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Biobased aromatic building blocks for coating applications

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Aromatic monomers are key building blocks for many polymer resins for coatings applications. The rigid structure results in improved thermal and mechanical properties of the coatings, such as high hardness or scratch-resistance to name but a few. However, most of the available aromatic building blocks are very inexpensive monomers obtained from petrochemical resources. To enhance the sustainability of coatings materials, bio-based alternatives are of high interest for both industry and academia. This short review aims to highlight very recent work on biobased aromatics for coatings applications.

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Bio-based building blocks, sustainable coatings, aromatic monomers, bio-based polymer resins.

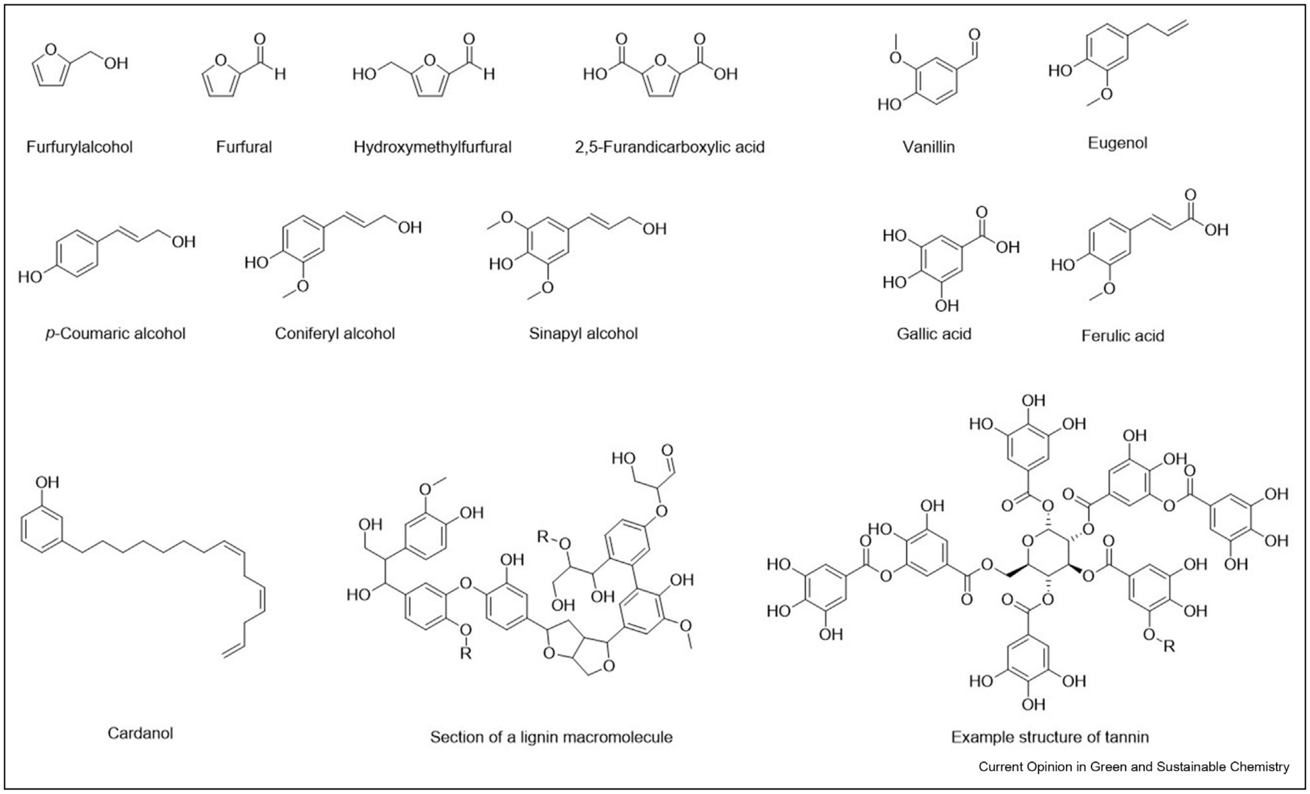
Introduction

Polymers resins for coatings applications are traditionally derived from renewable building blocks, such as vegetable oils, shellac or rosin for wood varnishes and printing inks. However, with the development of synthetic polymers, new resins with improved properties were developed that resulted in countless applications of this type of materials in our daily modern life. From the petrochemical monomers used for these new coatings, aromatic building blocks gained particular significance, as they allow for good mechanical and thermal properties of the final coatings. For instance, the use of phenol was not only important for the invention of thermosetting plastics, but also for condensation resins that are still used in large quantities for example in wood fiber boards [1]. Bisphenol-A or novolac epoxy resins, on the other hand are responsible for the mechanical performance of many epoxy resins [2]. But also other less prominent examples, such as alkyd resins, (unsaturated) polyester resins, and high performance polyurethanes are highly dependent on building blocks such as phthalic acid, isophthalic acid, styrene or toluene-2,4-diisocyanate to name but a few [3]. In the endeavor to develop novel bio-based polymer resins that can compete with these commercial products, replacements for the aromatic building blocks are of utmost importance. In this respect, several aromatic building blocks from renewable resources have drawn attention over the last years, such as furan-based building blocks, vanillin, cardanol, lignin and monomers derived thereof (Figure 1). This review aims to highlight the most recent advances in the last two years in the field of bio-based aromatic building for coatings applications and discuss the potential of the individual building blocks derived from renewable resources.

Furan-based building blocks

