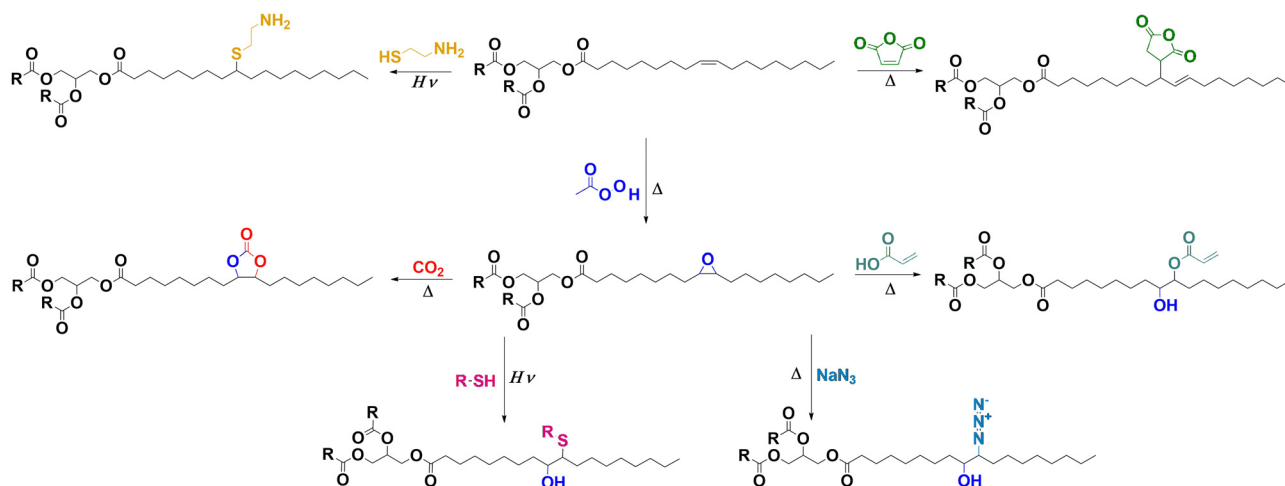

Fig. 4 Some possible modifications to the renewable compound structure (triacylglycerol only representing one oleic chain).

enhanced by 20% between 2022 and 2023, this estimate is around 10% up to the end of 2024.[11] Additionally, some challenges are present in this field and must be surmounted, for instance:[67,68]

I. Understanding better the relationship between renewable compounds and polymers' final properties.

II. Enhancing the reaction yield by respecting a greener methodology.

III. Enhancing the mechanical properties of renewable polymers, being similar to commercial polymers.

IV. Turning the process cheaper for industrial development and applications.

V. Avoiding biomass used for human food.

VI. Developing novel polymers respecting circular economy.

Renewable polymeric materials have been researched by groups from different countries such as those headered by Pescarmona,[69,70] Mija,[71,72] Sangermano,[73,74] Caillol,[75,76] Monticelli,[77,78] Avérous,[79,80] Song,[81,82] and Dove,[83,84] among others.

Although there is progress in the area, questions arise in this field: can the lipid be used in both photo and thermal polymerization? And what are the challenges involved?

Replying to these questions, the lipid compounds can be used for polymerization; however, previous modifications should occur to improve their reaction. In pristine form, they are low reactive and demand higher time or energy to produce polymers by a radical reaction. At first glance this can be a disadvantage, however, we as chemistries should overcome this little obstacle by developing new cleaner routes in order to obtain reactive molecules. After chemical modification, these compounds can present different solubilities or viscosities,

which can give drawbacks to efficient polymerization. Nevertheless, this question is easy to answer considering monomeric formulations and mid-temperature. Therefore, the present article has been written to assist the research and shed light on difficulties and advances in the renewable polymeric materials field. Therefore, an outline with recent articles has been selected to discuss the relationship between renewable materials and properties/applications.

2 Advances in materials

2.1 Lipid-biomass-based photoinitiators and monomers in the additive manufacturing

Among the polymerization processes, one of the most attractive is photopolymerization, since it is performed at room temperature, it does not demand solvent and generally achieves high conversions quickly, resulting in lower values of energy than the polymerization performed under the conventional thermal process. Therefore, the photopolymerization is in complete accordance with the 2nd (Atom Economy) and 6th (Design for Energy Efficiency) Principles of Green Chemistry.[85] In this method, the polymerization is triggered by exposing the monomeric mixture to the light. The type of these reactions depends on the reactive sites present in the system: monomer structure and the initiating species, which are generated after the light excitation of the photoinitiator (PI) or photoinitiator system (PIS), in which other components can be presented beside the PI. As a result, large types of reactions can be performed (Fig. 5(a)).[86–89]

Our group has been working mainly with the radical photopolymerization, in which the photoinitiation process can be
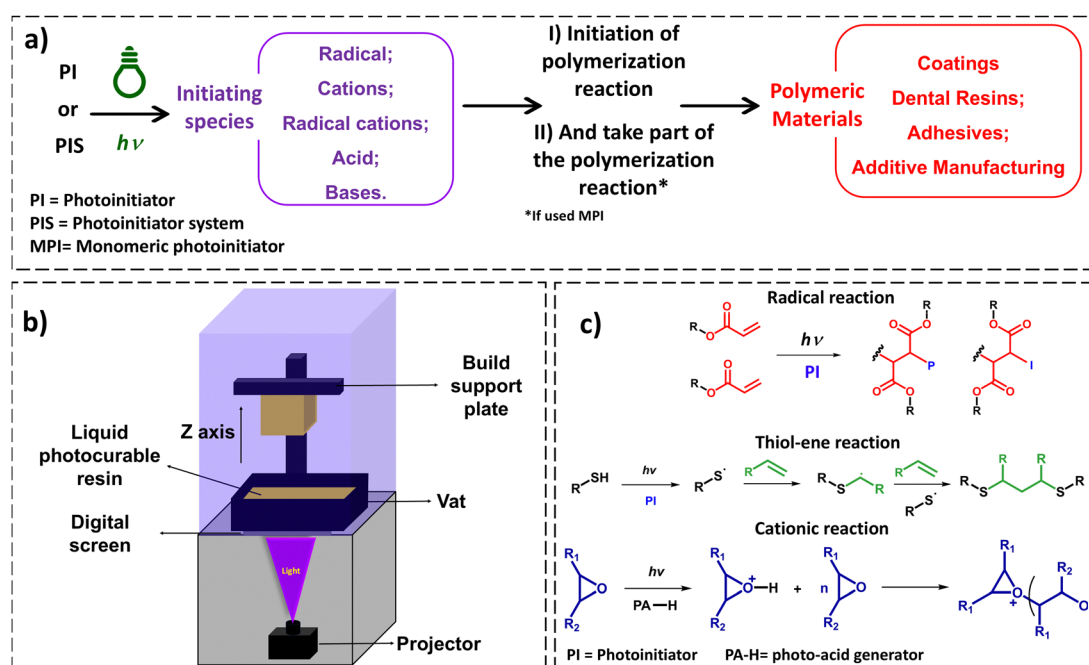

Fig. 5 (a) Simplified scheme of generation of initiating species and how they can undergo *n* photopolymerization, (b) schematic of the DLP printing system and (c) scheme of some reactions that can be explored in DLP 3D printing.

distinguished in type I and type II, depending on how the radical is generated. When the molecule is excited by the light to the triplet state and then results in homolytic cleavage providing a radical, the photoinitiation is a type I and is a PI. In type II, the radical generation occurs after hydrogen abstraction, therefore involving more than one molecule and being considered as a PIS. The molecule excited by the light (called initiator) achieves the triplet state and then abstracts the hydrogen from the other molecule (called co-initiator), resulting then in the radical generation. As a result, type I initiation is usually faster than type II. However, most of the type I compounds absorb in the ultraviolet region, while the initiators in type II can absorb in the visible region of electromagnetic spectrum. Hence, the type II photoinitiator allows the use of a wide range of molecules already present in nature, or those derived from them, and enables the use of less energetic light sources than UV, such as those in the visible and near-infrared regions.[87–89]

Based on this, the lipid molecules are potential candidates for use as initiators in type II photopolymerization. We have shown the use of abietic acid (one of the abietanes present in rosin gum) in a PIS, in which it was the photoinitiator and ethyl-4-(dimethylamino)benzoate (EDB) was the co-initiator in a renewable monomeric mixture containing 0.5% of each of them.[60] It was verified that after 300 s, the PIS under UV and blue lights achieved monomeric conversion (MC%) into polymers equal to 85% and 41%, respectively, implying that other tests can be performed aiming to improve lipid molecules as photoinitiators.

