RSC Advances

REVIEW

Naturally occurring phenolic sources: monomers and polymers

Cite this: RSC Adv., 2014, 4, 21712

Bimlesh Lochab,*[a] Swapnil Shukla[a] and Indra K. Varma[b]

Exploration of sustainable alternatives to chemicals derived from petro-based industries is the current challenge for maintaining the balance between the needs of a changing world while preserving nature. The major source for sustainable chemicals is either the natural existing plant sources or waste generated from agro-based industries. The utility of such resources will supplement new processed materials with different sets of properties and environmental friendliness due to their biodegradability and low toxicity during preparation, usage and disposal. Amongst other polymers used on a day-to-day basis, phenolic resins account for vast usage. Replacement of petro-based monomers such as phenol and its derivatives either partly or completely utilized for the synthesis of such resins is ongoing. Extraction of natural phenolic components from cashew nut shell liquid, lignin, tannin, palm oil, coconut shell tar or from agricultural and industrial waste, and their utilization as synthons for the preparation of bio-based polymers and properties obtained are reviewed in this paper. This review article is designed to acknowledge efforts of researchers towards the "3C" motto – not only trying to create but also adapting the principles to conserve and care for a sustainable environment. This review paper describes how extraction, separation and recovery of desired phenolic compounds have occurred recently; how substituted phenol compounds, unmodified and modified, act as monomers for polymerization; and how the presence of sustainable phenolic material affects the properties of polymers. There are about 600 references cited and still there is a lot to uncover in this research area.

Received 8th January 2014
Accepted 24th March 2014

DOI: 10.1039/c4ra00181h

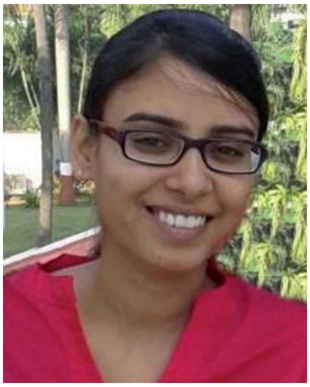
www.rsc.org/advances

---

[a] Department of Chemistry, School of Natural Sciences, Shiv Nadar University, Greater Noida, UP, India. E-mail: bimlesh.lochab@snu.edu.in; Fax: +91 120 266 3810; Tel: +91 120 266 3801

[b] Centre for Polymer Science and Engineering, IIT, Delhi, New Delhi, India. E-mail: ikvarma@hotmail.com; Tel: +91 9582972226

Bimlesh Lochab obtained an MS (1997–1999) and MTech (1999–2000) from IIT, Delhi, India. She held a Felix scholarship for her DPhil degree (2002–2006) from the University of Oxford on the topic of polymers for electro-optic applications under the supervision of Professor Paul Burn. She did her PDF at the University of Oxford and University of Nottingham, UK. After her return to India, she received the Young Scientist Award to research on cardanol-based benzoxazine polymers. In 2012, she joined, as an Assistant Professor, Shiv Nadar University (SNU), UP, India. Her research interests include polymers using intermediates from sustainable origin; dendritic architectures and polymers for PVs and OLEDs, and nanoparticles for nanocomposite applications.



Swapnil Shukla completed her BSc and MSc degrees in chemistry at the University of Delhi, India. Her specialization during the MSc was organic chemistry. She is currently in the second year of her PhD programme at Shiv Nadar University, UP, India. She is pursuing research in the field of green polymers based on renewable sources and synthesized in accordance with the tenets of green chemistry under the supervision of Bimlesh Lochab. Her research interests involve exploration of the realms of sustainable chemistry with an emphasis on synthesizing polymeric materials.

1. Introduction

For over a decade, there has been a continuous surge in petro-product prices due to a greater dependence and high depletion rate of non-renewable fossilized reserves. Concurrently, there is increased awareness about environmental protocols for a greener earth, which could be achieved mainly by a reduction of greenhouse gases and through the generation and use of biodegradable products.

Exploration and utilization of alternative renewable feedstocks of monomers for the chemical industry – in particular, the polymer industry – is a necessary step towards sustainable development. This provides new significant synthetic aspects and helps to produce partly green goods with a finite content of renewable or recyclable material extracted without odour problems and less use of fossil fuel reserves.

Previous literature[1] showed the utility of polymers based on naturally occurring plant oils such as soya bean, castor, linseed, sunflower, mustard, palm oil; amines such as fatty amines; polyols such as glycerol, ethylene glycol; alkenes such as limonene; diacids such as succinic acid, citric acid, tartaric acid *etc.* However, there is a need to explore alternative materials that are generated either from waste or from substances of non-food origin. The main aim should be exploration of the possibility to produce sustainable polymers on a large scale and economically that can compete successfully with petro-based polymers. Over the past two centuries, there has been a change in the dependence of sources of raw materials for chemical industries with time and it showed a closed loop cycle.[2] Renewable feedstocks were of interest in the early 1850s, but non-renewable coal tar-based materials were simultaneously explored and reached maximum usage in the 1930s. In the meantime, natural gas- and oil-based resources started gaining importance from 1930 onwards. However, the associated problems such as dwindling and not easily replenished feedstocks of non-renewable resources have necessitated the use of renewable feedstocks, thereby closing the loop. Currently, research efforts are focused on either partial or complete replacement of chem-stocks of petro-based industries.

There are several problems associated with extracting desired monomers or chemical intermediates from naturally occurring renewable resources.[3] The main limitations are (i) poor knowledge about the occurrence, chemical content and composition in the natural source, (ii) the varying percentage with species, geographical area, and climatic conditions, (iii) the same chemical extraction process cannot be applied from species to species, (iv) requirement for optimization of extraction process, (v) extraction of desired chemical recovered from the usual complex chemical composition involves higher costs, (vi) low percentage of the desired chemical species requires further processing costs and (vii) development of non-destructive techniques to analyse and quantify the content easily.

In this review article, we will focus on phenols derived from easily renewable natural resources such as cashew nut shell liquid (CNSL), lignin, tannin, palm oil and coconut shell tar (CST) or from agricultural and industrial waste and their use as monomers with or without modification for the synthesis of sustainable polymers. The hydroxyl functionality, side groups and aromatic rings available in these naturally occurring phenolic derivatives could be tailored to design new monomeric structures which need to be explored.

Several classes of phenolic polymers have been developed in the past hundred years. The first synthetic phenolic resin was developed more than a century ago by Baekeland.[4] Since then, phenols have been utilized for the preparation of other polymers such as polyesters, polycarbonates, epoxy resins, poly(phenylene oxide), polyurethane, *etc.*

Indra K. Varma obtained her MSc and DPhil degrees from the University of Allahabad, India, and PhD and DSc from the University of Glasgow, UK. She joined Dept. of Chemistry, IIT, Delhi, India in 1966 as a faculty member and taught at UG and PG levels for almost 40 years. She has published more than 250 papers and holds 5 US patents. She guided 45 students for their PhD degrees. Her research interests are synthesis and characterization of bio-polymers, degradable polymers, polymer composites, and enzymatic synthesis of polymers. She has written several chapters in books and recently acted as co-author of a book entitled "The science and technology of fibrous composites".

2. Sources of naturally occurring phenol

Earlier, the waste generated by agro-based industries, such as empty fruit bunches,[5] seed,[6,7] fibre, shell,[8] wood and bagasse,[9] was mainly utilized either as a local source of energy by incineration[10] or as natural fertilizer. The waste is found to be rich in phenolic derivatives such as cresol, catechol, guaiacols, syringol, eugenol *etc.* which can promisingly substitute petro-based phenol in phenolic polymers. The sources of naturally occurring phenolic compounds that will be considered are CNSL, lignin, tannin, palm oil and CST.

2.1 Cashew nut shell liquid (CNSL)

CNSL is a reddish brown viscous liquid, with the honeycomb structure of the shell of cashew nuts obtained from cashew trees grown in coastal areas of Asia and Africa, Mozambique, India and Brazil. India is a leading exporter of CNSL and had exports of 13 575 MT in 2011–12, and is expected to increase by nearly 1500 MT per annum.[11] The estimated growth rate in demand is 7 to 8% per annum. The noxious saps of numerous members of the Anacardiaceae, such as Japanese lac, poison ivy, CNSL, *etc.*, contain phenolic compounds in which a benzene ring is substituted with long unsaturated alkyl side-chains.[12]

2.1.1 Structure. CNSL is an alkyl phenolic oil contained in the spongy mesocarp of the cashew nut shell from the cashew tree *Anacardium occidentale* L. It is a by-product of the cashew nut processing industry, obtained as a dark brown, viscous, vesicant liquid.

CNSL is derived from the most diffused roasted mechanical processes of the cashew and is a powerful phenolic pollutant of the cashew agro industry. It is a mixture of anacardic acid (71.7%), cardanol (4.7%), traces of cardol (18.7%), 2-methylcardol (2.7%),[13] and the remaining 2.2% is unidentified polymeric material, as shown in Fig. 1.

The pentadecyl alkyl side chain (R) of each of these constituents may be saturated, mono-olefinic, di-olefinic or tri-olefinic with a high percentage of the components having one or two double bonds per molecule of CNSL. In total, it is a mixture of 16 phenolic components with varying percentages.

Amongst other components in CNSL, anacardic acid is a highly corrosive and poisonous material. It is of less use commercially but has medicinal effects such as antimicrobial,[14] antitumour[15] and molluscicidal activities. It is a potential enzyme inhibitor for tyrosinase[16] and acetytransferase[17] and showed other potential therapeutical[18] and antioxidant[19] benefits.

The presence of dual functionalities in cardanol and cardol, namely phenolic and long-chain alkyl/alkylene moieties, has been widely utilized as such or modified further for applications[20,21] mainly as plasticizers,[22–25] adhesives,[26] fuel additives,[27] surfactants,[28–35] resin additives[36–39] and intermediates which act as precursors for other chemicals such as in the formation of cardanol-based fullerenes and porphyrin derivatives.[40,41] They also act as material for a variety of soft nanomaterials[42] such as nanotubes, nanofibers and gels.[43] Cardanol and cardol are the major constituents of cashew nut shell liquid and show both high cetane number and heating value (36–40 MJ kg^{-1}) equivalent to that of fuel oil along with excellent solubility in diesel[44] and light lubricating oils. The presence of strongly polar phenol group also induces antioxidant properties thereby contributing to high stability at room temperature. However, storage at high temperature leads to polymerization accounting for increase in oil viscosity.[45]

2.1.2 Extraction and characterization. Extraction of CNSL from cashew nut shell and isolation of its components are carried out by techniques such as solvent extraction, pyrolysis, heat and supercritical carbon dioxide extraction. CNSL is commercially produced in two ways and available in two grades.[46] (i) *Natural grade*: the cold-processed CNSL, obtained by solvent extraction of cashew nut shells, has anacardic acids (60–70%) and cardols (20–25%)[47] as major components. (ii) *Technical grade*: the hot-processed/heat-extracted CNSL, which oozes out of the shells during roasting of the nuts for separation of the kernels. The major components of the hot-processed CNSL are cardanols (60–70%) and cardols (20–25%) with minor quantities of 2-methylcardols.

Tyman *et al.*[48,49] investigated solvent extraction of CNSL from the shell material using organic solvents (carbon tetrachloride, light petroleum, or diethyl ether) and extracted CNSL in 15–30% yield using long extraction times ranging from 1 to 14 days. Higher yields of CNSL can be achieved by changing the polarity of organic solvents, using longer extraction runs, and using finely ground shells. However, this method requires harsh mechanical pre-treatment and, further, use of organic solvents tends to extract undesirable coloured compounds from the shell material. Thus, the use of organic solvents for separating CNSL from cashew is mainly suitable for small-scale analysis rather than for large-scale processing due to use of organic solvents which accounts for the high cost and non-green solution. In another procedure, solvent extracted CNSL using Soxhlet apparatus[50,51] was separated into various constituents, namely anacardic acid, cardanol and cardol, using alanine as an extractant to facilitate the separation of monohydric and dihydric phenols and removal of polyhydric phenols. Decarboxylation of anacardic acid in CNSL can also be achieved in toluene as solvent using Dean-Stark apparatus in 3 h. Cardanol was obtained in 50% yield when decarboxylated CNSL was heated at reflux in methanol–formaldehyde–diethylenetriamine (200 : 20 : 3 v/v/v) solution for 2 h.[49]

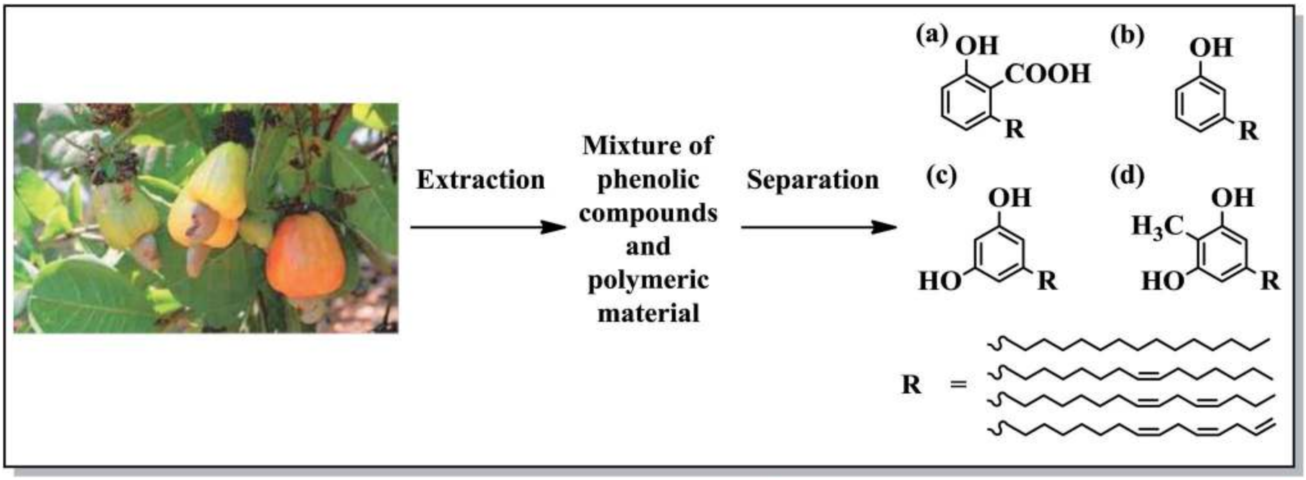


Fig. 1 Components in CNSL: (a) anacardic acid, (b) cardanol, (c) cardol, and (d) 2-methylcardol.