The use of furan-based building blocks as thermosetting coatings is by no means new. First reports on the polymerization of furfuryl alcohol date back to the 1970s [4]. However, due to its relevance as biobased building block, the chemistry of furfuryl alcohol and its applications as thermoset and composite matrix has been recently reviewed [5,6]. Furthermore, a general overviews over furan-based resins and polymers were lately reported [7,8]. The aldehyde group in both furfural and HMF makes these aromatic molecules also interesting as formaldehyde alternative in polycondensation resins. In this respect, Moualhi et al. reported the synthesis of range of thermosets by a reaction of resorcinol with furfural and methylfurfural and other bio-based aldehydes achieving tensile strengths up to 74 MPa [9]. As another recent example Hithesh et al. studied the use of phenol-furfural composite with functionalized graphene oxide as anti-corrosion coating for mild steel [10]. As far as FDCA is concerned, immense research efforts were dedicated to its applications as replacement of terephthalic acid in thermoplastic polyesters. On the other hand, only little research was dedicated towards the implementation of FDCA in the coatings field.

Figure 1



Aromatic building blocks used in the synthesis of polymer resins.

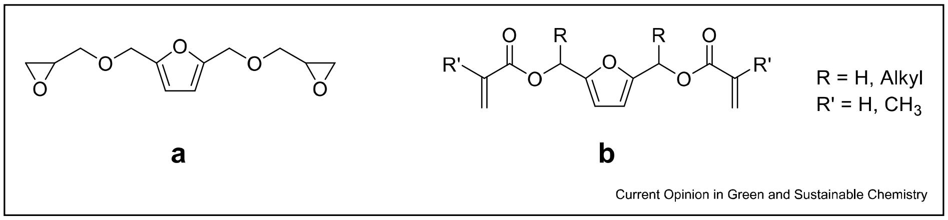
Papadopoulos et al. recently compared the performance of polyurethane dispersions derived from polyols with either isophthalic acid or FDCA [11]. They could show that the incorporation of FDCA leads to higher hardness and T_gs compared to the isophthalic acid counterparts. As far as UV-curing coatings are concerned, Pezzana et al. utilized the diallyl ether of furan dimethanol together with different thiols in UV-induced thiol–ene reactions [12]. The resulting coatings showed superior T_gs compared to similar materials derived from other bio-based building blocks. The same group examined the mono- and diglycidyl furfuryl alcohols in cationic UV-curing coatings (Figure 2A) [13]. Furthermore, the group of the Dean Webster recently reported the synthesis of a set of furanic di(meth)acrylates (Figure 2B) and tested their application as reactive diluents with a UV-curing urethane acrylate oligomer. The bio-based monomers showed that their implementation improved the hardness and the T_g of the cured materials [14]. Later, they also tested these monomers as diluents for UV-curing additive manufacturing [15]. Diglycidyl furfuryl alcohol or 2,5-bis[oxiran-2-ylmethoxy)methyl] furan was also used as bisphenol A alternative in epoxy resins with maleic acid as hardener with properties competitive with commercial materials [16].

As far as the availability of furan-based building blocks is concerned, furfural and furfuryl alcohol are produced for decades in industrial quantities at very competitive prices. For FDCA on the other hand the prices are still very high (around 500 €/kg), despite industrial interest and confirmed technical feasibility by academic, as well as industrial research projects. Therefore, industrial applications are still very limited. However, a breakthrough is expected in near future due to large scale plants (5 kT/y) are being built [17], which is predicted to bring down the costs of FDCA to acceptable levels, at least for premium markets where higher prices for coatings are accepted by costumers and end-users.