Although tertiary amines are considered good co-initiators in type II photopolymerization from the point of view of chemical reactivity due to the facility in which its hydrogen can be abstracted, most of them can present health hazards, increasing the risks during handling and also incorporating it into the polymer structure.[90–92] Aiming to improve this, our group has tested glycerol instead and using the camphorquinone (CQ, absorption between 400–500 nm) as the initiator in four different dimethacrylate systems: diurethane dimethacrylate (UDMA), triethylene glycol dimethacrylate (TEGDMA), bisphenol a ethoxylate (bis-EMA), and bisphenol a glycerolate (bis-GMA).[28] Although glycerol is an alcohol (soluble in water), it is a by-product from the triglyceride used in biodiesel production, and therefore it is important to propose an application for it. It was verified that after 300 s of exposition under blue light (430–490 nm), the CQ/glycerol did not affect the MC% of systems with UDMA (35% of glycerol in the monomeric mixture) and bis-GMA (16% of glycerol in the monomeric mixture) significantly compared to the respective systems using CQ/EDB. Our group has also tested the use of curcumin (instead of CQ) in systems with UDMA/glycerol with and without EDB (a fully-bio-based PIS) and verified that independent of the amount of glycerol, the achieved MC% was very similar in systems with and without EDB.[29] Throughout the photopolymerization process, the glycerol can result in a initiating species starting the polymerization or this initiating species can dehydrate, resulting in an alkene structure, which can also undergo polymerization.[28]

Therefore, these results show the potential use of PIS with a high bio-based content or fully bio-based in photopolymerization. This can be enhanced by testing these PIS systems using renewable monomers such as those derived from triglycerides and terpenes.

Further advance in the photopolymerization that has been arising is the development and utilization of monomeric photoinitiators (MPIs) and polymeric photoinitiators (PPIs), in which the initiating species are generated by light, due to the chromophore groups present in their structures. For MPI, besides starting the polymerization, these groups can also undergo polymerization (Fig. 5(a)). Consequently, it is possible to decrease the amount of external PI or PIS, which generally are smaller molecules that can migrate through the final polymeric material. As a result, four benefits are observed when the MPI or PPI is used in photopolymerization.[89,93,94]

I. A decrease in polymer toxicity.

II. Decreasing or avoiding the problem of PI (or PIS) non-miscibility in the monomeric mixture.

III. No colour changing of polymeric material with time.

IV. Odours reducing from the degradation of residual PI or PIS.

The acrylated vegetable oil can act as MPI, and we have recently shown that the acrylated macaw vegetable oil after 300 s of light exposure achieved MC% = 75% (UV-light, 370 nm) and MC% = 46% (blue light, 430–490 nm). However, the polymerization rates were low when compared to the CQ/EDB systems (Type II), which achieved the highest rates only in 10 s and stabilized the MC% higher than 90% after 50 seconds in both irradiation sources.[60] Similar results were observed when the photopolymerization was evaluated with passion fruit acrylated vegetable oil; however, in the presence of a PI (TPO), the MC% stabilized in the first 10 s under UV-light.[61] In both studies, it was demonstrated that the acrylated vegetable oils can act as MPI.

Therefore, the finding of lipid molecules for photoinitiators that present high conversions is still a challenge. In addition, we have already pointed out that maleinized vegetable oils present the aggregation-induced emission (AIE) effect, demonstrating its excitation under UV-light.[23] Thus, monomers and polymers with the AIE effect are promising compounds for photopolymerization reactions.

Overcoming these challenges related to the utilization of PI, PIS, MPI and PPI could enhance the application of these systems. They can be combined with lipid-based monomers, resulting in a high bio-based content or fully-bio-based systems with different properties, such as high hydrophobicity, since the main characteristic of lipids is their non-solubilization in water.

Here, we will focus on the photopolymerization of lipids for use in additive manufacturing (AM), also known as 3D printing, which has emerged as a new and potential tool for producing materials with complex architectures.

In the AM, the desired object can be initially designed by using specific software, and then the data must be converted in a correct format (e.g. STL format) and transferred to the printer,

which starts to manufacture the object layer by layer along the Z-axis with high accuracy, resolution, and design complexity. Due to these features, AM processes are extensively employed in several fields such as building, aerospace, automotive, biomedical, and others.[95]

Among the AM field, digital light processing (DLP) presented in Fig. 5(b) is an important component of vat-polymerization techniques. In this technique, photocurable liquid resins are used to produce polymeric materials when exposed to the light projected by a light source, such as a digital micromirror device (DMD). Furthermore, the DLP technique offers advantages compared with other AM techniques such as short printing preparation time, energy saving, printing resolution and fidelity to the designed object. Therefore, in order to reach the maximum DLP printing efficiency, some important parameters must be considered:

I. The resin viscosity should be adequate for printing.

II. Time of photocuring of each layer.

III. Resin stability should disable the boiling process or extreme exothermic reactions.

IV. Photoinitiators should be selected to absorb the correct light wavelength.

Photopolymerization reactions are the base of the DLP (and other processes that use light to produce polymers), thus during the printing process, radical species or cations are generated by the light after the photoinitiator cleavage (in the case of radical species) or photo-acid generation (in the case of cation species).[96] Therefore, during the development of photocurable resins, the wavelength that the photoinitiator absorbs and the functional groups which can promote the crosslinking during the propagation and termination steps must be carefully selected. Some functional groups such as acrylics, epoxides, and thiols (displayed in Fig. 5(c)) are extensively used in the formulations of resins for DLP printing due to their high reactivity and interesting properties presented by the polymers generated.[97] Based on the structural characteristics of non-renewable resins/monomers, a new and bio-based class of photocurable and renewable resins has been developed in order to substitute completely or increase the bio-based content of fossil-based 3D printing resins/monomers.

The production of new bio-based resins/monomers must aim for the main features of these fossil-based products already developed as much as possible to be considered for the AM fields. At the same time, it is expected that the thermal and mechanical properties of the final polymers are similar or better than those originating from non-renewable resources. In this context, lipid biomasses such as triglycerides, terpenes, and terpenoids (and derived) appear as potential renewable sources for the development of fully bio-based or high-bio-based-content photocurable monomers/resins with features that fit adequately for AM.

Recently, we have reported the acrylation of epoxidized macaw vegetable oil (EMWO) using acrylic acid (a cheap acrylic monomer that in its pure form does not present stability to be photopolymerized). According to the ^{1}H-NMR analysis, the percentage of acrylic groups attached to the triglyceride chain

in this reaction was 66.6. The acrylated macaw oil (AMVO) was then photopolymerized with different type II photoinitiators under UV (370 nm) and blue (430–490 nm) light, and the monomer conversions (MC%) and the polymerization rates (R_p) were studied by mid-infrared spectroscopy analysis (MIR). Therefore, the acrylated macaw palm oil with camphorquinone (initiator) and ethyl-4-(dimethylamino)benzoate (EDB) presented the highest MC% and R_p values under both irradiation sources after 10 seconds of exposition. After 50 seconds under light exposition, both monomeric systems presented MC% values higher than 90%. Furthermore, both materials obtained were characterized and presented thermal and mechanical properties comparable to those produced from fossil sources. Thus, this renewable monomer could be applied for 3D printing, and act as a potential substitute for acrylated soybean oil (an edible oil) in formulations containing other classical acrylic monomers such as UDMA, TEGDMA or HEMA.[60] However, the formulations based on these non-renewable acrylic monomers must be optimized in order to increase the number of bio-based monomers and reduce the fossil-derived components in the resins.

In our recent study, passion fruit vegetable oil, which is extracted from the passion fruit seed and considered non-edible and a by-product of the juice industry, was epoxidized and acrylated achieving 72.6% of acrylic groups incorporated into the triglyceride chain. The MC% and R_p values of a monomeric mixture containing acrylated passion fruit oil (APFO) and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) – type I photoinitiator-were evaluated when exposed to UV irradiation (365 nm). Then, the monomeric system reached a conversion of 86% and a polymerization rate of 89.3 s^{-1} as in 10 s (Fig. 6(a) and (b)). Moreover, the viscosity of APFO is 1612 ± 1 mPa s. which is in accordance with expected viscosity values for 3D printing resins (0.1–10 Pa s). The adequate viscosity allows unreacted resin to refill the vacant spaces in the vat after the rise of the built support plate and to flow out of the object avoiding the decrease in the printing resolution. Thus, APFO was successfully tested as a matrix resin (without any other acrylic monomer in its formulation) in a DLP printer using different TPO amounts (0.5 wt%, 1.0 wt%, and 2.0 wt%). The polymeric materials obtained (the cubes presented in Fig. 6(c)) were then characterized and no substantial difference in their thermal and chemical (MC% values) properties was observed (Fig. 6(d) and (e)). Furthermore, although the MC% values reach around 65% after printing, materials obtained present regular and homogeneous surfaces (as shown in Fig. 6(f) and (g)) and physical–chemical properties comparable to commercial polymers produced from non-renewable resources such as poly(n-butyl methacrylate).[61] Meanwhile, the monomer conversion (fast curing time) is an important parameter in the 3D printing field that can be improved whenever possible, and high values must be searched in order to enhance the final properties of the 3D printed materials.