Typically, the composition of heat-extracted CNSL is approximately 52–60% cardanol, 10% cardol and 30% polymeric material. In the heat-extraction procedure, CNSL is extracted from shell at a high temperature in the range 80–200 °C. Once it reaches a temperature of 180 °C, it is kept for 2–3 h to ensure occurrence of the decarboxylation process. During this process, the percentage of cardanol is increased to ~68% at the expense of thermal decarboxylation of anacardic acid. Heat-extracted CNSL is often further processed by distillation at reduced pressure to give distilled technical grade with removal of the polymeric material. The composition of the distilled technical grade CNSL is about 78% cardanol, 8% cardol, and 2% polymeric material.

Extraction by vacuum pyrolysis at 500 °C and 720 mmHg mainly yields cardanol and cardol along with substituted phenols and phthalates. Maximum yields of about 40% (~16% obtained up to 150 °C plus 24% obtained on pyrolysis) have been achieved.[44,52]

Green extraction procedures such as the use of supercritical carbon dioxide (Sc-CO_2) were also explored for the extraction of CNSL. It was found that a flow rate of 4–5 kg h^{-1} at 40 °C and 250 bar yielded 19% phenolic lipids in 17.5 h.[53] The process conditions were further modified and optimized, and it was found that the fraction mainly contained cardanol (70–90%) with traces of anacardic acid and cardol at a flow rate of 0.8–1.3 kg h^{-1} at 50 °C and 300 bar in 0.9 h.[54] A much higher percentage of cardanol (85%) was obtained at 300 bar and 60 °C using Sc-CO_2 extraction. The yield obtained was much higher than that of the technically distilled grade CNSL.[55] Chemical degradation, especially decarboxylation of the anacardic acid, did not occur during the extraction with Sc-CO_2 solvent in the pressure profile separation method.[54,56] The latter method involves penetration, dissolution, expansion and rupture of the shell matrix due to depressurization of the CO_2 to increase mass transfer and phase contact area. CNSL extracts obtained with the pressure profile method using pressurization–depressurization steps with CO_2 at a flow rate of 5 L min^{-1}, 60 °C at standard atmospheric pressure and followed by depressurization to 0.1 MPa contained cardanol (19–22%), cardol (26–32%) and anacardic acid (46–52%).

Extraction of cardanol from natural grade CNSL requires separation of anacardic acid as a salt followed by the use of different solvents to separate other components. Anacardic acid can be isolated from CNSL by its precipitation as either calcium[57] or lead[58] anacardate on treatment with corresponding hydroxides. The salt of anacardic acid was filtered, dried and treated with hydrochloric acid to release free anacardic acid from the mixture. The acid-free CNSL was treated with liquor ammonia and extracted with hexane–ethyl acetate (98 : 2) to separate the mono-phenolic component, cardanol. Subsequently, ammonia solution was extracted with ethyl acetate–hexane (80 : 20) to obtain cardol.[59] Anacardic acid can also be separated from solvent-extracted CNSL by column chromatography using silica gel with ethyl acetate–hexane (1 : 3 v/v) and triethylamine (0.5%) as eluent mixture to elute cardanol and cardol followed by elution with acidic (acetic acid, 1%) eluent mixture.

Separation of cardanol especially from cardol is based on physical processes such as vacuum distillation[6] or a chemical process,[13] or a chemical treatment has been described in the literature.[47,60] 3-Pentadecadienylphenol was obtained as the main fraction when CNSL was distilled at 205–219 °C at 1.5 mmHg.[6]

The purity and identity of components and their derivatives were confirmed by HPLC[53,57,58,61] and mass analysis,[27] and IR,[52] ^{1}H-NMR[27,52,58] and ^{13}C-NMR[52] spectroscopies.

In HPLC purification of CNSL, a gradient elution system was used either with a mixed solvent such as acetonitrile–water–acetic acid in the ratio 80 : 20 : 1;[57,62] or 66 : 22 : 2 with tetrahydrofuran (THF)[58] or THF[61] alone at a different flow rate of 1.8, 2.7 or 0.8 mL min^{-1}, respectively. HPLC trace showed four different peaks at retention times ranging from 3.5 to 10.7 min corresponding to first elution of cardanol–triene (39.6%) followed by other fractions namely diene (20.2%), monoene (31.4%), and saturated (2.7%) akyl side chain, respectively.

GC-MS analysis showed m/z at 304 and 320 corresponding to saturated cardanol and cardol, respectively.[62] Tyman *et al.*[58] reported m/z ratio of cardanol, cardol and 2-methylcardol with monoene, diene, and triene constituents at 304.1, 302.2, 300.1, 298.1; 320.2, 318.2, 316.2, 314.2; 334.4, 332.4, 330.4, 328.4 respectively. The four m/z values which differ by 2 units for each component confirm the presence of four different alkyl chains which differ by a double bond. ESITOF MS[27] also showed m/z at 297 [$(M - H)^-$ of cardanol], 299 [$(M - H)^-$ of cardanol], 301 [$(M - H)^-$ of cardanol], and 303 [$(M - H)^-$ of cardanol] which further confirms the variation in double bonds in side chains.

The FTIR spectrum of cardanol[52] showed characteristic peaks due to O–H stretch (3363 cm^{-1}), C–H vibration of the unsaturated hydrocarbon moiety (3010 cm^{-1}), C–H asymmetric and symmetric stretching vibrations of alkyl side chain (2930, 2849 cm^{-1}), C=C and aromatic stretching bands (1601, 1454 cm^{-1}), terminal vinyl group (907 cm^{-1}) and also the vinyl peak (630 cm^{-1}). In another publication, C–H vibration peaks at 994, 976, and 912 cm^{-1} were ascribed to the conjugated *cis*–*trans* double bond, non-conjugated *trans* double bond, and terminal vinyl group in polycardanol, respectively.[63]

A typical ^{1}H-NMR spectrum[27,52,58] of cardanol diene showed signals due to terminal –CH_3 groups centered at 0.85 (CH_3, t), long aliphatic side chain methylene protons in three different environments observed at 0.88–1.59 (n-CH_2, m, 27H), 1.85–2.25 ($CH_2CH{=}$, m, 4H), and 2.9 [$CH_2(CH{=})_2$, m], benzylic protons at 2.56 (CH_2Ar, t, 2H, J = 7.4 Hz), olefinic protons at 5.05–5.42 ($CH{=}$, $CH_2{=}CH$–, m, 4H), and aromatic protons as a multiplet at 6.63–6.80 (HAr, m, 3H) and 6.95–7.05 (HAr, m, 1H). ^{13}C-NMR[52] spectra for cardanol diene and cardol monoene were reported with aliphatic signals ranging from 11 to 38 ppm and aromatic ones from 112 to 155 ppm, respectively.

Both CNSL and cardanol are considered sustainable, low cost and largely available natural resource by-products. Cardanol possesses interesting functional structural features that allow chemical modification to generate a range of amphiphiles and useful monomer structures.

2.2 Lignin

Lignin is an aromatic polymer that is mainly found in the cell walls of secondarily thickened cells, making them rigid and impervious. It is synthesized in plants by enzyme-catalysed oxidative combinatorial coupling of 4-hydroxyphenyl propanoid units.[64,65] The molecular weight of lignin ranges between 600 and 15 000 kDa. Lignin is usually exploited as an energy source in paper mills and bio-ethanol industries and it is a residue of alcohol and sugarcane industries, and paper and pulp mill waste water discharge. Nearly 40–50 MT per annum waste lignin is generated by the pulp and paper industry. These wastes are chiefly used as an energy source by combustion and only 5% is used for other purposes.[66]

2.2.1 Structure and source of chemicals. Lignocellulosic biomass is made up of three main components, hemicellulose, cellulose and lignin, of which the lignin fraction can account for up to 40% of the dry weight. Lignin is an amorphous biopolymer in which hydroxyphenyl propane units are connected with ether and partial carbon–carbon bonds in a helical structure.[67] Lignins are highly functionalized bio-macromolecules possessing primarily alkyl–aryl ether linkages, aliphatic and aromatic hydroxyl groups and low polydispersity, which offer potential for high value-added applications in renewable polymeric materials development. Lignocellulosic materials have been proposed as large-scale renewable resources for chemicals and sugars to reduce society's dependence on non-renewable petroleum-based feedstocks.

The major chemical functional groups in lignin include hydroxyl, methoxy, carbonyl and carboxyl in various amounts and proportions, depending on genetic origin and extraction processes. Phenolic chemicals can be obtained from lignin by chemical disassembly processes.

Although lignin is the most abundant natural phenolic polymer, its phenol activity is extremely low due to etherification of phenolic hydroxyl groups of lignin precursors in the biosynthetic process. The basic building blocks of lignin can be schematically simplified into "C9" units each made up of a phenolic moiety bearing three aliphatic carbons. The aromatic components are moreover differently substituted by methoxy groups, whereas the aliphatic portions are characterized by the variable presence of C═C unsaturations, hydroxyl functionalities, and other less frequent substituents.[68–70] A representative structure of lignin[71] is shown in Fig. 2.

The polyphenolic structure of lignin is chemically stable and therefore vigorous reaction conditions are needed to modify or transform its structure. The presence of oxygen during transformation prevents its depolymerisation into simple green monomers. The highly reactive radical reaction intermediates during thermal conversion result in oligomeric products of increased molecular weight, *e.g.* tars or solid chars. Utilisation of reactive additives[66] such as radical scavengers, *e.g.* phenol, supercritical water–phenol mixtures; reactive hydrogen-containing compounds, *e.g.* tetralin, 9,10-dihydroanthracene; and hydrogen in the presence of metal catalysts prevents degradation of vinyl and allyl substituents by means of hydrogenation

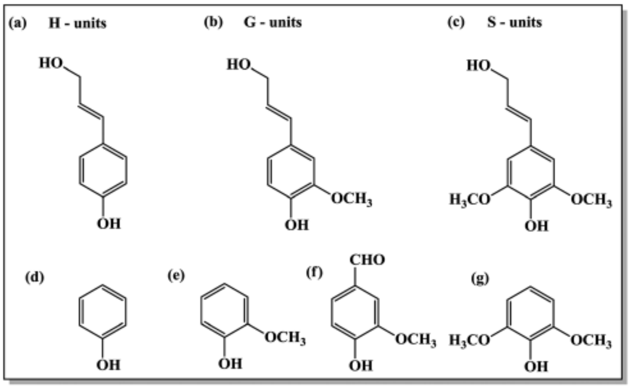


Fig. 3 Lignophenol: basic units. (a) H: *p*-coumaryl alcohol (*p*-hydroxyphenyl derivative), (b) G: coniferyl alcohol (guaiacyl derivative), (c) S: sinapyl alcohol (syringyl derivative). Structures of phenols derived from basic units are (d) phenol, (e) guaiacol and (f) vanillin, and (g) syringol from (a), (b) and (c) respectively.[65,71]

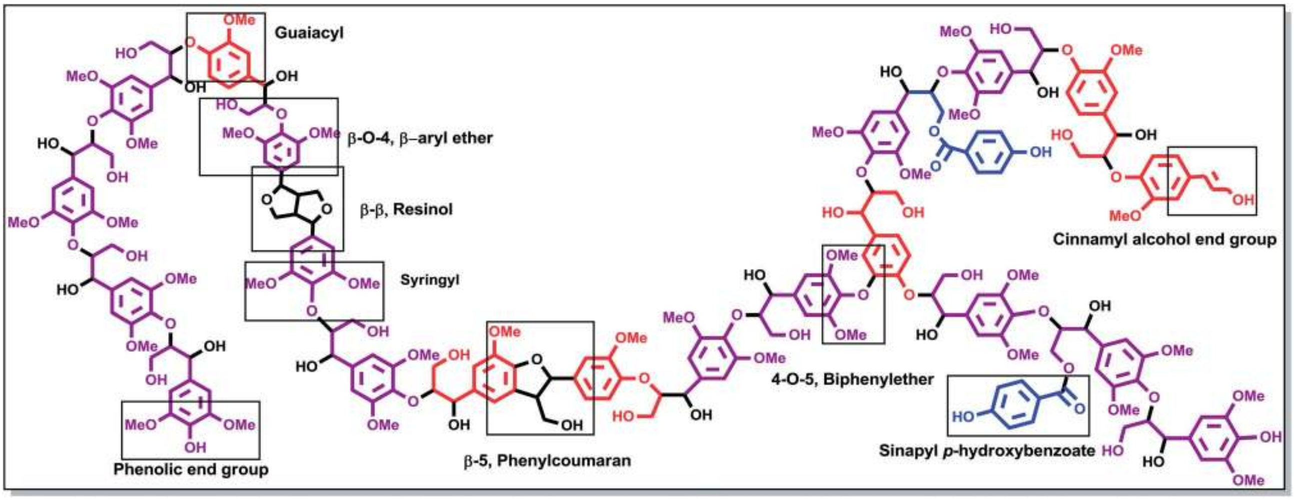


Fig. 2 Structural representation of a lignin polymer from poplar wood, as predicted from NMR-based lignin analysis.[71]

and capping radicals. Lignin pretreatment, dissolution and catalytic treatment is an important area for production of substituted phenols and other important chemicals.[72] The basic aromatic phenols[66,73,74] obtained from lignophenols are structurally represented in Fig. 3.