Lignin-based building blocks

Lignin is by far the most abundant aromatic biopolymer and is produced on large quantities as side product of the pulp and paper industry. However, the very heterogenous structure makes it a very challenging feedstock and despite immense research efforts from both industry and academia over the last decades, the material use of lignin is still quite limited. As far as coatings applications of lignin are concerned, academic research has been recently reviewed [18–21]. Latest research activities in this field focus on the integration of special

Figure 2



Digylcidyl furfuryl alcohol and furan-based di(meth)acrylates used in UV-curing coatings.

functionalities to the coating by using modified lignin additives. Henn et al. demonstrated the use of acetylated lignin nanoparticle (LNP) for superhydrophilic antifogging coatings [22]. LNP dispersions prepared were applied on glass, which lowered the contact angle of water from 29° ± 6° of uncoated glass compared to 9° ± 4° of the coated glass. Another study from Diogenes et al. describes the use of acetylated kraft lignin to improve the anticorrosive ability of epoxy coatings for carbon steel [23]. The preparation of novel lignin-based micro/nano structure coatings with superhydrophobic properties was described by Liu et al. [24] They modified lignin with 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTES) to obtain PFDTES-grafted lignin. The functionalized lignin powder was mixed with an epoxy resin and applied on different substrates. The prepared lignin-based coatings showed excellent repellency to water with a contact angle of 164°. However, it is noteworthy to mention that the use of perfluorinated particles is not very sustainable and should be avoided. Another approach based on dual-size lignin micro-nanospheres (LMN) was reported by Ma et al. [25] They produced nano-LMNs (n-LMN) and micro-LMNs (m-LMN) via antisolvent precipitation and tested these nanospheres also as additives in epoxy coatings [26]. Thermoset coatings based on glyoxylic acid lignin and poly(ethyleneglycol)diglycidylether with antioxidant and UV-protective effect with high visible transparency were developed by Boarino et al. [27] They fabricated free coating films with tunable mechanical properties having a lignin content of up to 70 wt%. Such coatings films are attractive for sustainable food packaging. Besides the mentioned examples of using chemically modified lignin in functional coatings, there is also ongoing research in using unmodified lignin as additive for sustainable antiviral [28], antifouling [29] and flame retardant [30] coatings. The application of lignin-based materials in coatings is still limited despite immense research efforts. However, some commercial examples start entering the market, such as lignin-based dispersants and emulsifiers derived from lignosulfonates for example [31]. This shows that the use of lignin in coatings applications is indeed possible and it is expected that further research will eventually lead to a broader material use of lignin in the coatings field.

Vanillin-based building blocks

Vanillin is commonly used in food and variety of cosmetic compounds because it is inexpensive and available. The presence of aldehyde group and phenolic hydroxyl group makes this precursor highly versatile for further functionalization to be exploited in polymerization reactions [32,33]. Recently, Mahajan et al. synthesized divanillin (DV) which was used as a partial replacement for polyethylene glycol an industrial diol for polyurethane (PUR) synthesis [34]. In this work hydroxyethyl methacrylate was attached to incorporate unsaturation exploited for UV-curing process. The synthesized resin was dispersed in water and applied on a wooden panel. The achieved PUR coatings showed an enhancement of pencil hardness and scratch hardness by increasing the DV content. The 30% incorporation of DV allows to obtain the highest pencil hardness (2H) and scratch hardness (0.90 kg) among all the DV formulations. Several epoxidized vanillin derivatives have been reported as potential biobased epoxy resins for high-performance polymers and composites. The functionalized precursor was thermally cured as well as UV-cured [35,36]. The crosslinked materials showed high T_g (above 60 °C) and high mechanical performance with a Young's modulus of 837 MPa. Hakkarainen reported the synthesis of vanillin epoxy thermosets characterized by good thermal and mechanical properties and they studied the thermal reprocessability and chemical recyclability under acidic conditions at room temperature [37]. The achieved thermosets exhibited good thermo-mechanical properties and are stable in common organic solvents. Furthermore, the authors showed that the materials can be thermally reprocessed through compression molding with good recovery of the mechanical properties. Finally, the synthesized thermosets showed rapid and complete chemical recyclability to water-soluble aldehydes and amines by imine hydrolysis at room temperature in 0.1 m HCl solution. Li et al. reported the synthesis of vanillin-phosphorus based epoxy coatings showing high thermal stability and flame retardancy [38]. This research provides a novel direction for the preparation of epoxy reactive flame retardant from bio-based resources as raw materials and a reference for the application of epoxy resin in the field of wood flame retardant coating. Industrial applications in the very price competitive coatings field are still limited, mainly due to cost limitations compared to similar aromatic building blocks derived from petrochemical sources. However, some building blocks, such as methacrylated or epoxidized vanillin are commercially available [39]. Despite the higher prices, these monomers could find application in specialty coatings applications, where higher prices are tolerated.