Epoxidized vegetable oil also offers a high potential for use in 3D printing with a photocuring system, by radical or cationic reactions. Based on these possibilities, epoxidized Baru
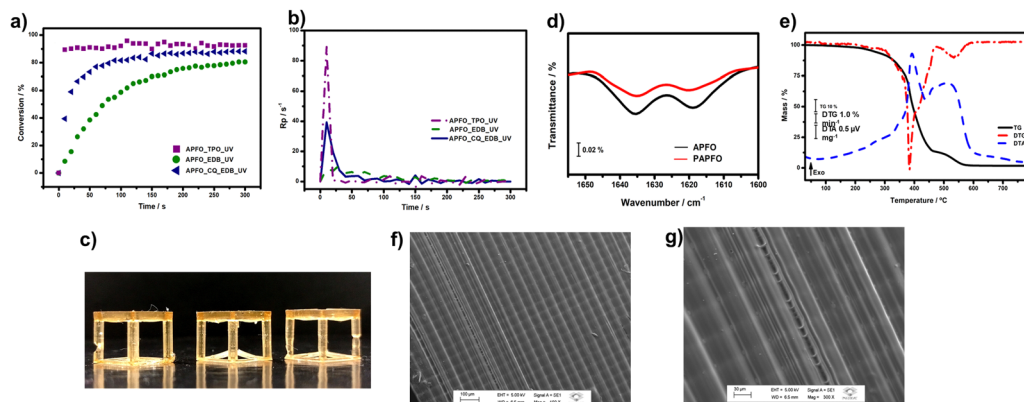
Fig. 6 (a) Monomer conversion and (b) polymerization rate of APFO under UV-light (365 nm). (c) Three-dimensional polymeric materials obtained by 3D printing using APFO with different quantities of photoinitiators. (d) MIR spectra comparing the C=C bands of APFO and the 3D printed polymer in the presence of 0.5 wt% of TPO and (e) simultaneous thermogravimetry-differential thermal analysis curves and surface micrographs at different magnifications: (f) 100× and (g) 300° of the same polymer. Adapted from ref. 61, copyright 2024 Springer Nature.

oil (EBO) was reacted with fumaric acid in the presence of tetrabutylammonium bromide (TBABr) as a catalyst. The product obtained was then photopolymerized under UV irradiation (370 nm) in the presence of type II photoinitiator. This system showed a low MC% value (29.4%) after 300 s, which is associated with the steric hindrance of internal double bonds that decrease the radical formation and consequently decrease the monomer reactivity. To overcome this situation, the monomer reactivity was increased by formulating a monomeric mixture with the addition of classical methacrylic monomers such as UDMA and TEGDMA, which present terminal double bonds. Subsequently, the best MC% value observed was related to the system containing UDMA (98.4%) under the same conditions (UV irradiation for 300 seconds). The final polymers were characterized and interesting properties such as thermal stability (up to 200.0 °C), solvent resistance, luminescence, flexibility, and dye adsorption were observed.[98] Although these monomeric mixtures reach high monomer conversions after 300 seconds under light exposition, this time is considered high for 3D printing processes; thus, some parameters such as the viscosity of the monomeric system can be adjusted by adding reactive diluents that can increase the chain mobility and consequently increasing the monomer reactivity and decreasing the curing times.

Cationic polymerization can also be utilized in the formulation of renewable epoxy resins for 3D printing as shown recently by Bergoglio and coworkers,[99] which explored the concept of dual-vat DLP 3D printing to obtain multi-materials employing epoxidized linseed oil (ELO) and vanillin alcohol diglycidyl ether (DGEVA) in the formulation of bio-based resins containing a cationic photoinitiator. Multi-material printing allows for the development of integrated materials with different properties and can be processed in a dual-vat system containing two different resins. This system is based on a moving platform that switches the vats along the X axis when the desired thickness of the material printed is reached. It allows the same object to be printed with the characteristics of two different resins.

According to the results reported, a synergic behavior in the multi-materials was observed by the shifting in the glass transition to higher temperatures and an enhancement in the mechanical performance. Furthermore, the shape-memory property of the multilayer polymers was investigated, and the ability to change the shape under an external stimulus (temperature) was observed, making these 3D-printed materials suitable for industrial applications. This new multi-material 3D printing approach using bio-based epoxy resins brings considerable opportunities to create or improve the properties of renewable materials. Thus, the polymer field will benefit from the use of other lipid biomass-derived precursors such as those presented in this work.

Terpenes and terpenoids are a versatile lipid biomass class that can be potentially used in 3D printing processes due to their structure characteristics. The presence of double bonds in the chains of these compounds allows the use of thiol–ene reactions to produce polymers by photoinitiation, and consequently, their use in 3D printing as bio-based resins. Weems and collaborators[100] have recently employed different terpenes and terpenoids (limonene, terpinene, linalool, nerol, and geraniol), a four-arm thiol (pentaerythritol tetrakis(3-mercaptopropionate) – PETMP), and a type I photoinitiator (Irgacure 819) in the formulation of photocurable resins. Based on a ^{1}H-NMR and photoreology screening, they suggested that limonene and linalool-based resins are suitable for stereolithographic 3D printing due to the high reactivity (the crosslinking was reached after 5 seconds under 3D printing conditions) for thiol–ene addition while geraniol, nerol, and terpinene can be used as additives for shrinking reduction. One interesting approach carried out to overcome the low viscosity of some monomers was the employment of the thiol–ene reaction to produce prepolymers with higher viscosities. After the 3D printing, they concluded that linalool was the most effective monomer for printing being able to produce porous Hart's cubes (displayed in Fig. 7(b)). Despite the high reactivity of limonene, the 3D printability of the monomer (without its respective pre-polymer) is
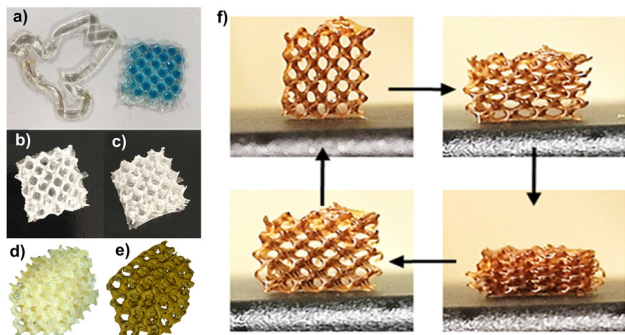
Fig. 7 (a) Examples of pseudo-3D-printed materials from limonene monomers (without its pre-polymer). The respective Hart's cubes from (b) linalool and (c) limonene pre-polymer resins. Adapted from ref. 100, copyright 2019, Royal Society of Chemistry. Optical microscopy (d) and reassembled microCT (e) images of linalool-derived scaffolds produced by DLP 3D printing and, (f) 4D behavior of the linalool-derived thermoset, including the representative 4D behavior of a printed scaffold showing original and secondary shapes as well as intermediate steps. Adapted from ref. 101, Copyright 2021, American Chemical Society.

limited and pseudo-3D structures (with non-complexity in the z-axis) could be printed as shown in Fig. 7(a). However, the limonene-derived resin printability was improved by printing its respective pre-polymer, and a similar porous structure obtained using linalool was achieved (Fig. 7(c)). This work offers a valuable perspective on the challenges and use of terpenes in AM and how to overcome some important limiting factors for the formulation of bio-based resins. Meanwhile, with the aim of expanding the applicability of terpenes in 3D printing, investigating alternative thiols, photoinitiator systems, and blends can help address current limitations and improve their suitability for this technology.

In another work, linalool was utilized as a base for the development of photocurable resins after reaction with allyl bromide and three isocyanates (diisocyanate, isophorone diisocyanate, and methylene diphenyl diisocyanate). This innovative approach allowed the formulation of greener resins to be applied in DLP 3D printing to produce scaffolds by thiol–ene reactions. Although the formulated resins presented different photocrosslinking times with no inhibitory effects during the photocuring, the polymers obtained presented high spatial resolution and tunable physical properties, and displayed four-dimensional (4D) shape-memory behaviors, as shown in Fig. 7(d)–(f). For a better understanding, 4D printing combines 3D printing and smart material behaviors (stimuli-responsive) and produces objects that are space-time dependent and can change their shape during a certain time when exposed to external stimuli.[102] Furthermore, the thermosets from the monomers with urethane derivatives (those provided by the isocyanate structures) showed enhanced thermomechanical and physical properties (including shape memory or 4D behavior).[101] Extending beyond 3D printable polymer production, the thiol–ene reaction in conjunction with a greener monomer development can allow the development of smart materials. However, a high bioderived (or bio-based) content

must be searched and compounds that can substitute isocyanates are a potential solution for it; meanwhile, finding suitable candidates is still a challenge to overcome.