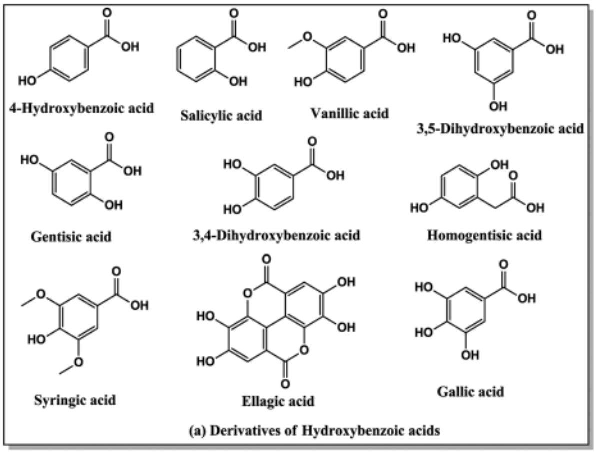
The three basic units – namely, (a) H: *p*-coumaryl alcohol (*p*-hydroxyphenyl), (b) G: coniferyl alcohol (guaiacyl) and (c) S: sinapyl alcohol (syringyl) – are differentiated by the presence and position of methoxy groups. In comparison to H units, the aromatic ring of S and G unit substituted phenols is more electron rich to facilitate electrophilic attack but that of phenolic H unit derivatives is less sterically hindered for ring substitution.

Generalized chemical structures of sustainable and valuable aromatic chemicals obtained by cleavage of aryl ethers and aryl–alkyl linkages from lignin are shown in Fig. 4.

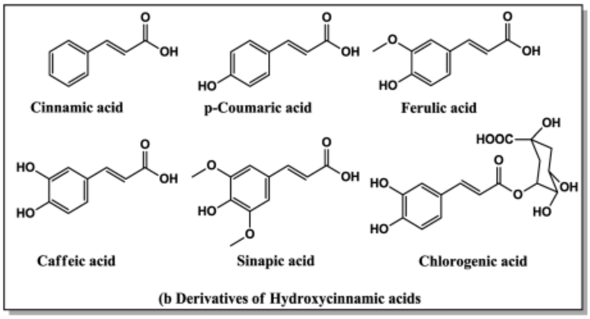
The lignin fraction in these materials contains numerous phenolic components, mainly acids such as ferulic (FA), *p*-coumaric (PCA), syringic, vanillic and *p*-hydroxybenzoic acids. FA and PCA are the major phenolic compounds present in sugarcane bagasse.[75] In addition, there are certain substituted phenolic compounds with alkyl/alkylene chains present in palm, soybean, maize, sunflower, rapeseed *etc.* These classes of phenolic compounds are called tocols such as alpha-, beta-, gamma-tocophenols and tocotrienols (Fig. 5).

2.2.2 Nature of wood. Lignin, the second major component of cell walls of hardwood and softwood as well as lignocellulosic fibres of annual plants, is a highly branched and amorphous macromolecule, whose structure varies with the vegetable species. Lignins are complex aromatic biopolymers that vary in composition and structure as a function of genotype, phenotype, and environment, as well as with the cell type and maturity of the plant tissue, and genetic improvement of plants.[76,77]

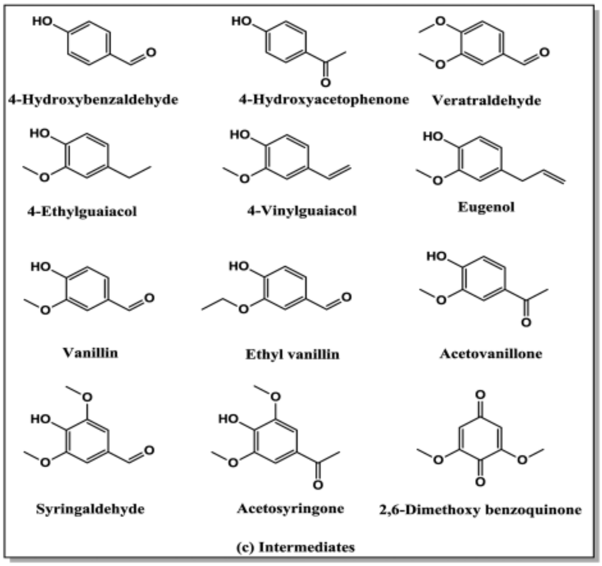
The H, G, and S units are not discrete within either a cell or a given lignin molecule, and the compositional ratios of these three moieties can vary significantly. This inherent complexity and heterogeneity of lignin, both in structure and composition, make it extremely difficult to develop a conversion technology that can efficiently and cost-effectively process a wide range of sustainable feedstocks. Genetic engineering strategies are involved to design lignin polymers so that the development of feedstocks can be tailored for efficient biofuel production, and optimal and selective chemical feedstock production.[78]



(a) Derivatives of Hydroxybenzoic acids



(b Derivatives of Hydroxycinnamic acids



(c) Intermediates

Fig. 4 Naturally occurring phenolic compounds from various biological origins obtained from lignin as derivatives of (a) hydroxybenzoic acids, (b) hydroxycinnamic acids and (c) intermediates.[75,176,186,187,233]

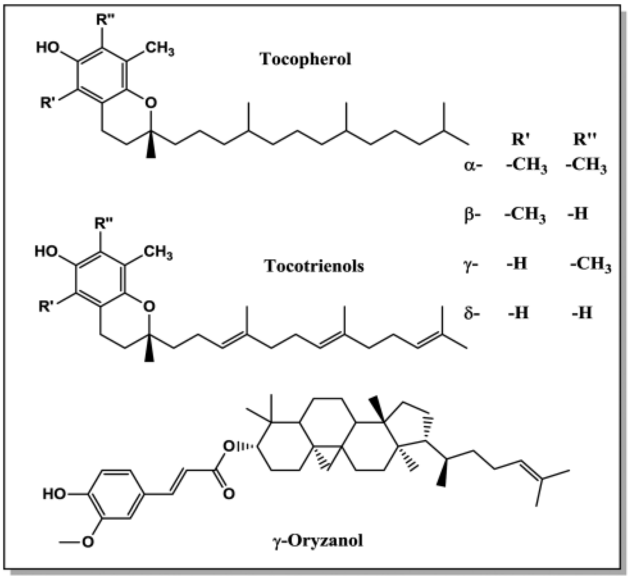


Fig. 5 Phenolic derivatives present in rice bran and other plant-derived oils.

Major constituents of some wood- and agricultural-based materials are shown in Table 1.[73,79–87]

Hardwood is derived from trees like aspen, poplar, birch, elm, and maple, while softwood is from pine, spruce, cedar, fir, larch, Douglas fir *etc.* The composition of the cell wall changes with the kind of tree or plant, but, in general, 40–45% of wood is cellulose, 25–35% hemicellulose, 15–30% lignin, and up to 10% other compounds. Apart from woody biomass, many other biomass feedstocks have been used in the production of phenolic precursors. The distribution of the various constituents varies depending on their origin, ranging from Gramineae (grass and cereals, non-woody biomass) to gymnosperms (softwoods) and angiosperms (hardwoods). Moreover, the lignin content of softwoods is generally higher than the lignin content of hardwoods (Table 1). Grasses are built up from H, G, and S units; softwood lignins essentially consist of G units with low levels of H units; hardwood lignins contain G and S units with traces of H units[88–91] (Fig. 3), except for commelinid monocots which have high abundance of hydroxycinnamic acids.[70,92]

Lignins from monocot grasses incorporate G and S units at comparable levels and more H units than dicots.[65] Softwoods may yield more reactive phenolics than hardwoods due to the relative lack of S units with one methoxy group in softwood-derived liquids compared to G units with two methoxy groups derived from hardwoods. Lignin extracted from sugarcane bagasse[93] has the major proportion of H units in comparison to other sources. The most widely employed feedstocks to date for the production of pyrolytic lignins are hardwoods and softwoods due to consistency, widespread availability and extensive referencing. In addition, lignin and lignin-enhanced biomass are difficult to characterise and to process thermochemically. It was observed that the amount of S and G decreases with increase in pyrolysis temperature, guaiacol derivatives are formed at lower temperatures, while syringol derivatives, phenol and catechol are formed at higher temperatures. Guaiacols undergo secondary decomposition reactions to form catechol.[94]

Table 1 Constituents of lignocellulosic wood and specific fibres[73,79–87]

Wood/fibre	Polysaccharides[a] (wt%)	Lignin (wt%)
Softwood		
Bark[73]	30–48	40–55
Wood[73]	66–72	25–30
Pinus radiata[b,80]	—	28
Pinus taeda[79]	—	27–30
Hardwood		
Bark[73]	32–45	40–50
Wood[73]	74–80	18–25
Eucalyptus regnans[60]	—	23–33
Fagus sylvatica[27]	52–68	40–31
Fibre[82]		
Jute	75–91	12–13
Sisal	76–92	10–14
Plant materials[,83]		
Alfalfa (*Medicago sativa* L.)	—	12–15
Red clover (*Trifolium pratense* L.)	—	7
Bromegrass (*Bromusinermis Leyss.*)	—	10–13
Cornstalk (*Zea mays* L.)	—	8
Oat straw (*Avena sativa* L.)	—	14–17
Wheat straw (*Triticum aestivum* L.)	—	14–18
Cereal straw[82]	53–76	12–20
Barley straw[84] (*Hordeum vulgar* L.)	65–73	15–16
Paddy straw[85]	56	6
Rice husk[86]	51–57	16–24
Sugarcane bagasse[87]	80–75	20–25

[a] Cellulose and hemicellulose. [b] Wood meal. c. g kg^{-1} cell wall determined by Klason method.