Cardanol-based building

Cashew nutshell liquid (CNSL) is an abundant by-product from agricultural wastes, that contains mainly four components: anacardic acid, cardanol, cardol, and 2-methyl cardol [40]. Furthermore, CNSL is a non-edible oil which can be recovered at low cost because of an abundant availability. Therefore, the derivatized phenol-containing building blocks from CNSL can be used in various coatings applications, such as epoxies, alkyds, phenolic and epoxy resins, polyol, benzoxazine, vinyl ester polymers [41]. Recently, Vijayan et al. synthesized solvent-free sustainable colorless cardanol-based polyurethane coatings, copolymerizing with hydroxy-terminated polydimethylsiloxane (HTPDMS) without using any metal catalysts [42]. The resulting coating exhibited a high transparency up to 92–96% in the visible light, high hydrophobicity, with a value of contact angle with water of 103°, a T_g value of 98 °C and a high corrosion resistance, showing no sign of corrosion even after 50 days of immersion in salt water. Zhang et al. reported the good anti-corrosion performance of an epoxy coating prepared in the presence of epoxy cardanol as reactive diluent [43]. The anticorrosion behavior can be attributed to the optimization of the crosslinkable formulation which allowed to achieve high epoxy group conversion, good dispersibility of graphene oxide (GO) and enhanced GO-epoxy resin interfacial bonding. All these factors helped to obtain coatings with good anticorrosion properties. The group of Wadgaonkar also recently reported the preparation of CNSL-based epoxies [44]. They were able to show that the glass transition temperature decreased with increasing CNSL content, while the thermal stability was not affected. Kalita et al. reported the synthesis of cardanol ethyl vinyl ether (CEVE) which was polymerized exploiting the ability of the cardanol to undergo autoxidation [45]. The polymers were cured oxidatively at both ambient and elevated temperatures (120 and 150 °C) resulting in crosslinked materials characterized by good tensile properties (12.2–26.6 MPa) and pendulum hardness (15–40 sec.). Functionalized methacrylated cardanol was studied both in homopolymerization and copolymerization with methyl methacrylate in emulsion polymerization. The same functionalized precursor was exploited for coating application with UV cross-linking via thiol–ene chemistry. The cross-linked coating exhibit promising thermal and mechanical resistance properties [46]. Considering that the global production of CNSL is well above one million tons per year with a low environmental foot print, cardanol can be considered a bio-based alternative not only for coatings from both, economic and environmental point of view [47].

Other aromatics

Despite the structural similarity of eugenol to lignin-derived monomers, such as coniferyl alcohol, the main source of eugenol is not lignin, but it is extracted from clove oil and other natural oils. The group of Sylvain Caillol recently reviewed the use of eugenol for polymer applications [48]. Furthermore, the group of Dean Webster has used this biobased aromatic compound for the synthesis of poly(vinyl ether)s or epoxy resins [49,50]. The latter showed similar hardness of the final coating as a bisphenol A-derived epoxy resin. Furthermore, phenolic acids, such as gallic or ferulic acid are not directly used as bio-based replacements for petrochemical aromatic building blocks, as the phenolic OH is not reactive in standard esterification procedures. However functionalized building blocks have been used in the past also for coatings applications [51,52]. Recently, these monomers in combination with chitosan have been studied as active building blocks for antioxidative food packaging films and coatings [53]. As another very interesting group of aromatic compounds, different tannins have been utilized in coatings applications. Tannins is the term for a number of different polyphenolic compounds that can be extracted from a wide range of tree barks or leaves are traditionally used in the tanning of animal skins into leather [54]. The use of this family of polyphenols in polymeric applications has been reviewed previously [55,56]. As far as coatings are concerned, Kumar and coworkers recently reported the use of different Red sanders bark extract in UV-protective wood coatings [57]. Furthermore, phosphorylated tannin-particles have been used as intumescent fire protection coatings [58].

Conclusions

This short review summarized the most important bio-based aromatic monomers and the recent scientific literature on their use as building blocks for coatings applications. In several cases, the novel coating systems exhibit promising material properties that have the potential to compete with commercial products based on petrochemical sources. However, further research efforts of academia, as well as industry are needed to identify new potential sources for aromatic building blocks, to modify the latter so they can be used as monomers in polymer resins, and to design the polymer resins so they exhibit properties suited for coatings applications. In addition to the mere properties of the final coatings, also techno-economical and sustainability studies are needed to ensure that biobased coatings will be able to penetrate the market, commercially compete with existing market products, and have indeed an improved environmental footprint.

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 article.

Data availability

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

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