Based on our achievements and the recent advances reported in the literature, it is clear that the lipid biomass presents a high potential to contribute to AM development. The use of these renewable resources has generated a class of materials with greener and more sustainable characteristics. In addition, the 3D printed polymers have presented interesting properties for industrial and technological fields. However, there are some important challenges reported above to overcome. Based on this, our group has been working to extend the use of these biomass-derived polymers incorporating the photopolymerization reactions discussed in this work and the novel approaches reported for the other scientists. Thus, we are making important advances that will overcome the main challenges and contribute to the development of photocurable resins for DLP 3D printing while the materials obtained will contribute significantly to the circular economy due to properties such as self-healing, recyclability, and smart behaviour.

2.2 Lipid biomass-based vitrimers

Thermoplastics and thermosets represent the two primary categories of plastics.[103–106] Thermoplastics can be melted and reprocessed at high temperatures, whereas thermosets cannot be easily reprocessed after their initial formation.[103–107] Additionally, thermosets generally offer greater mechanical strength, thermal stability, and solvent resistance than thermoplastics.[103–107]

These distinctions are assigned to their differing structures, which directly influence their properties. Thermoplastics are made up of linear polymer chains held together primarily by intermolecular forces.[104–108] In contrast, thermosets are composed of three-dimensional (3D) networks with covalent cross-links. These cross-links are not easily broken, even at elevated temperatures, which often lead to the decomposition of the material before it melts. This characteristic results in the low capability of thermoset reprocessing.[103–108]

In this way, the development of recyclable polymers is a major research focus today, driven by environmental concerns and issues related to non-renewability, which had attracted the attention of researchers globally.[104–109]

Therefore, the current challenge is to develop high-performance, recyclable polymeric materials that combine the advantages of both thermoplastics and thermosets. These efforts have led to the development of a new class of polymers known as Covalent Adaptable Networks (CANs).[18,103–105]

CANs feature covalent cross-links similar to those in thermosets; however, they become reversibly dynamic when exposed to stimuli such as heat, pressure, light, or changes in pH. In the absence of these stimuli, CANs maintain thermoset-like properties such as enhanced strength and durability.

In contrast to traditional thermosets, which are generally non-recyclable, CANs are potentially recyclable due to the dynamic nature of their cross-links.[103,105,109–111] Furthermore, CANs can exhibit a range of desirable properties, such as
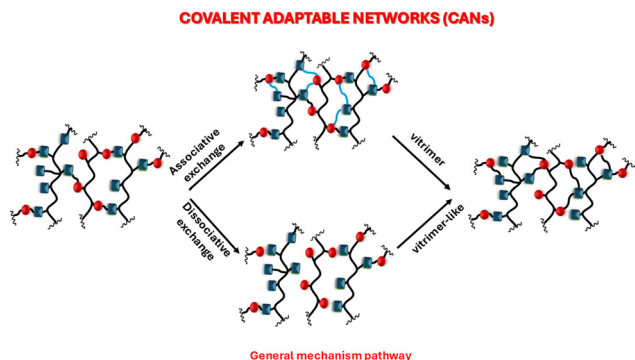
Fig. 8 General mechanism of associative and dissociative bond exchange.

flexibility, shape memory, and self-healing capabilities. These materials not only reduce the consumption of non-renewable resources but also offer benefits such as recyclability, weldability, reconfigurability, ease of chemical degradation, and biocompatibility.[103,105,109–111]

CANs are typically categorized into two types based on their exchange mechanisms: dissociative and associative (Fig. 8). However, classifying them only by the type of chemical bonds can be misleading, as bond exchange may occur through either mechanism depending on the specific conditions.[18,103–105,108]

In a dissociative mechanism, dynamic bond cleavage occurs, followed by the formation of new covalent bonds. As a result, there is a decrease in crosslinking density, which facilitates stress relaxation and flow.[18,103–105,108] However, the associative mechanism maintains a constant crosslink density. Bond breaking occurs only when new bonds are formed, leading to a permanent degree of connectivity.[18,103–105,108]

Associative CANs exhibit a unique linear viscoelastic behaviour, comparable to that observed in inorganic materials such as vitreous silica.[103,105–112] This characteristic led Leibler and coworkers to name this dynamic polymer material "vitrimer" in 2011.[112]

This behaviour can be attributed to the nature of their dynamic cross-links, which remain nearly constant regardless of external stimuli. Consequently, the viscosity-temperature relationship of these materials follows an Arrhenius-like dependence.[84,103,105–112]

Vitrimers behave as viscoelastic liquids, exhibiting stress relaxation at high temperatures, which allow these materials to flow. Upon cooling, the kinetics of the exchange reactions slow down, and the structure becomes fixed, resulting in a permanent topology similar to that of a solid and behaving like a thermosetting polymer.[103,104,112]

Moreover, dissociative CANs may be classified as vitrimers; however, they are temperature-dependent, as the rate of new bond formation must exceed the rate of bond cleavage.[18,103,104,112] Two main primary thermal events can be observed in vitrimers. The first one is related to a glass transition temperature (T_g), typically occurring at subambient temperatures, at which polymer chain segmental movement transitions the material from a rigid state to a moldable state, whereas the second event corresponds to the topology-freezing transition temperature (T_v). Above T_v, the polymer shifts from a viscoelastic solid to a viscoelastic liquid, promoting rapid bond exchange and enabling structural recovery.[18,103–108]

Both thermal events, T_g and T_v, originated from different interactions; therefore, their values are independent. Typically, T_g is lower than T_v, resulting in the vitrimer transition from a rigid solid below T_g, to an elastic solid between T_g and T_v, and then, finally to a viscoelastic liquid above T_v. In some cases, T_v may be lower than T_g, which suggests that no extensive segmental motion occurs, turning exchange reactions impossible. Consequently, the network can be considered fixed in the polymeric material.[18,105–108]

Several chemical reactions including transesterification, imine bond exchange, Diels–Alder reactions, disulfide exchange, transamination, and coordination reactions can afford bond exchange in vitrimers. When considering CANs and vitrimers, the chemical and reactivity aspects of the material are critical. The rates of bond formation and cleavage at a given temperature significantly influence the balance between bound and unbound states, thereby affecting material properties.[18,103–111,113]

Furthermore, the architecture and dynamic characteristics of the decrosslinked states contribute to the rheological profile. Thus, these materials have proven to be an excellent case study for investigating the relationship between chemical reactivity and the dynamic properties of polymeric materials.

As reported before, lipid biomass represents a promising resource for new vitrimers, reducing the dependence on petroleum-based materials.

Vegetable oil (VO) versatility allows several chemical modifications. The alkenes in VO can be converted into epoxide groups by using oxidizing agents such as hydrogen peroxide, peracids, or O_2 in the presence of catalysts. Then, the epoxidized vegetable oil (EVO) can react with several groups, for example, cyclic anhydrides or diacids to form cross-linked structures containing free hydroxyl (OH) groups. This enables the polymer to be reshaped or welded at the topology-freezing transition temperature (T_v) via transesterification reactions between the ester and free OH groups.[18,109,114–116]

One of our group studies reported the use of Macaw and Baru vegetable oils, which were first epoxidized and subsequently carbonated (Fig. 9(a)). By varying the loading of the aluminium (salen) complex catalyst, along with the reaction time, CO_2 pressure, and temperature, conversions of 100% were achieved.[22]

Both carbonated oils were reacted with amines such as 1,6-diaminohexane, lysine, and 4,4′-methylenebis (cyclohexylamine) to produce weldable poly-hydroxyurethanes. It was observed that polymers synthesized from lysine exhibited more selective reactions and higher cross-linked structures, resulting in fewer side reactions involving glyceride groups.[22]