Among grasses, the Poaceae family is rich in hydroxycinnamates, namely ferulates (*trans*-4-hydroxy-3-methoxycinnamate) and *p*-coumarates (*trans*-4-hydroxycinnamate).[95] Lignin obtained from other non-woody biomass, *i.e.* wheat straw and sakanda grass (*S. munja*), of Indian origin (ALM lignin) is reported to be richer in phenols as compared to lignin residue (ETEK lignin) obtained as a by-product from ethanol production industry based on softwood of Swedish origin.[96]

Besides hardwood, softwood and non-woody biomass lignins being structurally different in their phenolic component ratios, they also differ in their linkages with cellulosic components. This accounts for their different properties and the strategies for extracting the phenols from them. The difference in aromatic ring structure in woody biomass affects the compositions of the types of linkages with phenylpropane units.[97] The biphenyl-type contents of the condensed structures are usually lower in hardwood lignins and require different pyrolysis conditions. The most abundant lignin linkage is the arylglycerol-β-aryl ether (β-O-4) linkage (Fig. 6a), consisting of two diastereoisomers: erythro and threo forms. Softwood lignin has an almost equal amount of the two forms but the erythro form is predominant in hardwood lignin.[98]

The hemicellulose component in hardwoods mainly contains xylan (*O*-acetyl-4-*O*-methylglucuronoxylan) units, while softwoods have galactglucomannan and xylan (arabino-4-*O*-methylglucuronoxylan) as major and minor components respectively (Fig. 6b).[99] The content of acetyl groups in hardwood hemicellulose is usually higher than that in softwood hemicellulose.[100,101] The chemical structures of hemicellulose in hardwoods and softwoods are different, accounting for different linkages in their backbones. In the case of hardwoods,

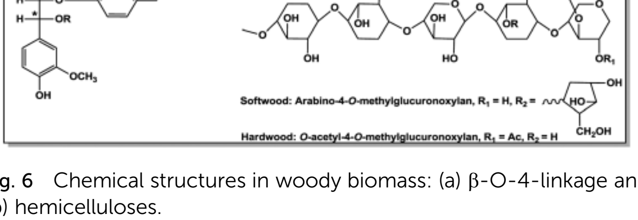


Fig. 6 Chemical structures in woody biomass: (a) β-O-4-linkage and (b) hemicelluloses.

xylan chains contain 4-*O*-methylglucuronic acid with α-(1 → 2) glycosidic linkages and *O*-acetyl substitution at C2–C3. Softwood xylans lack acetyl units and have arabinofuranose units linked by α-(1 → 3) glycosidic linkages.[102,103] In woody biomass, phenolic acids, mainly PCA and FA, have been found to form cross-links between lignins and polysaccharides; in non-woody biomass (wheat straw), PCA is mainly ester-linked while FA is ether-linked to lignin and ester-linked to hemicelluloses forming lignin–carbohydrate complexes (LCCs), as shown in Fig. 7.[104–107] In addition to PCA and FA, even *p*-hydroxycinnamic acids and diferulates[108] are abundant in non-woody plants to form cross-linkages between lignin and polysaccharides.[105,109–113]

Structural differences between softwood, hardwood and non-woody biomass account for different physical properties. Woody structure is physically larger, structurally stronger and denser than agricultural biomass.[114] Softwoods are generally more resistant to hydrolysis as compared to hardwoods. Straw lignin is known to possess characteristic alkali solubility and alkali treatments have been used to increase the digestibility of the complex lignocellulosic chemical network.[115,116] The solubility of straw lignin in alkali has been attributed mainly to the presence of significant amounts of H residues, which are bound to lignin as *p*-coumarate units.[91] Non-woody biomass (straw, grasses or stalks) is more easily treatable than wood (milder temperatures and lower reaction times), and its fermentation conditioning steps are less expensive and efficient.[117–119] The thermoplastic region of softwood lignin is in the range 170–175 °C and that of hardwood in the range 160–165 °C. Softwood lignin has stronger intermolecular hydrogen bonding between the phenolic and biphenol moieties thereby restricting their thermal mobility and leading to a higher glass transition temperature (T_g) than that of hardwood lignin. Softwood kraft lignin (SKL) shows a T_g of 119 °C higher than that of hardwood kraft lignin (HKL) 93 °C.[120] Differential scanning calorimetry (DSC) analysis of pine softwood, eucalyptus hardwood and switchgrass showed the softwood to be the most recalcitrant material and thereby requiring alternative strategies prior to its use as a source for phenols and fuel.[121]

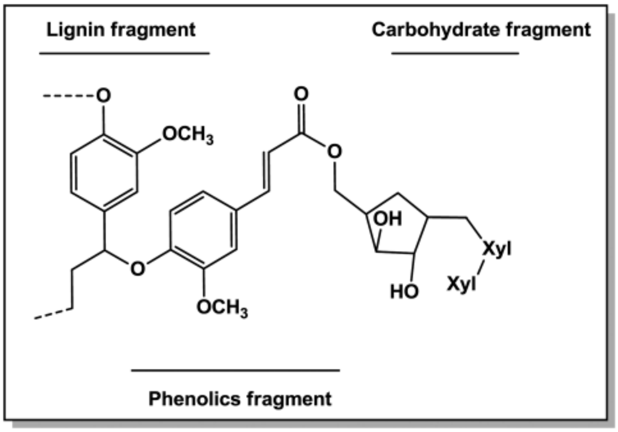


Fig. 7 Lignin–phenolic carbohydrate complex (LCC) in wheat straw (non-woody biomass).

Photodegradation of softwood hinoki (*Chamaecyparis* sp.) and hardwood maple (*Acer* sp.) lignin revealed that the phenolic hydrogen abstraction reaction was faster than the β-aryl ether linkage cleavage resulting in the formation of more non-conjugated carbonyl products than hardwood. In addition, the guaiacyl structure in hardwood degraded faster than the syringyl unit.[122]

2.2.3 **Extraction.**

Several processes have been used for the extraction of lignophenols from lignin. These include phase separation, pyrolysis, thermochemical methods, ultrasonic irradiation, solid state fermentation (SSF), enzymatic modification *etc.*

Lignin exists in plants as a complex polymer and has attached polysaccharides, cellulose and hemicellulose. To liberate lignin-derived phenols requires a pre-treatment step which involves removal of polysaccharides followed by conversion of lignin to high molecular weight lignophenols and low molecular weight substituted phenols. The nature of biomass dictates the pre-treatment strategy and conditions, through a depolymerisation process. In general, hardwood requires harsher conditions than softwood and non-woody biomass. The extent and rate of depolymerization influence pre-treatment time and temperature. For example, ionic liquid pre-treatment is effective in terms of depolymerizing switchgrass and pine at 120 °C, and at 160 °C for eucalyptus.[121]

Phase separation is a process where cellulose and hemicelluloses are hydrolyzed to sugars and lignin is converted to a light-colored functional phenolic polymer, lignophenol. The first step in the phase-separation process is based on solvation of lignocellulosic materials by phenol derivatives, resulting in successive cleavage of ether linkages of lignin, swelling and hydrolysis of carbohydrate by concentrated acid. The second step is cleavage of Cβ-aryl-ether linkages by switching functions of lignophenol under mild alkaline conditions. The third step is demethylation of the aromatic methoxy groups in the presence of boron tribromide from lignophenol depolymerised products. The methoxy group of guaiacyl arylcoumaran was effectively demethylated to give catechol type arylcoumaran dimer. In the process, native lignin was modified by phenol derivatives to selectively grafted benzyl position, the most reactive sites, to give 1,1-bis(aryl)propane type lignin-based recyclable polymer, a lignophenol that has the original inter-unit linkage of lignin and has high phenolic content and may partially substitute phenol in resins (Fig. 8).[69]

Through the phase-separation process, lignocellulosics are converted and separated into lignin-based polymers (lignophenols) and hydrolyzed carbohydrates. The resulting lignophenols have unique properties such as high phenolic content, very light colors and high stabilities. The phase-separation procedure involves the addition of drops of bio-oil to a large amount of water, followed by filtration and drying of the filtrate, the resulting insoluble fraction being commonly referred to as pyrolytic lignin devoid of cellulose and hemicellulose.

It was observed that lignophenols are converted to monophenols only under hydrothermal conditions after the phase-separation process. Cupric oxide[123,124] oxidized lignin to form aromatic phenol derivatives such as vanillyls (vanillin,

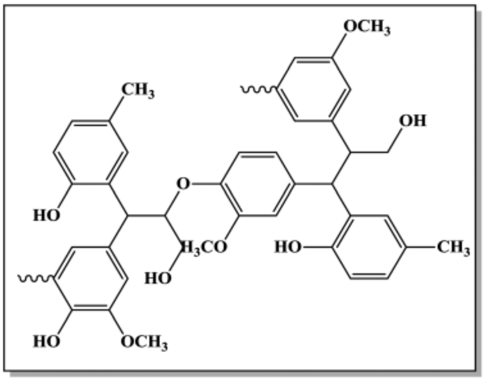


Fig. 8 Conversion of native lignin to lignophenol derivatives ligno-*p*-cresol.[69]

acetovanillone, and vanillic acid) and syringyls (syringaldegyde, acetosyringone, and syringic acid). Other inorganic salts including organometal compounds such as methyltrioxorhenium (MTO), salen complexes, polyoxometallates (POMs), metalloporhyrins, and enzymes[125] such as laccase and peroxidase oxidise lignin to several other organic compounds.[126]

Liquefaction of lignocellulosic materials such as corn,[127] sawdust, woodchips, agricultural residues and peat moss represents another route for obtaining phenolic resin precursors. It is generally performed under high pressure (10–20 MPa) at 290–350 °C and followed by a separation process.

Lignin depolymerisation under pyrolytic conditions leads to high amount of char generation and poor yield of low molecular weight chemicals. However, there has been particular interest in the use of such pyrolytic lignin as a renewable resin from pyrolysis of biomass due to the high yield of pyrolytic lignin and its ease of assimilation into phenol formaldehyde formulations.[73] Fast pyrolysis, as its name suggests, is carried out in the absence of air, and is a relatively recent thermochemical conversion technology. Fast pyrolysis trials were carried out in a small vortex reactor with a capacity of 10–20 kg h^{-1} operated at 480–520 °C to produce optimum yields of pyrolysis oil (55 wt% on a dry basis). The vortex reactor transmitted very high heat fluxes to the biomass causing primary depolymerisation of the constituent polymers into monomers and oligomers. In fluidised bed pyrolysis, though it is not a pure pyrolysis process as a small amount of air is employed, the oxygen only represents of the order of 5% of stoichiometric combustion requirements and the process is therefore quite close to standard fast pyrolysis. Identified compounds are claimed to be all polymerisable with, on average, two positions available for methylene linkages *versus* three for phenol. Rapid Thermal Processing (RTP™) is a method of preparing phenolic precursors by liquefying wood, bark and forest and wood industry residues using a patented fast pyrolysis process. Pyrolysis time (oven dried/N_2/600 °C/40–600 s) dictates the nature of products from monomers, *i.e.* phenolic derivatives (<120 s), to polyaromatic hydrocarbons (>120 s).[128] Pyrolysis reaction pathways have been determined for model compounds to postulate lignin chemical decomposition.[129] The pyrolysis kinetics[130] of lignin using thermogravimetric analysis (TGA) has also been studied to understand the formation of compounds as a function of both rate and change of temperature. Fast pyrolysis of lignocellulosic biomass produces a renewable liquid fuel called pyrolysis oil that is the cheapest liquid fuel (as elaborated on in Section 2.2.5) produced from biomass today, which can be converted into industrial commodity chemical feedstocks.[131] Reviews have been published on fast pyrolysis processes of lignin,[132] on applications of fast pyrolysis liquids including resins and on the production of monomeric phenols by thermochemical conversion of biomass. The production of monomeric phenols through hydrogenation of lignin has been the subject of much research, some of it indicating the potential for substantial yields of phenol and benzene. When heated, lignin component depolymerises to form monomeric and oligomeric phenolic compounds. Lignocellulose biomass on treatment with flash pyrolysis and steam gasification yields substituted phenols, the nature of the phenol generated depending upon temperature of treatment.[133] The importance of kinetic study, degradation mechanism, and chemical products obtained based on the type of thermal treatment have been reviewed.[94] Gani *et al.*[134] studied the effect of lignin and cellulose content on pyrolysis and combustion behaviour for woody (hinoki sawdust, larch bark and palm oil fiber) and non-woody agriculture biomass (rice husk, sugarcane bagasse, rice straw and corn stalk). Pyrolysis of softwood and hardwood lignins showed substantial mass loss occurred at 400–500 °C due to loss of propyl, methoxy and hydroxyl moieties. At pyrolysis temperature ≥500 °C, lignin was converted into fused polyaromatic complexes and it changed to a coke-like product at ~900 °C.[135]

In addition to fast pyrolysis, vacuum pyrolysis has been investigated as a means of producing phenolic resin precursors from lignocellulosic materials. In comparison to fast pyrolysis, longer residence times, of the order of 40 s, are employed in vacuum pyrolysis. The vacuum suppresses condensation reactions in the vapour, as the concentrations of reactants and therefore reaction rates are lower.

Thermal treatment in a hydrogen atmosphere leads to formation of chemicals like phenols, while an oxidative atmosphere produces phenolic aldehydes and acids. Catalytic treatment of lignin[102,136] mainly hydrodeoxygenation (HDO) process led to formation of higher percent of phenolic compounds under comparatively milder conditions.[137–141] Lignin depolymerisation using a catalyst system such as silica-alumina, and further catalytic cracking lead to formation of phenols,[142,128] alkoxyphenols, coke and aromatic hydrocarbons.[143–151] In general, the structure of lignin extracted from each method varies with the nature of the wood and processing conditions such as temperature, solvents, reaction time, catalyst, concentration *etc.* Catalytic processing of lignin depends upon the nature and morphology of the catalyst such as acidity and pore size. For instance, silicalite catalyst favours formation of alkoxyphenols due to stabilization of such structures by the catalyst under fast pyrolysis of lignin; however, the absence of such catalysts leads to higher char formation.[73,152] This process will lead to the formation of lignin samples with varying functional groups, both amount and nature (phenolic and aliphatic hydroxyl groups), molecular weight, polydispersity index, and anti-oxidant activity.[153]

Thermochemolysis is a chemically assisted pyrolysis with the use of chemicals such as tetramethylammonium hydroxide (Py/TMAH) has been used to characterize a variety of natural polymers, including lignin.[154–159] Chen *et al.*[160] reviewed the production of monomeric phenols from thermolysis of lignin. Thermochemolysis product of guaiacyl dehydrogenation polymer in the presence of TMAH led to the formation of (*E*)-5-formyl-2,3,3′,4′-tetramethoxystilbene as major product.[161]

Alternatively, the purification process needs modification due to generation of multi-component and multi-functionality organic compounds. Techniques such as ultrafiltration and nanofiltration of retentate of waste water from a thermo-mechanical pulp mill showed potential of recovery of 11 kg of hemicelluloses and 8 kg of aromatic compounds (lignin) per tonne of pulp.[162] The cost of lignin production from non-woody lignocellulosic feedstock (*Miscanthussinensis* L.) *via* ultrafiltration of lignin fractions obtained by organosolv pre-treatment is estimated as € 52 per tonne.[163] Lignin recovered from different industries has different sets of properties which may be attributed to the presence of residue materials such as water and coexisting carbohydrates. For example, industrial hydrolysis lignin obtained from bio-ethanol production plants showed a lower T_g (−25 to 90 °C) value than that of other industrial lignins, such as kraft lignin or lignosulfate.[164]

The scaling up of a high-temperature process for recovery of chemicals from lignin may not be viable on a commercial scale due to high energy requirements. Therefore, low-temperature processes are preferable to obtain desired chemicals from degradation of lignin. Greener methods such as use of supercritical and ionic liquid solvents[165] over organic solvents, use of enzymatic hydrolysis over metal/acid/alkaline catalysts and use of microwave reactors[166] over traditional reactors are explored either for extraction of lignin from lignocellulosic biomass or for recovery of chemicals[165] from lignin.

Lignin decomposition is also facilitated by green solvents, mainly supercritical water (Sc-H_2O).[167] The decomposition product was found to contain catechol (28 wt%), phenol (8 wt%), *m*- and *p*-cresol (8 wt%) and *o*-cresol (4 wt%) along with other phenolic substituted compounds.[168] Catechol undergoes further decomposition in Sc-H_2O to form phenol as suggested by a change in percentage of phenol at the expense of catechol.[169] Catalytic hydroprocessing of lignin into liquid products in supercritical ethanol overcomes the problems associated with the low lignin conversion (<20%) and char formation at higher temperatures in hot compressed water.[170] Organosolv lignin undergoes depolymerization during a catalytic hydrothermal process with catalysts such as Ni/active carbon and Ru/γ-Al_2O_3 leading to significant reduction of char formation and high yield of degraded lignin with weight average molecular weight of 568 g mol^{-1} and number average molecular weight of 181 g mol^{-1} upon treatment in water–ethanol and pure ethanol media under sub/supercritical condition in hydrogen atmosphere.[171]

Treatment with ionic liquids, such as 1-butyl-3-methylimidazolium chloride (BMIMCl) and 1-allyl-3-methylimidazolium chloride (AMIMCl),[172] $Mn(NO_3)_2$ in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [EMIM][CF_3SO_3][173] and renewable cholinium amino acids [Ch][AA][174] either under microwave irradiation and/or pressure is a good source of either lignin or lignin-based phenols or cellulosic compounds. Treatment with the ionic liquid 1-ethyl-3-imidazolium acetate breaks lignin aggregates into nm-size subunits of different shapes.[175]

Enzymatic processes such as SSF are bioprocesses for synthesis of phenolic compounds from agro-industrial residues and plants including cereal and vegetable wastes such as straw, bagasse, stover, cobs, husks.[176] The process involves digestion of organic polymer molecules by enzymes. The degradation of organic matter is both enzyme- and condition-specific, such as temperature, moisture, concentration, incubation time *etc.* The different weight percent of lignocellulosic biomass ratio mainly of cellulose, hemicelluloses and lignin dictates the digestibility. Lignin obtained by enzymatic hydrolysis could be a novel source for the production of many aromatic phenolic compounds under ambient conditions.[177] Enzymes originating from both fungi[178–180] such as phenol oxidases (manganese and lignin peroxidases), laccase or their isoenzyme and bacterial strains[181,182] such as *Streptomyces viridosporus* T7A, *Nocardia*, and *Rhodococcus* are known to oxidise lignin G and H units to produce compounds such as ethyl salicylate, coumaric, cinnamic and ferrulic acids, gentisate, 3-hydroxybenzyl alcohol *etc.*[183] Therefore, in order to achieve selectivity or to increase the percentage of specific organic compounds from enzyme-assisted degradation of lignin, the development of improved microbial strains has arisen as an attractive and important area for research.[184] The mechanism of biodegradation of wheat straw by *Streptomyces viridosporus* T7A was studied and the observed functional group changes in the lignin structure were mainly carbonyl and methoxy groups.[185] Enzymatic modification of lignophenols is a potential way to convert lignin into chemicals for industrial applications.[186] Phenolic compounds comprise a variety of odorants which can form, be degraded or be modified during processing. Vanillin and other aromatic aldehydes are produced from lignin degradation during wood cooperage and can be released into the wine during barrel ageing.[186,187]

2.2.4 Characterization techniques. Concentrations of lignin from wood pulp samples can be determined[188] both by non-invasive[77,189] and invasive methods.[78,190] The non-invasive methods are based on the fact that the chemical structure of lignin allows it to absorb electromagnetic radiation in specific regions. The characteristic features of spectra in a specific region (wavelength, wavenumber or chemical shift) will be proportional to the amount of lignin in a sample determined by either utilizing molar extinction coefficient (UV-visible spectroscopy), or overlap intensities of modified and unmodified matrix infrared (IR) and near-infrared spectroscopy[191,192] or integration of specific peaks in solid state nuclear magnetic resonance (NMR) spectra[193] with a sample of known lignin content. The non-invasive methods dictate whether the extraction of lignin from wood is economical and cost-effective.

On the other hand, invasive methods are based on volumetric titrations or gravimetric techniques using specific chemical treatments such as acetyl bromide or thioglycolate.

The lignin content was estimated by the gravimetric Klason procedure.[194] The lignin structure can be investigated by chemical methods such as thioacidolysis,[195,196] copper oxide oxidation,[197–204] nitrobenzene oxidation (NBO), and derivatization followed by reductive cleavage (DFRC).[205] The composition (H/G/S) of the lignin polymer and its quantification were achieved by DFRC method using pyrolysis-gas chromatography-mass spectrometry (GC-MS). This involved NBO, pyrolysis (GC-MS), thioacidolysis and DFRC.[206] This analytical process involves lots of time for preparation and analysis due to it being a multi-step process. A streamlined thioacidolysis method and near-infrared reflectance-based prediction modeling allows quicker analysis.[207]

A spectroscopic technique such as FTIR, NMR *etc.* is used to differentiate the nature of wood. FTIR spectra of softwood box (*Buxus sempervirens*) and hardwood aspen (*Populus tremula*), in the fingerprint region 1800–800 cm^{-1}, showed prominent differences in the transmittance values. A reduced intensity of the band at 1740 cm^{-1} is slightly greater in aspen than in box, which can be attributed to a greater number of acetyl groups in the case of the former.[208,209] The difference in the guaiacyl content between softwood and hardwood is elaborated by a doublet detected at 1610–1595 cm^{-1}, while there is only one band at 1595 cm^{-1} respectively.[210] Generally, hardwood shows equally intense peaks at 1595 and 1510 cm^{-1}, attributed to the predominant syringyl unit, while, in softwood, the band at 1510 cm^{-1} is more intense than at 1595 cm^{-1}, attributable to a higher content of guaiacyl units.[211] In SKL, the 1269 cm^{-1} band (guaiacyl ring breathing with carbonyl stretching) is more intense than the 1214 cm^{-1} band and there is no syringyl absorption at 1327 cm^{-1}, whereas the opposite is true for hardwood lignins; that is, a weak 1269 cm^{-1} band, a strong band at 1215 cm^{-1}, and a syringyl absorption at around 1327 cm^{-1}. The presence of a syringyl unit in hardwood lignin is also evident from the higher intensity of the band at 1462 cm^{-1}.[120] The presence of higher percentage of methoxy groups in hardwood is indicated by the peak near 1600 cm^{-1} due to aromatic –OCH$_3$ stretching.[210,211]

NMR spectroscopy provides information about the structural configuration, quantification, chemical composition, and linkages present in lignin samples.[212–214] ^{13}C–^{1}H correlated (HSQC, HMQC)[215,216] and ^{13}C-NMR[217–221] both solution and solids state are reported in the literature to elucidate the structure of lignin. NMR studies confirmed the higher concentration of methoxy signals in HKL as compared to SKL due to predominance of both G and S units in the former. It is observed that purified isolated lignins, namely, "cellulolytic enzyme lignin", give good quality spectra as they are devoid of cellulosic component. Cell wall lignin polymers and polysaccharides in the native state are also identified and characterized during hydrothermal treatment of wheat straw lignin using solution state 2D-NMR spectroscopy.[222] Non-woody biomass such as corn stover was studied for the structural changes shown by lignin and LCCs characterized by alkaline nitrobenzene oxidation, ^{13}C-NMR, and ^{1}H–^{13}C HSQC NMR studeis.[223]

The composition and nature of lignin phenols are also determined by the compound-specific radiocarbon analysis (CSRA) technique.[224,225]

Microscopy techniques such as confocal microscopy along with histochemical Mäule staining provide indication for S units in composition of lignin at a cellular level.[226,227] The H/S/G composition can also be determined by laser capture micro-dissection combined with the microanalysis of lignins.[227]

Mass spectrometry (MS) techniques such as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS)[228,229] were used for the analysis of the depolymerized fragments of lignin polymers, structural determination of monolignols, and syringyl to guaiacyl (S/G) ratio[230] in order to obtain information on the complex polymer structure of lignin present in plant cell walls. It was found that rupture of inter-unit linkages at 8-O-4′, 8-1′, 8-5′, and 8-8′ in lignin showed m/z 137 and 151 due to guaiacyl ring.[229] FT-ICR MS of wheat straw lignin showed some regularity with a difference of 44.026 m/z (C_2H_4O) units suggesting lignin is not a completely random polymer.[230,231] Other MS techniques such as jet-cooled thermal desorption molecular beam (TDMB), secondary ion MS (SIMS), and synchrotron vacuum-ultraviolet secondary neutral MS (VUV-SNMS) were also used to understand the fragmentation mechanism of monolignols under different energetic processes. The positive ion SIMS spectrum of coniferyl alcohol showed characteristic peaks at m/z 137 and 151.[232] A study on wheat straw lignin using atmospheric pressure photoionization quadrupole time-of-flight mass spectrometry (APPI-QqTOF-MS) provided evidence that grass lignin is composed of repeating phenylcoumaran units, which are formed from two di-coniferyl units linked by the C8–C′5 covalent bond and the ether C7–O-4′ linkage, forming a furan-like ring attached to an aromatic coumaran ring.[233] Py-MBMS of grass bagasse gave a distinctive fragmentation pattern with high m/z 114 consistent with expected xylan enrichment, and fragments at m/z 150 and 120 indicated coumaryl derivatives, presumably from the hydroxycinnamic acid groups, PCA and FA.[234]

Simple techniques such as GC-MS analysis of pyrolysed softwood and hardwood samples confirmed the presence of syringyl and guaiacyl groups in hardwood and softwood lignin.[235] Non-wood fibers such as hemp, flax, jute, sisal and abaca, and alkali lignins have been analyzed. Hemp and flax have low S/G ratios, while jute, sisal and abaca show high S/G ratios, as revealed by Py-GC/MS and FTIR analysis. Py/TMAH showed a significant amount of PCA in the abaca lignin and much lower cinnamic contents in the other lignins. This analysis also confirmed that PCA is attached to cell walls through ester bonds, while FA is attached through ether linkage, except in sisal where the linkages are found to be reversed.[236] Softwood lignin pyrolysis afforded coniferyl derivatives while hardwood lignin gave coniferyl and sinapyl derivatives and grass lignin *p*-vinylphenol as confirmed by GC-MS studies.[237]

Thermal characterisation such as DSC[120,121] and TGA and thermorheological analysis can also provide insight about the nature of wood. The yield of carbon generated from SKL and soda hardwood lignin was found to be 37% and 34%, as analyzed by TGA studies at 900 °C.[238] The viscosity of softwood and hardwood lignins was found to be considerably different due to their different chemical structures and molecular weights, the former showing a lower value of 2.8 poise and the latter of 3.5 poise at 1.8 s^{-1} at 225 °C.

2.2.5 Lignin pyrolysis oil. The properties of lignocellulosic biomass such as carbon neutrality, relative abundance, renewability and non-food competition[239,240] mean that it is considered as an important primary feedstock for generation of renewable fuels and chemicals. Amongst various possible extraction techniques, pyrolysis has come up as an economically viable option for the generation of lignin pyrolysis oil by virtue of low capital and operating costs.[241] Apart from addressing the sustainability issue, lignin pyrolysis oils have also been of economic relevance due to their attractive fuel selling price of $ 2.48 per gallon, as supported by PNNL (Pacific Northwest National Laboratory).[242,243] The cost of the final oil product is in the range $ 2.11–3.09 per gallon, depending on the source of biomass.