Thermal analysis revealed that the synthesized polymers are thermally stable above 200 °C. Differential Scanning Calorimetry (DSC) analysis indicated two main thermal events related to T_g and T_v, which as evaluated, were reversible. Moreover, these polymers could be reshaped and healed into different forms when exposed to red light at 660 nm (Fig. 9(b)).[22]
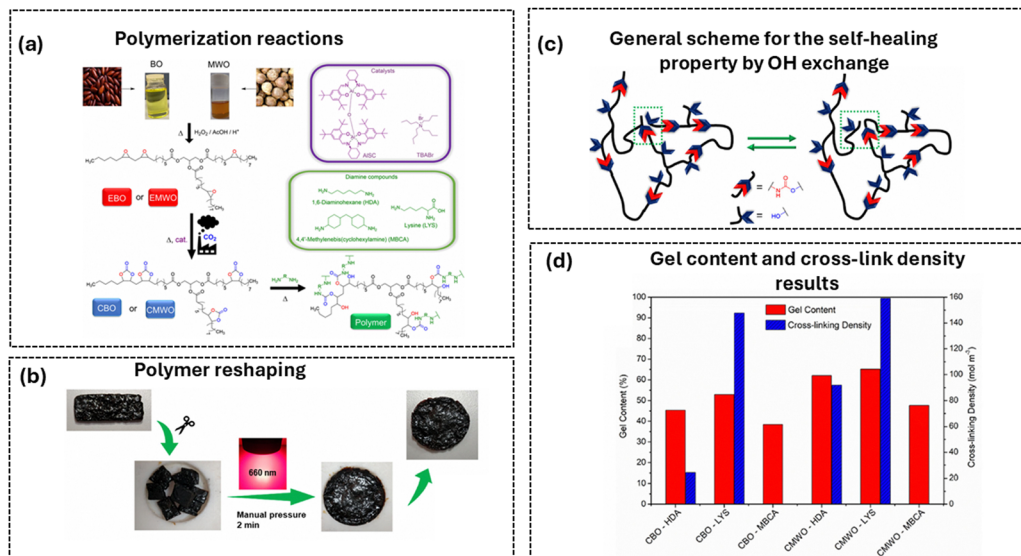
Fig. 9 (a) Polymerization reaction scheme, (b) polymer reshaping under 660 nm light, (c) general scheme of bonding exchange, and (d) gel content and crosslinking density results. Adapted from ref. 22, copyright 2022, Wiley.

As illustrated in Fig. 9(c), bond exchange was achieved *via* a transcarbomoylation reaction evolving urethane and OH groups from the polymer structure. The polymer containing lysine demonstrated a 100% Gel Content, indicating a complete cure and a fully cross-linked structure (Fig. 9(d)).[22]

Recently, Thakur and colleagues reported vitrimers with reversible cross-links derived from epoxidized methacrylated castor oil, employing itaconic acid as a curing agent. The resulting material demonstrated shape memory and self-healing properties, attributed to its ability to undergo transesterification exchange. Notably, the material showed a loss of tensile strength only after three reprocessing cycles, primarily due to the potential for oxidation or other undesired side reactions during the hot-pressing processes.[117]

The preparation of thermosets based on epoxidized vegetable oils (EVOs) has attracted considerable attention in recent years. However, most of these materials cannot be recycled once they become cross-linked.[18,22,109,114]

In 2020, Mija and colleagues reported for the first time the development of epoxy thermosetting resins like vitrimers, which incorporate dynamic disulfide covalent bonds. These resins were synthesized by copolymerizing twelve EVOs with 2,2'-dithiodibenzoic acid as the hardener.[114]

This study demonstrates the three key properties of 3R: reprocessability, repairability, and recyclability.[83,103,114] The researchers observed that the epoxy content in the EVOs significantly influences the final thermo-mechanical properties of the recycled material, whereas in this case, those with a lower epoxy content facilitate reprocessing. Additionally, the disulfide exchange and transesterification reactions ensure the shape memory of these materials.[114]

Since epoxy resins are extensively used in various critical industrial applications, including coatings, adhesives, composite matrices, and electronic components, these findings are of considerable importance. They not only have significant sustainability implications but also offer substantial economic benefits.[114]

Another study introduced a bio-based epoxy vitrimer synthesized by curing epoxy soybean oil with fumaropimaric acid (FPA), a rosin derivative. The incorporation of FPA enhanced the glass transition temperature of the ESO-based-vitrimer, exceeding room temperature.[118] FPA was used as a curing agent, significantly improving the mechanical properties of the ESO-based vitrimer. Additionally, the vitrimer material demonstrated self-healing capabilities, triple-shape memory, and reprocessing abilities due to the dynamic transesterification of covalent bond exchanges.[118]

Our research group has also contributed a study on new renewable disulfide polyesters that were successfully synthesized by heating the mixture and avoiding the use of solvents or catalysts (Fig. 10(a)).[24]

Maleinized grape-seed oil (MGSO) was able to react with nucleophiles such as amines or alcohols, resulting in highly cross-linked polyamides, polyimides, and polyesters. The results demonstrated the successful production of biomass-renewable polyesters with enhanced properties such as luminescent, flexible and shape memory (Fig. 10(b)).[24]

Moreover, it was observed that an increase in disulfide content led to a decrease in thermal stability and accelerated degradation, as confirmed by thermogravimetric analysis.

Furthermore, these materials exhibited greater resistance to elastic deformation, showing a higher Young's modulus (Fig. 10(c) and (d)). These thermal properties can be attributed to the crosslinking density, which gets reduced with the increase in disulfide content.[24]

Marco Sangermano, Matteo Bergoglio, and Sandra Schög published a review in 2023, discussing the scientific strategies reported in the literature for developing bio-based epoxy
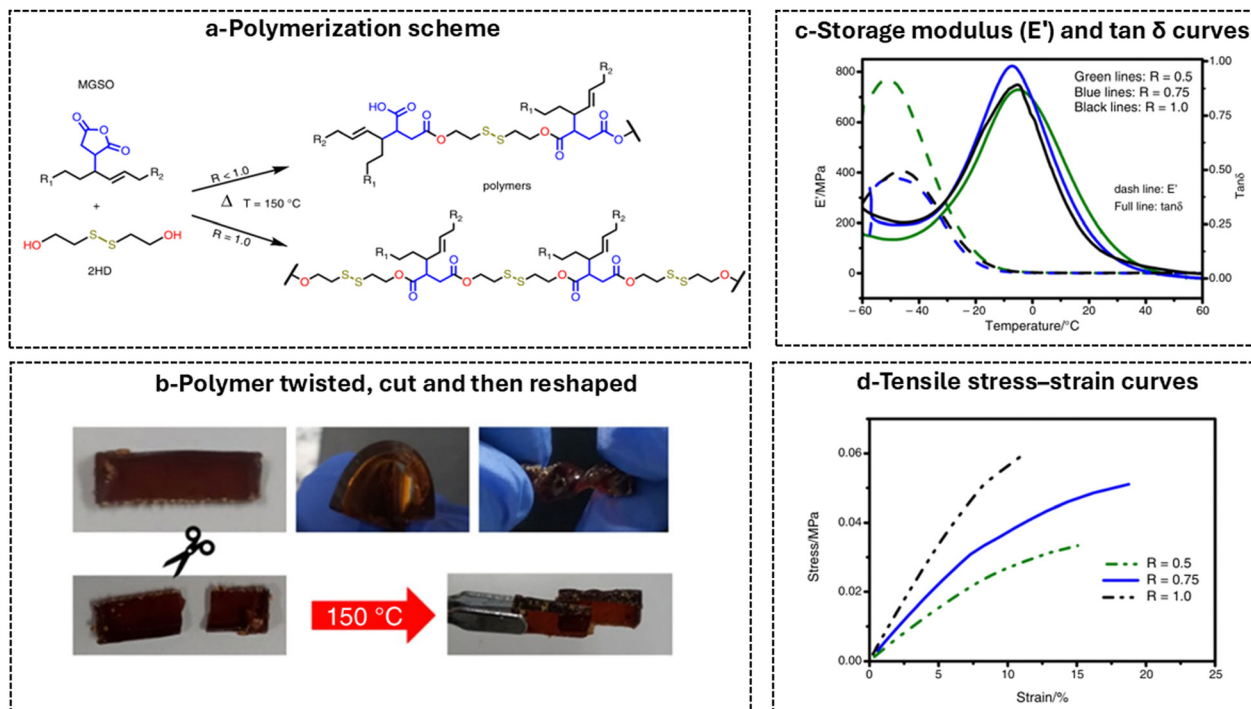
Fig. 10 (a) Polymerization reaction scheme, (b) polymer cut and reshaping under heating, (c) storage modulus (E') and δ curves, and (d) tensile−stress curves. Adapted from ref. 24, copyright 2024, Springer.

vitrimers extending beyond vegetable oils. The authors highlighted the use of terpenes, lignin, cellulose, and vanillin, among others, as bio-based building blocks for epoxy thermosets, showing them as alternatives to bisphenol-A-based formulations.[109]

In this regard, Federica Zaccheria and coauthors published a study on free thermosetting resins prepared from vegetable oils including soybean, hempseed, and linseed oils, by mixing and using terpenic comonomers such as limonene and α-myrcene.[119] The bio-based thermosets avoided styrene, a traditional fossil-based diluent. The authors observed that resins containing α-myrcene exhibited the best mechanical resistance, regardless of the oil used.