Amongst prominent lignocellulosic fractions, cellulose is primarily used for pulp and paper production (5–36 × 10^8 T per annum).[244] Cellulose[245,246] and hemicellulose can be also hydrolyzed to fermentable sugars that can be either fermented to produce ethanol or butanol, or transformed by hydrogenation or dehydration methods to yield intermediates important for chemical syntheses and fuel purposes. The upgrading strategies are different for lignins being phenolic in nature, whereas cellulose and hemicelluloses are polysaccharides. Bio-oil yielded from lignocellulosic biomass *via* the fast pyrolysis technique comprises both water-soluble and insoluble fractions, of which the former with high oxygen content is derived from cellulose and hemicellulose fraction of biomass. Cellulose being a pure polymer of glucose can be converted to high-quality bio-oil. Under rapid pyrolytic conditions, pure cellulose yields levoglucosan which can easily be hydrolyzed to glucose, but, generally, due to the presence of small amount of alkali, hydroxyacetaldehyde is formed instead.[247] Catalytic pyrolysis of cellulose has also confirmed it to be the highest hydrogen producer amongst all the biomass components.[248] Apart from thermal treatment, microbial methods[249] and chemo-catalytic conversions[250,251] have also been explored to effect the conversion of cellulose to biofuel. Cellulose and hemicellulose have received widespread attention as possible fossil fuel alternatives due to their easy convertibility[252] but lignin has largely remained underutilized except for possible applications in paper pulping, bioethanol fermentation or as a low-value fuel because of its inhomogeneity and resistance to degradation.[253] The conditions for pyrolysis of lignin to generate oil depend on feedstock composition and experimental conditions, such as temperature, residence time and nature, morphology and type of catalyst, which are different from its use for generation of chemical intermediates as discussed in Section 2.2.3. The pyrolysis products from lignin contain mainly water-insoluble heavy oil (65–85 wt%),[254,255] whereas tannin and cellulose yield mostly water-soluble light oil, which contains >60 wt% of water and water-soluble components such as methanol, levoglucosan and catechol. In comparison to lignin, pyrolysis of tannin and cellulose yields ~78 wt% and ~85 wt% of light oil respectively.[256,257] This accounts for the analysis and development of new and different process technologies for conversion of lignin to pyrolysis oil in comparison to whole lignocellulosic biomass in terms of chemistry, mechanism, upgrading, catalysts *etc.*[258]

In comparison to traditional oils, pyrolysis oils have high oxygen and unsaturated content in addition to several other drawbacks, such as poor volatility, corrosiveness, viscosity, thermal instability, high coking tendency, low heating value, and immiscibility with petroleum fuels.[131] This hampers the prospects of their commercialization, thereby necessitating the utilization of upgrading technologies that convert pyrolysis oils to potential substitutes for diesel and gasoline. The upgrading process stabilizes the pyrolysis oil and reduces or eliminates the inferior properties mentioned above, enhancing its compatibility with gasoline. Several upgrading techniques, ranging from catalyst cracking, to HDO, to hydrotreatment, are being explored.

Zeolite cracking is one of the most widely explored catalytic upgrading routes for pyrolysis oil. It was found that H-ZSM-5 zeolite improves lignin depolymerization[143] and leads to complete deoxygenation[143,147,149] of liquid phase producing simple aromatics and naphthalenic structures. Modification of ZSM-5 zeolite with substitution of metals such as nickel, cobalt, iron, and gallium resulted in the highest amount, ~16 wt%, of hydrocarbons.[259] Also, pyrolysis of several biomasses such as corn stalks, cassava rhizome, hybrid poplar wood, rice husks and pine wood with ZSM-5 zeolites resulted in a lowering of oxygen content. The use of nickel salt additive along with zeolite resulted in an improvement in the decomposition of aliphatic hydroxyl, carboxyl, and methoxy groups and ether bonds in lignin.[260] The variation in the ratio of Si : Al in zeolites has shown a profound effect in cracking reactions during thermal treatment of biomass. The lowering of Si : Al ratio in H-Beta zeolites resulted in formation of less organic oil, more water, and polyaromatic hydrocarbons.[261] The pyrolysis of SKL in the presence of various H-ZSM-5 zeolites with different $SiO_2 : Al_2O_3$ mole ratios ranging from 23 : 1 to 280 : 1 at 600 °C was studied. H-ZSM-5 zeolites lead to an almost complete decomposition of aliphatic hydroxyl and carboxyl groups and the content of polyaromatic hydrocarbons in pyrolysis oil was found to decrease with an increase in $SiO_2 : Al_2O_3$ ratio. Also, an 8–16% decrease in the molecular weight was observed in the presence of zeolites.[262] Mixing of H-ZSM-5 with organosolv lignin extracted from prairie cordgrass (PCG) in a ratio of 5 : 1 at 650° C resulted in a 13 wt% yield of PCG lignin. Aspen (woody biomass) showed a two-fold increase in the total aromatic hydrocarbon yield obtained from organosolv lignin pyrolysis in the presence of H-ZSM-5, as compared to PCG lignin (non-woody biomass). However, the content of oxygen in the volatile emissions during catalytic pyrolysis was found to be lowered in case of PCG, as compared to aspen, thereby enhancing the quality of pyrolysis oil.[263] Zeolite frameworks also influence the pyrolysis mechanism. FAU and BEA zeolites were found to improve the cleavage of aromatic–methoxy and other ether bonds in lignin yielding pyrolysis oil with gasoline-range molecular weight. Hence, upgraded pyrolysis oil could be used as a precursor of gasoline and possible substitution of petrochemicals. Similarly, other zeolite frameworks, such as MFI, FER and MOR zeolites, could more efficiently decompose the carboxyl groups, thereby reducing the acidity of pyrolysis oil and making it more suitable for use as a biofuel.[264] The cost-effectiveness of the zeolite cracking process can be achieved because of the low amount of hydrogen gas required and the use of a regular non-pressurized reactor. However, the produced oil is of low quality[265] and shows higher coke content. Moreover, although zeolite is effective in deoxygenation of small oxygen-containing molecules such as aldehydes and ketones, its capability is limited for deoxygenation of phenolics due to its small pore size.[266,267] This is accounted for by the difference in reaction pathway governed by reactivity–selectivity principle. When the pore size is small, selectivity increases but reactivity decreases due to different diffusion rates. Zeolites can also be used as catalyst supports for such a process. It was observed that the modification of zeolite into a mesoporous structure significantly increased the reactivity. The dehydration and transalkylation reactions mainly occur on the acid site. In addition, the stronger acidity or bonding with reactants reduces the desorption rate and lowers the reaction rate which implies that acidity and surface area are two key parameters for support material characterization.

HDO is another popular upgrading process which involves hydrogenation of the unstable unsaturated bonds and reduction of oxygen in the pyrolysis oil. It produces high-quality oil, but it requires hydrogen under pressure as one of the major reactants. In contrast to zeolite cracking, the cost of hydrogen and pressurized reactor reduces the viability of this process. Commonly used catalysts in the HDO process are sulfided and transition metal catalysts. Sulfided catalysts such as NiMoS/Al_2O_3, CoMoS/Al_2O_3 *etc.* are more often used due to their low costs compared to other transition metal catalysts. Although widely used for petroleum materials, this class of catalysts suffers from certain disadvantages owing to the unique nature of pyrolytic oils. The presence of water and high oxygen and coke content[268] in raw pyrolytic oil[269,270] are the factors which may lead to rapid catalyst deactivation resulting in poor yields. In comparison to sulfide catalysts, transition metal catalysts, such as platinum, palladium, ruthenium, rhodium, *etc.* can easily be utilized in the presence of water. They also show higher reactivity for hydrogenation and require moderate reaction conditions.[271,272] But this class of catalysts also suffers from certain disadvantages such as high costs due to demanding catalyst recycle techniques and its sensitivity to sulfur present in kraft lignin. Therefore, feedstock requires special treatment to remove the sulfur before treatment with the HDO process.

Spectroscopic techniques are widely employed to elucidate chemical structure and composition of lignin pyrolysis oil as compared to chromatography and MS techniques. The simplest and most commonly used GC technique can detect only 10–40% of the content of pyrolysis oil due to its complex nature.[273,274] The addition of flame ionization detection to GC leads to an improvement in detection by 30%.[275] NMR methods such as ^{1}H-NMR, ^{13}C-NMR,[275] HSQC-NMR and ^{31}P-NMR were found to be better characterization techniques for both chemical structure elucidation and quantification. ^{31}P-NMR spectroscopy is a widely used technique, for both studying chemical changes during pyrolysis of biomass and quantification of hydroxyl groups. This analysis is based on the phosphitylation of hydroxyl groups with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) to form phosphorus groups linked to the bio-oil.[276] The effect of catalyst (zeolites) on the pyrolytic mechanism,[262,264] variation in the bio-oil quality with the nature of biomass (woody *vs.* non-woody),[263] order of bond cleavage,[277–284] primary cleavage products,[254,277–286] favourable decomposition steps,[254,277,279,287] efficacy of a particular extraction methodology[255] *etc.* were investigated using these spectroscopic methods. GPC analysis is another technique employed to determine optimal pyrolytic conditions of temperature, time duration,[254] nature of catalyst[264] *etc.*, thereby enhancing the properties of pyrolytic oil.

2.3 Tannins

Tannins are natural phenolic structures present in numerous wood species particularly in the southern hemisphere.[288] They are useful for helping plants to fight against insects and fungi. Furthermore, their astringent character limits the consumption of tannin-rich vegetables by herbivorous animals.[289] Although distributed all through the cytoplasm of any vegetal cell,[290] the highest concentration of such compounds is generally found within tree barks including black mimosa bark (*Acacia mearnsii*), quebracho wood (*Schinopsis batansae*), oak bark (*Quercus* spp.), chestnut wood (*Castanea sativa*), pines (*Pinus radiata* and *Pinus nigra*), fir *etc.* Brazil, India, Zimbabwe and Tanzania are amongst the leading producers of mimosa tannin, Argentina of quebracho tannin and Slovenia of chestnut wood tannin, amongst others.[288] The qualitative and quantitative analytical differences between tannins from plant polyphenols of other types arise from their affinity to bind with proteins, basic compounds, pigments, metallic ions and macromolecular architectures including anti-oxidant activities, *etc.* The specific binding properties are utilized for their quantification protocols. As a result of which, the quantification of tannins is based on their binding activity unlike the analysis of polyphenols.[291]

Traditionally, tannins have found use in leather manufacturing due to their ability to precipitate proteins in animal hides.[288] Other uses for tannins range from cement plasticizers, ore floatation agents, wine additives to pharmaceutical applications. Also, tannins are explored as green renewable material for novolac adhesives,[292] and for formation of resole resins. Their utilization for partial replacement of petro-based phenols in wood adhesive formulation has led to a reduction of pressing and gelation time and also lowered formaldehyde emissions, adding to their ecological relevance.[293]

Tannins can be classified as hydrolysable tannins (HTs) and condensed tannins (CTs) (Fig. 9).[292] The molecular weights of vegetable tannins range between 500 and 3000 Da.

HTs are sourced from chestnut (*Castanea sativa*), myrabolans (*Terminalia* and *Phyllantus*), divi–divi (*Caesalpina coraria*), tara, algarobilla, valonea, oak *etc.* They contain either gallatotannins (monoester, Fig. 9a) or ellagitannins (diester) which on hydrolysis in acidic/basic or enzymatic conditions produce glucose and gallic or ellagic acids. In addition to gallic and ellagic acids, other phenolic acids such as valoneic,

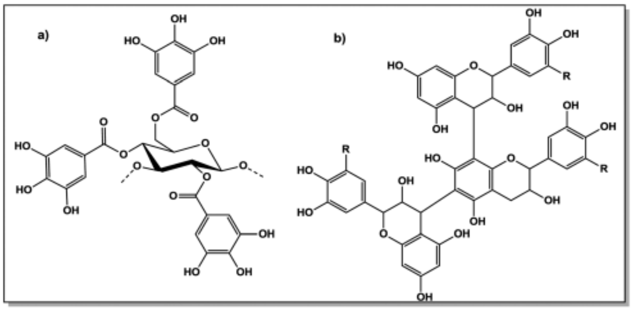


Fig. 9 Chemical structure of (a) hydrolysable tannin (HT) and (b) condensed tannin (CT; when R = H, catechin).

nonahydroxytriphenoic, hexahydroxydiphenoic and flavogallonic acids have also been obtained due to the hydrolysis of ester linkages in HTs (Fig. 10).

The presence of ester linkages explains the susceptibility to acidic, alkaline and enzymatic hydrolysis. However, HTs are not as commercially viable as CTs due to their lack of macromolecular structure, low level of phenol substitution, low nucleophilicity, limited worldwide production and relatively high price. The commercial HTs obtained from chestnut tannin extract contain positional isomers castalagin (14.2%) and vescalagin (16.2%), positional isomers castalin and vescalin (6.6%), gallic acid (6%) and pentagalloyl glucose monomer (3%).

CTs constitute more than 90% of the total world production of commercial tannins (2 × 10^5 tons per year).[294] The main sources of CTs are wattle or mimosa (*Acacia*), quebracho (*Schinopsis*), hemlock (*Tsuga*), sumach (*Rhus*) and various pine (*Pinus*) species. CTs are polymers of a mixture of either flavan-3-ols or flavan-3,4-diols and are most frequently linked *via* either C4–C6 or C4–C8 bonds (Fig. 11).[295,296] They are also called as flavolans or proanthocyanidins such as procyanidins, propelargonidins, prodelphinidins, profisetinidins and prorobinetinidins.[297] Catechin, gallocatechin and epigallocatechin are all precursors of CTs. The structure of flavonoid monomer is represented in Fig. 11.

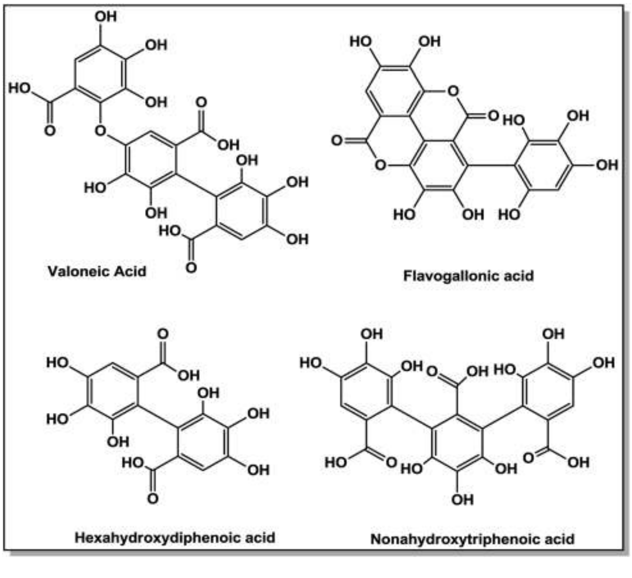
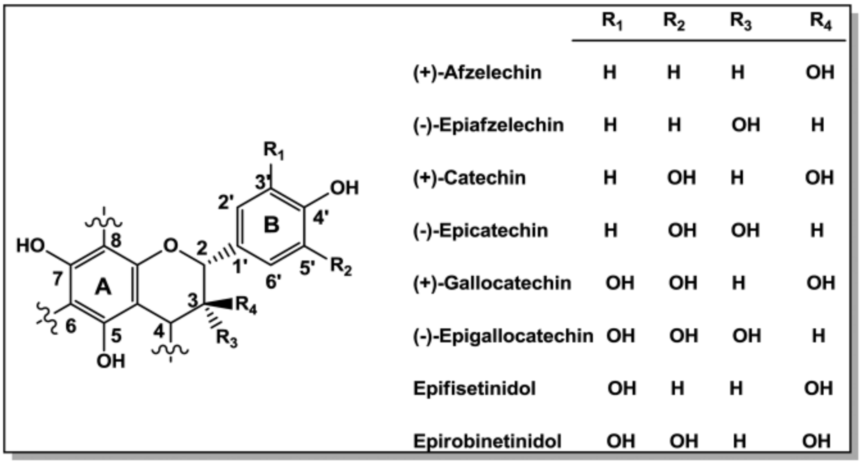


Fig. 10 Phenols and phenolic acids obtained in low molecular weight fractions of HTs.[288]

The flavonoid structure (Fig. 11) comprises two aromatic rings, namely A- and B-ring, which differ in number of hydroxyl groups. A-ring may have one (resorcinol) or two (phloroglucinol) hydroxyl groups while B-ring can have two (catechol) or three (pyrogallol) hydroxyl groups. In addition to this structural variation, A- and B-ring can be linked resulting in formation of different flavanoid monomer structures which differ in reactivities. Such difference in number and position of hydroxyl groups in the two rings dictates their reactivity towards aromatic electrophilic substitution reaction: the A-ring tends to be more reactive than the B-ring.[294] Mimosa tannins are mainly based on prorobinetinidine, being the association of a resorcinol A-ring with a pyrogallol B-ring. In mimosa bark tannin extract, the repeating units are mostly 4,6-linked and sometimes 4,8-linked. In mimosa bark, 70% of CTs contain A- and B-rings as resorcinol and pyrogallol, 25% contain resorcinol and catechol, respectively, while the remainder are the non-tannins (carbohydrates, hydrocolloid gums and small amino and imino acid fractions).[294] The hydrocolloid gums account for the high viscosity of tannin extract even though they are present in low (3–6%) amounts. The properties of CTs depend on the structure of monomer units, degree of polymerization (DP) and the linkage between flavan-3-ol units accounting for a considerable range of structural variation.[298] CTs are oligomeric compounds characterized by sequences of units bearing two or more OH groups per aromatic moiety with DPs varying considerably (2–30) from species to species.[299,300] The soluble extract fraction of mimosa and quebracho tannins contains oligomers of flavonoid units (2–11)[294,301] with an average DP of 4–5, while pine tannins have ~30 units with an average DP of 6–7.[302] The most common classes are the procyanidins, which are chains of catechin, epicatechin, and their gallic acid esters, and the prodelphinidins, which consist of gallocatechin, epigallocatechin, and their galloylated derivatives as the monomeric units.[303] In CTs, the presence of and number of phenolic –OH and free aromatic ring position account for high reactivity and their economic usage for the preparation of adhesives, resins and other applications, apart from the traditional leather tanning for which HTs are well suited. CTs have the capability to replace up to 90% of phenols in phenolic resins.[304] In general, tannins can be structurally modified by acetylation, hydrolysis, condensation, and polymerization reactions.[305–308] They may also be copolymerized with isocyanates, formaldehyde, aminoplast or phenolic resins to yield thermosetting binders for particle panels.[294,304,308]

In addition to the commonly used classification into HTs and CTs, tannins can also be categorized into Type A and Type B based on the chemical structure variation with seasonal changes. Polyphenols of constant chemical structure are categorised as Type A and polyphenols of variable composition as Type B. All ellagitannins are of Type A. The structures and compositions of Type B tannins from a particular plant species behave in a transient manner which varies with season, growth



	R_1	R_2	R_3	R_4
(+)-Afzelechin	H	H	H	OH
(-)-Epiafzelechin	H	H	OH	H
(+)-Catechin	H	OH	H	OH
(-)-Epicatechin	H	OH	OH	H
(+)-Gallocatechin	OH	OH	H	OH
(-)-Epigallocatechin	OH	OH	OH	H
Epifisetinidol	OH	H	H	OH
Epirobinetinidol	OH	OH	H	OH

Fig. 11 Mononmeric unit containing flavonoid units.

conditions of the plant, and extraction methods. Examples of Type B tannins are HTs from Chinese and Turkish gallotannin.[291,309]

2.3.1 Extraction and characterization. Similar to cardanol, isolation of tannins from biomass utilizes extraction techniques such as conventional methods,[310] extraction[311] and green methods such as utilization of microwaves and ultrasonic waves,[312,313] and sub-critical solvents.[314]

In conventional methods, the effect of solvent polarity on the extraction of gallic acid, ellagic acid and corilagin from *P. niruri* was studied using polar solvents such as water, water–ethanol mixture, ethanol, and non-polar solvents such as hexane. The yield of extraction was found to be maximum in polar solvents such as water (26%), followed by aqueous ethanol (27%) and least in hexane (~2%) due to higher salvation of polar tannin phenolic structures.[315] Other solvent systems such as acetone and diethyl ether either alone or in combination with water and ethanol were also reported for the extraction of phenolics from pomegranate aril.[316] Industrial tannin production largely employs and prefers the hot water extraction technique over organic solvents to reduce both VOC emissions and cost. This process requires extraction at 70 °C with longer extraction times, and high water to solid weight ratio. These parameters require optimization to improve both the yield and quality of tannin extract. However, poor extraction efficiencies may be accounted for as due to dilute extraction conditions, prolonged heating duration or use of temperatures >70 °C which may lead to degradation of phenolics.[317] Norway spruce (*Picea abies*) bark appears to be a promising source of tannins by industrial extraction (10.7%), and extraction yield was scaled up to a promising 50% with strict temperature control at a pilot scale.[318]

An alteration in pH of aqueous extracting solvent from neutral to slightly alkaline using aq. Na_2CO_3 (10%) showed an increase in extractive concentration from 25% to 49%. This increase in extractive percentage was due to partial cleavage of pyran rings of phlobaphens (~polyphenols) assisted by alkaline pH resulting in enhanced water-soluble intermediates. However, with an increase in concentration of base in the solvent, there is a simultaneous increase in undesirable non-tannin components which is found to inhibit the utility of extract for adhesive applications.[319] It was found that an alteration of the nature of the base to a mixture of aqueous $Na_2SO_3 : NaHSO_3$ (1 : 1, 0.25%) and NaOH (1%) at 70/80 °C also led to extraction of tannin. The function of NaOH is to increase the alkalinity to improve tannin yields in the extract while the sulfite–bisulfite mixture leads to a decrease in extract viscosity thereby stabilizing the extracted mass.[320] A bi-component solvent system, acetone–water with bisulfite, method is also reported for tannin isolation.[321]

Microwave-assisted extraction (MAE) offers several advantages over conventional extraction techniques: shorter extraction times, lower solvent consumption, better efficiency and higher yields.[322] Rosemary (*Rosmarinus officinalis*) biomass subjected to MAE in the presence of alcohol such as methanol and ethanol showed a two-fold higher extraction yield (951 mg of chlorogenic acid/100 g) as compared to ultrasound-assisted extraction (UAE). However, the extraction yields of microwave and Soxhlet extraction were found to be similar.[323] Besides usage of naturally occurring sources, grape pomace residues obtained from wine manufacturing units are also found to be rich in CTs. Their extraction using conventional methodology requires harsher conditions (100 °C, high base concentration of 2.5–7.5%),[324] while optimal MAE conditions are milder (100 °C, 1 : 8 solid to solvent ratio, 1.25% Na_2CO_3, 8 min) and give higher polyphenolic and consequently tannin yields of 0.6, 1.6 and 1.5% for grape red marc, white marc and pomace, respectively.[325] *Agrimonia pilosa* Ledeb. known for its high tannin levels yielded 128.7 mg g^{-1} of tannin under MAE conditions optimized to irradiation power of 500 W, at a concentration of solvent to mass ratio of 35 mL g^{-1} at 30 °C in 15 min.[326] Response surface methodology (RSM) could be used as an important method for optimization of extraction process.[325,327] MAE process optimized by RSM for cherry laurel (*Prunus laurocerasus*) leaves suggested the most economic conditions of extraction are a power of 307.6 W, a very dilute concentration of 0.17 g mL^{-1} in 17.1 min.[328]

In addition to MAE, UAE is another promising technique for tannin extraction owing to lower equipment costs, simplicity of operation, and better extraction quality. Ultrasonic waves require shorter extraction times and lower temperature for leaching out of tannin as compared to other extraction techniques of maceration, hydrodistillation, low-pressure solvent extraction *etc.*, making UAE suitable for extraction of thermally sensitive organic compounds.[329,330] Cavitational effects of ultrasound waves facilitate the release of extractable compounds and enhance mass transport by disrupting the plant cell walls.[331] Highly solvating solvents lead to better swelling and account for higher extraction efficiency and/or reduced extraction times.[332] In myrobalan, a 4.5-fold enhancement in the extract yield (90%) was observed without external heating using ultrasonic treatment as compared to conventional methods (21%).[333] Quantitative extraction of polyphenols from jatoba (*Hymenaea courbaril* L.) bark using UAE process at 60 W, 50 °C, 40 min and a solvent to feed ratio of 20 showed improved yields as compared to a conventional agitation process.[334] A variation in ultrasonic method extraction parameters such as temperature (0–75 °C), output amplitude (20, 50 and 100%), duty cycle (0.2 s, 0.6 s and 1 s), quantity of sample (0.5–2.0 g), and total extraction time (3–15 min) was studied for tannin extraction of grapes. It was found that a 6 min extraction time using acidic pH (2) and ethanol–water (1 : 1) at 10 °C gave optimal tannin extraction yields,[335] whereas a conventional extraction process required stirring and 60 min to attain similar yields.[336,337]

Not only does the use of greener methods allow better yields at milder extraction conditions, but the utilization of either green or low-volatility solvents such as ionic liquids is also a current area of research into tannins to meet commercial requirements for material applications.[338,339] The extraction efficiency of HT materials from plant sources such as catechu (*Acacia catechu*) and myrobolan (*Terminalia chebula*) was found to be 85% using a distillable ionic liquid, *N*,*N*-dimethylammonium-*N*′,*N*′-dimethylcarbamate (DIMCARB), at room temperature, as compared to the conventional extraction methods which utilize bulk quantities of solvents.[338] Ionic liquid extraction of tannin from *Galla chinensis* using simultaneous UAE and MAE technique yielded ~630 mg g^{-1} of tannin content, which was ~22% more efficient than the conventional techniques, along with a reduction in extraction time from 6 h to 1 min.[340] Although ionic liquids have arisen as an attractive alternative to the existing solvents, due their high boiling points and solvation capability they suffer from the major drawback of requiring their removal to isolate the target compounds. Macroporous resin adsorption technology in addition to ionic liquid-based UAE and MAE increased the tannin content in *Galla chinensis* extract from 70 to 85% with a solvent recovery of 99%. Preliminary extraction of tannins by 1-butyl-3-methylimidazole bromide and its subsequent removal from *Galla chinensis* extract using macroporous resins have been reported.[341] The use of low temperature, greener processing conditions is also important for industrial scale-up methods. CTs undergo depolymerisation in the presence of thiols to form monomeric phenols under mild conditions at 40 °C in 2 h using ethanol as a solvent.[342]