Moreover, the presence of pinene resulted in the poorest performance, while limonene contributed to intermediate properties. In sum, these results indicated that the multiple double bonds in myrcene, which possess a higher reactivity, promote more effective copolymerization and crosslinking.[119]

These data show how different renewable materials can be applied to enhance or change thermal, mechanical, luminescent, shape-memory properties, and so on.

An interesting work focused on how the *cis/trans* stoichiometry influences the thermosetting properties of resins derived from *R*-limonene. This study, conducted by Louisy, Olivero, Michelet, and Mija, explored the use of limonene as a bio-based thermoset precursor. The authors separated *cis* and *trans* limonene epoxides and synthesized limonene dioxide named S-LDO and R-LDO.[120]

Their primary achievement was the successful obtention of a fully-bio-based thermoset from *cis*-LDO monomers, which were

copolymerized with glutaric anhydride in the presence of imidazole. Moreover, the thermosets derived from *cis*-LDO exhibited superior properties compared to those made from a mixture of LDO isomers. The mechanical results indicated that *cis*-LDO thermosets are more rigid, demonstrating a higher Young's modulus and lower strain at break.[120]

Although the research group has not discussed possible self-healing and shape-memory properties from these materials in this paper, this topic is highly relevant and requires attention in the design and characterization of new smart/self-healing materials.

Vitrimers have evolved from scientific curiosity to a wide range of applications in society. Their use in tissue engineering is notable. For instance, self-healing surgical implants can act as smart materials, capable of autonomously repairing minor damages within the body, thus reducing the need for additional surgeries.[103,121]

In civil engineering, these materials can be utilized as self-repairing concrete. This innovative application allows the concrete to autonomously heal cracks, which addresses a common and costly issue in construction. Consequently, this can lead to reduced maintenance costs and lower overall expenses, but contributes to a decrease in carbon dioxide emissions associated with concrete production.[122,123]

Vitrimers are promising in the electronics sector, and they can be used as reprocessable materials, and as self-repairing electronic circuits. It will avoid electronic waste, which is becoming a major global issue.[124–126]

Their applications also extend to 3D printing, allowing for innovative reshaping in manufacturing.[61] Additionally, the

aerospace and automotive sectors can greatly benefit from these materials.[124]

Several reversible bond exchange reactions can be utilized to achieve different properties and characteristics in vitrimers. Therefore, it is essential to better understand these parameters to determine how to apply these compounds and what properties to expect.

3 Summary and outlook

As described, lipid compounds (*e.g.* triglycerides and terpenes/terpenoids) are promising building blocks for monomers as polymers. These agree with the principles of green chemistry, the United Nations Sustainable Development Goals (goals 9, 12, and 13), and the circular economy. Consequently, they can be applied to advanced materials such as photoinitiators, additive manufacturing, and vitrimers.

These compounds are versatile; however, in their pristine form they are not quite suitable for application as monomers; therefore, a chemical modification is required to enhance reactivity. Therefore, it is crucial to plan and evaluate the ideal synthetic route considering atom economy, energetic consumption, hazardous, and time in order to maintain the greener aspect.

Lipid compounds can be tested as photoinitiator and photoinitiator systems since they are abundant, and generally absorb visible light, resulting in less energetic consumption. Moreover, monomers and polymers derived from them can act as photoinitiators decreasing or even avoiding the presence of residual small molecules that can interfere negatively with polymer properties.

By exploring formulations that combine fully-bio-based monomers with diverse chemical structures or that increase the bio-based content alongside non-renewable monomers, we can potentially enhance the mechanical properties of lipid-derived polymers while maintaining their renewable advantage. Vitrimer is an advanced material with a myriad of properties and possible applications. However, they demand further studies about how different exchanged reaction types can influence their final properties such as thermal, mechanical and solvent resistance. The relationship between structure and properties should be deeply investigated considering the material application. Moreover, the self-healing process still depends on higher pressures in most cases, which limits applications in our daily lives, and the scale-up process. However, new alternatives have been developed, such as vitrimer self-healing activated by, for example, red light at 660 nm; therefore, this alternative can overcome this challenge, reducing time and energy.

As described, these lipids are abundant and promising building block compounds in the polymer field. Although plenty of works report different materials (*e.g.* biomaterials, coatings, printing formulations, luminescent materials, shape memory, vitrimers and so on), there is a lot of research and development to be done in the scientific field considering the circular economy, greener design, and new modification routes and applications. The advancement of this area is essential for a sustainable and innovative world.

Author contributions

Rafael Turra Alarcon: conceptualisation, resources, writing – original draft, writing – review and editing. Caroline Gaglieri: conceptualisation, formal analysis, writing – original draft. Aniele de Moura: conceptualisation, formal analysis, writing – original draft. Gabriel Iago dos Santos: conceptualisation, formal analysis, writing – original draft. Éder T. G. Cavalheiro: conceptualisation, writing – review and editing. Gilbert Bannach: conceptualisation, writing – review and editing.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this feature article.

Conflicts of interest

There are no conflicts to declare.

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References

1 C. Kalirajan, A. Dukle, A. J. Nathanael, T. H. Oh and G. Manivasagam, *Polymers*, 2021, **13**, 1–27.
2 Y. W. Liu, B. Q. Hu, J. P. Guan, X. W. Cheng and R. Chen, *Polym. Test.*, 2024, **135**, 108467.
3 M. F. Cunningham, J. D. Campbell, Z. Fu, J. Bohling, J. G. Leroux, W. Mabee and T. Robert, *Green Chem.*, 2019, **21**, 4919–4926.
4 S. Wei, Z. Li, W. Lu, H. Liu, J. Zhang, T. Chen and B. Z. Tang, *Angew. Chem., Int. Ed.*, 2021, **60**, 8608–8624.
5 S. Nam and D. Mooney, *Chem. Rev.*, 2021, **121**, 11336–11384.
6 E. M. Maines, M. K. Porwal, C. J. Ellison and T. M. Reineke, *Green Chem.*, 2021, **23**, 6863–6897.
7 H. Sardon and A. P. Dove, *Science*, 2018, **360**, 380.
8 R. Geyer, J. R. Jambeck and K. L. Law, *Sci. Adv.*, 2017, **3**, 25–29.
9 K. Kümmerer, *Angew. Chem., Int. Ed.*, 2017, **56**, 16420–16421.
10 R. A. Sheldon and M. Norton, *Green Chem.*, 2020, **22**, 6310–6322.
11 Plastic Europe, 2024, **https://www.european-bioplastics.org/bioplastics-market-development-update-2023-2/**.
12 K. Kümmerer, J. H. Clark and V. G. Zuin, *Science*, 2020, **367**, 369–370.
13 V. G. Zuin and K. Kümmerer, *Nat. Rev. Mater.*, 2022, **7**, 76–78.
14 J. W. A. Langeveld, J. Dixon and J. F. Jaworski, *Crop Sci.*, 2010, **50**, S-142–S-151.
15 J. Guit, M. B. L. Tavares, J. Hul, C. Ye, K. Loos, J. Jager, R. Folkersma and V. S. D. Voet, *ACS Appl. Polym. Mater.*, 2020, **2**, 949–957.
16 S. Dahiya, R. Katakojwala, S. Ramakrishna and S. V. Mohan, *Mater. Circ. Econ.*, 2020, 1, DOI: **10.1007/s42824-020-00007-x**.
17 R. T. Alarcon, C. Gaglieri, G. Bannach and É. T. G. Cavalheiro, *Green Chem.*, 2024, **26**, 3261–3270.

18 C. Gaglieri, R. T. Alarcon, A. de Moura and G. Bannach, *Curr. Res. Green Sustainable Chem.*, 2022, **5**, 100343.

19 R. T. Alarcon, C. Gaglieri, K. J. Lamb, M. North and G. Bannach, *Ind. Crops Prod.*, 2020, **154**, 112585.

20 M. D. Guillén and A. Ruiz, *Eur. J. Lipid Sci. Technol.*, 2003, **105**, 688–696.

21 P. T. Wai, P. Jiang, M. Lu, Z. Cui, S. Feng and P. Zhang, *J. Anal. Chem.*, 2024, **79**, 233–240.

22 R. T. Alarcon, K. J. Lamb, É. T. G. Cavalheiro, M. North and G. Bannach, *J. Appl. Polym. Sci.*, 2023, **140**, 1–14.

23 R. T. Alarcon, C. Gaglieri, G. C. dos Santos, A. C. Moralles, N. H. Morgon, A. R. de Souza and G. Bannach, *ChemistrySelect*, 2021, **6**, 7838–7844.

24 C. Gaglieri, R. T. Alarcon, G. I. dos Santos and G. Bannach, *J. Therm. Anal. Calorim.*, 2024, DOI: [10.1007/s10973-024-13102-x](10.1007/s10973-024-13102-x).

25 C. Gaglieri, R. T. Alarcon, R. Magri, M. North and G. Bannach, *J. Appl. Polym. Sci.*, 2022, **139**, 1–13.

26 A. L. Vermiglio, R. T. Alarcon, É. T. G. Cavalheiro, G. Bannach, T. J. Farmer and M. North, *RSC Sustain.*, 2023, **1**, 987–993.

27 R. T. Alarcon, B. B. C. Holanda, A. R. Oliveira, A. G. Magdalena and G. Bannach, *Rev. Virtual Quim.*, 2017, **9**, 163–175.

28 R. T. Alarcon, C. Gaglieri and G. Bannach, *J. Therm. Anal. Calorim.*, 2018, **132**, 1579–1591.

29 D. S. B. L. de Oliveira, L. S. B. L. de Oliveira, R. T. Alarcon, B. B. C. Holanda and G. Bannach, *J. Therm. Anal. Calorim.*, 2017, **128**, 1671–1682.

30 O. A. B. Pires, R. T. Alarcon, C. Gaglieri, L. C. da Silva-Filho and G. Bannach, *J. Therm. Anal. Calorim.*, 2019, **137**, 161–170.

31 R. T. Alarcon, A. R. Oliveira and G. Bannach, Patent, BR102018008030-1, 2018.

32 Z. Y. Ben, H. Samsudin and M. F. Yhaya, *Eur. Polym. J.*, 2022, **175**, 111377.

33 S. Goyal, N. B. Hernández and E. W. Cochran, *Polym. Int.*, 2021, **70**, 911–917.

34 D. Kong, B. Yang, H. Yuan, C. Du and Y. Tan, *J. Mater. Sci. Technol.*, 2024, **213**, 268–275.

35 M. Porcarello, S. Bonardd, G. Kortaberria, Y. Miyaji, K. Matsukawa and M. Sangermano, *ACS Appl. Polym. Mater.*, 2024, **6**, 2868–2876.

36 R. Hu, W. Yao, Y. Fu, F. Lu and X. Chen, *Polymers*, 2025, **213**, 268–275.

37 J. Gershenzon and N. Dudareva, *Nat. Chem. Biol.*, 2007, **3**, 408–414.

38 K. Wijesekera and A. S. Dissanayake, in *Phytochemistry and Pharmacognosy of Medicinal Plants*, ed. M. Napagoda and L. Jayasinghe, De Gruyter, Berlin, Boston, 2022, pp. 65–94.

39 R. Bailón-Moreno, J. Romero-Noguera, F. C. Bolívar-Galiano, A. M. Yebra-Rodríguez and N. Pérez-Villares, *J. Cult. Herit.*, 2020, **45**, 10–24.

40 M. Pagliaro, A. S. Fabiano-Tixier and R. Ciriminna, *Green Chem.*, 2023, **25**, 6108–6119.

41 G. Cui, X. Yang, Z. Liu, M. Wei, T. Liu, H. Gu and L. Yang, *ACS Sustainable Chem. Eng.*, 2022, **10**, 11057–11068.

42 R. T. Alarcon, K. J. Lamb, G. Bannach and M. North, *ChemSusChem*, 2021, **14**, 169–188.

43 R. A. Lyubushkin, N. I. Cherkashina, D. V. Pushkarskaya, D. S. Matveenko, A. S. Shcherbakov and Y. S. Ryzhkova, *ChemEngineering*, 2023, **7**, 1–8.

44 M. Aguirre, S. Hamzehlou, E. González and J. R. Leiza, *Renewable feedstocks in emulsion polymerization: Coating and adhesive applications*, Elsevier Inc., 1st edn, 2020, vol. 56.

45 M. Palenzuela, D. Sánchez-Roa, J. Damián, V. Sessini and M. E. G. Mosquera, *Polymerization of terpenes and terpenoids using metal catalysts*, Elsevier Inc., 1st edn, 2021, vol. 75.

46 N. Luo, G. Ma and J. Qu, *Ind. Crops Prod.*, 2024, **222**, 119622.

47 S. Kugler, P. Ossowicz, K. Malarczyk-Matusiak and E. Wierzbicka, *Molecules*, 2019, **24**, 1651.

48 A. Llevot, E. Grau, S. Carlotti, S. Grelier and H. Cramail, *Eur. Polym. J.*, 2015, **67**, 409–417.

49 P. Gnanasekar, J. Chen, S. R. Goswami, H. Chen and N. Yan, *ChemSusChem*, 2020, **13**, 5749–5761.

50 N. P. Vidal, O. A. Adigun, T. H. Pham, A. Mumtaz, C. Manful, G. Callahan, P. Stewart, D. Keough and R. H. Thomas, *Molecules*, 2018, **23**, 2356.

51 A. Abbasi, W. Z. N. Yahya and M. M. Nasef, *Green Mater.*, 2020, **8**, 172–180.

52 M. Ionescu, D. Radojčić, X. Wan, Z. S. Petrović and T. A. Upshaw, *Eur. Polym. J.*, 2015, **67**, 439–448.

53 Y. Çakmak, E. Çakmakçi, N. K. Apohan and R. Karadag, *J. Cult. Herit.*, 2022, **55**, 391–398.

54 Z. Chu, Y. Feng, B. Xie, Y. Yang, Y. Hu, X. Zhou, T. Yuan and Z. Yang, *Ind. Crops Prod.*, 2021, **160**, 113117.

55 R. T. Alarcon, C. Gaglieri, O. A. de Souza, D. Rinaldo and G. Bannach, *J. Polym. Environ.*, 2020, **28**, 1265–1278.

56 C. Gaglieri, R. T. Alarcon, A. De Moura, R. Magri and G. Bannach, *J. Braz. Chem. Soc.*, 2023, **34**, 600–613.

57 C. Gaglieri, R. T. Alarcon, A. De Moura, R. Magri, L. C. Da Silva-Filho and G. Bannach, *J. Braz. Chem. Soc.*, 2021, **32**, 2120–2131.

58 R. Magri, C. Gaglieri, R. T. Alarcon and G. Bannach, *J. Polym. Res.*, 2021, **28**, 1–7.

59 R. T. Alarcon, G. Bannach and É. T. G. Cavalheiro, *J. Braz. Chem. Soc.*, 2025, **36**, e-20240068.

60 R. T. Alarcon, C. Gaglieri, K. J. Lamb, É. T. G. Cavalheiro, M. North and G. Bannach, *J. Polym. Res.*, 2021, **28**, 425.

61 G. I. dos Santos, C. Gaglieri, R. T. Alarcon, R. Magri, M. Hartlieb and G. Bannach, *J. Polym. Environ.*, 2024, **32**, 4748–4762.

62 M. Porcarello, C. Mendes-felipe, S. Lanceros-mendez and M. Sangermano, *Sustain. Mater. Technol.*, 2024, **40**, e00927.

63 L. Guo, K. J. Lamb and M. North, *Green Chem.*, 2021, 77–118.

64 J. Chen, G. Chiarioni, G. J. W. Euverink and P. P. Pescarmona, *Green Chem.*, 2023, **25**, 9744–9759.

65 K.-K. Tremblay-Parrado, C. García-Astrain and L. Avérous, *Green Chem.*, 2021, **23**, 4296–4327.

66 N. Uysal, G. Acik and M. A. Tasdelen, *Polym. Int.*, 2017, **66**, 999–1004.

67 A. Mtibe, M. P. Motloung, J. Bandyopadhyay and S. S. Ray, *Macromol. Rapid Commun.*, 2021, **42**, 1–28.

68 J. G. Rosenboom, R. Langer and G. Traverso, *Nat. Rev. Mater.*, 2022, **7**, 117–137.

69 G. Chiarioni, M. van Duin and P. P. Pescarmona, *Green Chem.*, 2023, **25**, 7612–7626.

70 P. P. Pescarmona, *Curr. Opin. Green Sustainable Chem.*, 2021, **29**, 100457.

71 C. Di Mauro, A. Genua and A. Mija, *Ind. Crops Prod.*, 2022, **185**, 115116.

72 A. Mija, E. Louisy, S. Lachegur, V. Khodyrieva, P. Martinaux, S. Olivero and V. Michelet, *Green Chem.*, 2021, **23**, 9855–9859.

73 L. Pezzana, S. Fadlallah, G. Giri, C. Archimbaud, I. Roppolo, F. Allais and M. Sangermano, *ChemSusChem*, 2024, **202301828**, 1–14.

74 M. Bergoglio, G. Palazzo, D. Reisinger, M. Porcarello, G. Kortaberria, S. Schlögl and M. Sangermano, *React. Funct. Polym.*, 2024, **200**, 105936.

75 N. C. Nepomuceno, C. Bakkali-Hassani, R. Wellen, S. Caillol and C. Negrell, *Eur. Polym. J.*, 2024, **212**, 113074.

76 A. Delavarde, S. Lemouzy, A. Lebrun, J. Pinaud and S. Caillol, *Molecules*, 2023, **28**, 7133.

77 L. Valle, L. Maddalena, G. Damonte, F. Carosio, A. Pellis and O. Monticelli, *Colloids Surf., B*, 2024, **236**, 113806.

78 F. Ferretti, G. Damonte, F. Cantamessa, R. Arrigo, A. Athanassiou, A. Zych, A. Fina and O. Monticelli, *ACS Omega*, 2024, **9**, 1242–1250.

79 L. Sougrati, S. Wendels, S. Dinescu, L. R. Balahura, L. Sleiman and L. Avérous, *Sustain. Mater. Technol.*, 2023, **37**, e00656.

80 N. Wybo, A. Duval and L. Averous, *Angew. Chem., Int. Ed.*, 2024, e202403806, DOI: 10.1002/anie.202403806.

81 X. Liu, X. Yang, S. Wang, S. Wang, Z. Wang, S. Liu, X. Xu, H. Liu and Z. Song, *ACS Sustainable Chem. Eng.*, 2021, **9**, 4175–4184.

82 S. Ye, W. Zhang, Z. Zhai, S. Shang, L. Huang, Z. Song and J. Jiang, *Langmuir*, 2024, **40**, 647–656.

83 O. King, M. M. Pérez-Madrigal, E. R. Murphy, A. A. R. Hmayed, A. P. Dove and A. C. Weems, *Biomacromolecules*, 2023, **24**, 4680–4694.

84 C. Jehanno, J. W. Alty, M. Roosen, S. De Meester, A. P. Dove, E. Y. X. Chen, F. A. Leibfarth and H. Sardon, *Nature*, 2022, **603**, 803–814.

85 P. Anastas and N. Eghbali, *Chem. Soc. Rev.*, 2010, **39**, 301–312.

86 T. Borjigin, J. Feng, M. Schmitt, D. Zhu, F. Morlet-Savary, P. Xiao and J. Lalevée, *Green Chem.*, 2023, **26**, 277–286.

87 G. Noirbent and F. Dumur, *Eur. Polym. J.*, 2021, **142**, 110109.

88 S. M. Müller, S. Schlögl, T. Wiesner, M. Haas and T. Griesser, *ChemPhotoChem*, 2022, **6**, 1–12.

89 P. I. Systems, *Photopolymerisation Initiating Systems – Google Książki*, The Royal Society of Chemistry, 2018.

90 A. S. Hamidi, M. A. Hadis and W. M. Palin, *Dent. Mater.*, 2022, **38**, 1330–1343.

91 E. Sprick, J. M. Becht, T. Tigges, K. Neuhaus, C. Weber and J. Lalevée, *Macromol. Chem. Phys.*, 2020, **221**, 1–5.

92 R. J. Wendland, M. T. Conway and K. S. Worthington, *J. Biomed. Mater. Res., Part A*, 2024, 1662–1674.

93 A. Jagtap and A. More, *Pollym. Bull.*, 2022, **79**, 8057–8091.

94 A. Spessa, R. Bongiovanni and A. Vitale, *Prog. Org. Coat.*, 2024, **187**, 108098.

95 N. Yaragatti and A. Patnaik, *Mater. Today: Proc.*, 2021, **44**, 4150–4157.

96 X. Xu, J. Yang, W. Jonhson, Y. Wang, A. Suwardi, J. Ding, C. Guan and D. Zhang, *Addit. Manuf.*, 2022, **56**, 102939.

97 A. Bagheri and J. Jin, *ACS Appl. Polym. Mater.*, 2019, **1**, 593–611.

98 R. Magri, C. Gaglieri, R. T. Alarcon, G. I. dos Santos and G. Bannach, *J. Polym. Res.*, 2023, **30**, 1–13.

99 M. Bergoglio, E. Rossegger, S. Schlögl, T. Griesser, C. Waly, F. Arbeiter and M. Sangermano, *Polymers*, 2024, **16**, 1510.

100 A. C. Weems, K. R. D. Chiaie, J. C. Worch, C. J. Stubbs and A. P. Dove, *Polym. Chem.*, 2019, **10**, 5959–5966.

101 D. Merckle, E. Constant and A. C. Weems, *ACS Sustainable Chem. Eng.*, 2021, **9**, 12213–12222.

102 P. Fu, H. Li, J. Gong, Z. Fan, A. T. Smith, K. Shen, T. O. Khalfalla, H. Huang, X. Qian, J. R. McCutcheon and L. Sun, *Prog. Polym. Sci.*, 2022, **126**, 101506.

103 J. Zheng, Z. M. Png, S. H. Ng, G. X. Tham, E. Ye, S. S. Goh, X. J. Loh and Z. Li, *Mater. Today*, 2021, **51**, 586–625.

104 S. Kamarulzaman, Z. Mao Png, E. Qi Lim, I. Z. S. Lim, Y. Liu and S. S. Goh, *Chem*, 2023, **9**, 2771–2816.

105 Y. Bei, Y. Ma, F. Song, Z. Kou, L. Hu, C. Bo, P. Jia and Y. Zhou, *J. Appl. Polym. Sci.*, 2022, **139**, 51977–51995.

106 V. Zhang, B. Kang, J. V. Accardo and J. A. Kalow, *J. Am. Chem. Soc.*, 2022, **144**, 22358–22377.

107 N. J. Van Zee and R. Nicolaÿ, *Prog. Polym. Sci.*, 2020, **104**, 101233.

108 M. Guerre, C. Taplan, J. M. Winne and F. E. D. Prez, *Chem. Sci.*, 2020, **11**, 4855–4870.

109 M. Sangermano, M. Bergoglio and S. Schögl, *Macromol. Mater. Eng.*, 2023, **309**, 2300371.

110 J. J. Lessard, G. M. Scheutz, S. Hyun Sung, K. A. Lantz, T. H. Epps and B. S. Sumerlin, *J. Am. Chem. Soc.*, 2019, **142**, 283–289.

111 A. V. Karatrantos, O. Couture, C. Hesse and D. F. Schmidt, *Polymers*, 2024, **16**, 1373.

112 D. Montarnal, M. Capelot, F. Tournilhac and L. Leibler, *Science*, 2011, **334**, 965–968.

113 W. Alabiso and S. Schlögl, *Polymers*, 2020, **12**, 1660.

114 C. Di Mauro, S. Malburet, A. Graillot and A. Mija, *ACS Appl. Bio Mater.*, 2020, **3**, 8094–8104.

115 Y. Yang, Y. Xu, Y. Ji and Y. Wei, *Prog. Mater. Sci.*, 2021, **120**, 100710.

116 Y. Zhu, W. Li, Z. He, K. Zhang, X. Nie, R. Fu and J. Chen, *Polymers*, 2024, **16**, 307.

117 Y. Zhang, M. Zhai, L. Shi, Q. Lei, S. Zhang, L. Zhang, B. Lyu, S. Zhao, J. Ma and V. K. Thakur, *Ind. Crops Prod.*, 2023, **193**, 116210.

118 Z. Luo, B. Yang, F. Liu, X. Pan and Y. Zeng, *ACS Appl. Polym. Mater.*, 2023, **5**, 8670–8678.

119 F. Bertini, A. Vignali, M. Marelli, N. Ravasio and F. Zaccheria, *Polymers*, 2022, **14**, 4185.

120 E. Louisy, S. Olivero, V. Michelet and A. Mija, *ACS Sustainable Chem. Eng.*, 2022, **10**, 7169–7179.

121 G. Kaur, P. Kumar and C. Sonne, *RSC Appl. Interfaces*, 2024, **1**, 846–867.

122 B. Han, X. Yu and J. Ou, *Self-Sensing Concrete in Smart Structures*, 2014, pp. 361–376.

123 M. M. Meraz, N. J. Mim, M. T. Mehedi, B. Bhattacharya, Md. R. Aftab, Md. M. Billah and Md. M. Meraz, *Alexandria Eng. J.*, 2023, **73**, 665–694.

124 V. Schenk, K. Labastie, M. Destarac, P. Olivier and M. Guerre, *Mater. Adv.*, 2022, **3**, 8012–8029.

125 K. Zhao, Y. Wang, J. Guo, S. Zhang and W. Niu, *Chem. Eng. J.*, 2022, **450**, 138285.

126 Z. Zhang, A. K. Biswal, A. Nandi, K. Frost, J. A. Smith, B. H. Nguyen, S. Patel, A. Vashisth and V. Iyer, *Nat. Sustain.*, 2024, **7**, 1–12.