Supercritical fluids can also be used as solvents for extraction as they provide an environmentally viable and commercially feasible option due to use of lower temperature and their easier removal, unlike ionic liquids, after completion of the extraction process by altering the operating conditions. The lower critical temperature (31 °C) and moderate critical pressure (7.28 MPa) of carbon dioxide make it an ideal solvent for compounds that may suffer thermal degradation, especially phenolics. In addition, CO_2 processing creates a medium without oxygen where oxidation reactions can be avoided, which is of paramount importance during antioxidant extraction.[343] The non-polar nature of carbon dioxide and polar nature of phenolic extracts is a problem for its usage as the sole extraction solvent. In order to enhance the polarity of carbon dioxide, alcoholic co-solvent such as methanol or ethanol showed better extraction yields.[343] The percentage of ethanol in Sc-CO_2 showed a profound effect on the chemical component extracted. Gallic acid, epigallocatechin and epigallocatechin gallate were extracted at 300 bar, 50 °C and 20% of ethanol while epicatechin yield was optimum at 250 bar, 30 °C and 15% of ethanol.[344]

Several methods are reported in literature to determine both the amount and analysis of CTs, HTs or total phenolics in a sample. In general, HTs are apparently more difficult to analyse than CTs due to their sensitivity to hydrolysis by acids, bases or enzymes. The nature of analytical data critically depends on appropriate sample preparation, storage conditions, extraction techniques and prior knowledge of the reactivities of tannins. The amount of tannins in a sample can be measured by general tannin assays, such as precipitation with metals[345] or proteins.[346] It is important to select appropriate assays for measurement of the quantity and activity of CTs.[347]

Colorimetric assays are widely used for comparison of tannin content in various samples. Most widely used colorimetric assays that are used to quantify tannins are based on reaction of phenolic moieties with a specific reagent and colour change is monitored and analyzed at specific wavelength by UV-visible spectroscopy.[348] Assays such as Folin Ciocalteu,[349] CUPRAC,[350] Trolox equivalent antioxidant capacity,[351] and free radical scavenging assays such as 2,2-diphenyl-1-picylhydrazyl (DPPH)[352–354] and oxygen radical absorption capacity (ORAC)[355] are well cited in the literature.

Characterization of tannic components in extracts is a complex process due to the coexistence of a large number of isomeric molecules and high molecular weight species. They are often unstable under heat, in acids and bases, or easily oxidized. Characterization techniques such as FTIR, NMR, MALDI-ToF along with chromatography techniques (HPLC, SEC) are useful tools to study, identify, and determine the purity the tannin composition in extracts. SEC is mainly used to determine average DP of CTs.

The nature of resin CTs or HTs can be analysed by UV-visible spectroscopy by determining the ratio of $\lambda_{\max} : \lambda_{\min}$ centered at 276 nm and 256 nm, respectively. It was found that HTs showed lower ratio values (1.03–1.35) while CTs showed a higher value in the range of 1.67–2.15.[356]

IR spectroscopy of tannin extract from grape pomace origins showed catechinic acid rearrangement under alkaline extraction conditions as suggested by the weak IR peak development at 1750 cm^{-1}. IR peaks at 1308, 1264 and 1212 cm^{-1} indicated pyran ring opening during the sulfitation process of flavonoid tannins.[357] The C=O or C–C stretch vibration in CR_2–CHR–$CR(SO_3)^{2-}$ was accounted for by the peak at 1260 cm^{-1},[358] while peaks at 1440 and 1495 cm^{-1} were due to C–H deformation and aromatic ring vibration[357] respectively. These peaks were only detected for extracts obtained with 1% NaOH along with $NaHSO_3/Na_2SO_3$ due to lower lignin content as impurity.[320]

The accurate analysis of tannins requires a combination of chromatography along with MS techniques. Chemical methods involve acid depolymerisation of CTs to form carbocation intermediate which is trapped with phoroglucinol and derivatized followed by capillary GC separation and detection by flame ionisation. Such processes are tedious; however, they are very sensitive and detect ~100 ng CT in a sample.[359] Mass spectrometry techniques such as LC-MS/MS and MALDI-ToF provide a good insight into the structural analysis of tannins. The fragment patterns *m*/*z* 301, 317, 285 were attributed to the fragment patterns of myricetin, quercetin and kaempferol, respectively, as confirmed from further fragment ions for quercetin (*m*/*z* 121, 151, 179, 245, 273, 301), myricetin (*m*/*z* 137, 151, 179, 271, 289, 299, 317) and kaempferol (*m*/*z* 187, 93, 285).[360] MALDI-ToF for non-purified industrially extracted maritime pine polyflavonoid tannin indicated procyanidin oligomers composed of catechin/epicatechin, epigallocatechin and epicatechingallate monomers. These oligomers contain 20–21 monoflavonoid units having catechingallate dimer (528–529 Da) as major repeat units which has lost both the gallic acid residues and a hydroxyl group along with a small proportion of fisetinidin units.[361] MALDI-ToF spectrometry demonstrated that grape pomace tannin extracts contained oligomers of up to 6 repeating flavonoid units, with dominant procyanidin and a minor amount of prodelphinidin units.[357] Post-source decay fragmentation of data obtained from MALDI-ToF allowed analysis of sequential loss of monomers from CT polymers. This technique confirms the that the major polymeric architecture present in willow (*Salix alba*) and lime leaf (*Tilia cordata*) contains procyanidin units, while spruce needle (*Picea abies*) and beech leaves (*Fagus sylvatica*) have both procyanidin and prodelphinidinin in varying ratios.[362] Two-dimensional chromatography (hydrophilic interaction chromatography with reversed-phase liquid chromatography) coupled with MALDI-ToF allowed analysis and accurate mass detection of procyanidins which comprise tannins up to a DP of 16.[363] HPLC-ESI-ToF allowed identification of major monomeric components of chestnut shell and pine bark tannin extract as catechin/epicatechin and dicatechin (*m*/*z* 289.08) and gallocatechin/epigallocatechin (*m*/*z* 305.07).[361] HPLC/DAD and MS provide both qualitative and quantitative analyses of polyphenols, HTs and CTs in extracts. Chestnut (*Castanea sativa*) bark samples showed first time detection of the presence of 1-*O*-galloyl castalagin along with other components vescalin, castalin, gallic acid, vescalagin, castalagin and ellagic acid which were separated, quantified and identified using HPLC-DAD/ESI-MS.[364] Normal-phase HPLC was found to be more suitable over reverse-phase for pine bark (*P. maritime* L.) tannic acid extract analysis and revealed that the extract was mainly composed of polyflavanols (containing 2–7 units) and tannic acid as glucose gallates (containing from 3 to 7 units of gallic acid).[365] Mass spectrometry profiling followed by preparative HPLC of the peel and flesh of mango fruits showed HT glycones as a major class of compounds. MS signals were observed at 332.07, 636.09, and 788.11 Da corresponding to galloyl-, trigalloyl-, and tetragalloyl-glucose, respectively. HPLC trace of these samples showed different peaks with different retention times corresponding to each *m*/*z* value suggesting the coexistence of isomeric structures.[366] Myrtle and pomegranate tannin extracts showed the [M − H] peak at *m*/*z* 343.2 (due to galloylquinic acid) and 169.2 (due to the loss of quinic acid),[367] at 633 (due to galloyl HHDP-glucose isomers), and [M − H] at *m*/*z* 481.3 and 483.2 (due to the loss of gallic acid) and 301.1 (due to lactonized form of the HHDP-unit, *i.e.* ellagic acid). The mass spectrum also confirmed the major tannic compound in pomegranate peel extracts: [M − H] peak at 1083.2 (due to β-punicalagin) and 781.2 (due to loss of 301 *m*/*z* fragment of ellagic acid).[368] The peel extracts and seed extracts showed a reversal in relative abundance of gallic–ellagic acid derivatives as 29 : 71 and 61 : 39, respectively.[369]

^{13}C-NMR spectroscopy confirmed the presence of procyanidinin in the leaves and needles of willow (*Salix alba*), spruce (*Picea abies*) and beech (*Fagus sylvatica*), while prodelphinidin was only present in the latter two. NMR signal between 70 and 90 ppm demonstrated the presence of stereoisomers (catechin/epicatechin; gallocatechin/epigallocatechin).[362] The proanthocyanidin tannins in quebracho (*Schinopsis lorentzii*) heartwood and black wattle (*Acacia mearnsii*) bark showed signals at 118 or 105 ppm due to the presence of catechols (quebracho) or pyrogallols (wattle) respectively.[370] ^{13}C-NMR analysis of chestnut tannin extract confirms procyanidins and prodelphinidins as major components with small amounts of prorobinetidins due to the presence of characteristic bands of a typical CT pattern.[371–374] The presence of carbohydrate content in tannins is confirmed from the characteristic signals at 65–85 ppm.[375]

2.4 Palm oil

Palm oil is an agricultural product from the palm tree (*Elaeis guineensis*) which is mainly produced in South-East Asian countries, such as Malaysia and Indonesia. Oil palm fruits lead to the formation of two types of oil derived from the mesocarp and the kernel. Indonesia and Malaysia are the leading producers of palm oil accounting for nearly 80% of world production, 21–23 MMT in 2013 by Indonesia alone.[376] In Malaysia, lignocellulosic biomass availability is nearly 47 402 dry kton per year. Agro-waste generated from the oil palm mill industry and agricultural fields (oil palm fronds, OPF and empty fruit bunches, EFB) is considered as a poor source for fertilizers and animal feed due to very low nitrogen content or incineration due to smoke problems. However, it is rich in lignocellulosic material and therefore can act as a renewable source of chemicals at low cost for green material applications.[377,378] The lignin and polysaccharide content variation in palm tree biomass is shown in Table 2.[379]

In general, palm waste has nearly 60–80% cellulose and 20–30% lignin content, making it a good source of both glucose[388] and phenolic compounds. Lignin content was found to be maximum in oil palm shells, followed by fibres, empty palm fruit bunches (EPFB), OPF and trunks. Iraqi phoenix date palm (*Austa omran*) showed the highest lignin content of 36% as determined by the Klason lignin method.[389]

Extraction of lignin from palm fruit essentially requires a pre-treatment step. This process allows the release of fermentable sugars from the plant polymers and an easy separation of lignin from cellulose in a lignocellulosic biomass. Hydrothermal treatment is generally used to obtain sugars and has been shown to enhance the enzymatic digestibility of the solid residue.[390,391] Glucose acts as a reserve source for second generation bio-alcohols, methanol, ethanol[392,393] using hot compressed water or ionic liquids,[394] acetic acid and substituted phenols. Thermal cracking mainly produced a solid residue and is not a suitable method for recovering desired chemicals.[128] Palm oil is obtained from palm shell by the fluidized-bed fast pyrolysis technique[2,73] with a maximum liquid product yield of 58 wt% at 500 °C. Fast pyrolysis[395] of EFB is a good method for obtaining renewable chemicals such as phenols, acetic acid, methanol, 2-furaldehyde and ethyl acetate, depending upon the nature of catalyst in catalytic cracking, pyrolysis temperature, ratio of steam to oil, time factor *etc.*[396]

Solid support catalysts such as zirconia-supported iron-based catalyst (Zr/FeO_x, $Zr–FeO_x$ or $Zr–Al–FeO_x$)[396,397] and rare earth metal exchanged Y-type (REY) zeolites[398] such as nickel supporting REY zeolites and FeOOH catalyst lead to formation of methanol, acetic acid, phenols, and ketones from oil palm shell waste. Unlike thermal cracking or when FeOOH catalyst is used alone, it was found there is generation of solid residue which prevents easy recovery of desired chemicals. Solid supports not only allow easy recovery but are also believed to enhance the activity of FeOOH catalyst.

Pyrolyzed palm shell oil contains a high percentage of phenol and its derivatives, such as substituted cresol, pyrocatechol, guaiacol, syringol, and eugenol (Fig. 12). Solvolysis liquefaction process of EFB in the presence of ethylene glycol followed by extraction in acetone showed the presence of phenol, syringol, eugenol, propenyl and propenoic substituted phenols, as confirmed by FTIR and analytical pyrolysis GC/MS analysis.[399]

Processes such as caustic pulping[400] or use of organic acids[401] (formic and acetic acids) lead to delignification of lignocellulosic biomass. The nature of the base in alkaline liquefaction also affects the nature of the product. Potassium carbonate favours phenol while sodium hydroxide mainly yields esters.[402] The organic acids act both as solvent and acid in the process. They are attractive due to significant amount of material dissolution at low processing temperature, no requirement for use of mineral acid catalyst and cause depolymerisation of lignin and hemicelluloses. Acidic phenolysis of oil palm EFB in the presence of phenol, and sulfuric acid as catalyst (8 wt% of phenol), showed 96% liquefaction at 150 °C in 90 min.[128] The reaction follows second-order kinetics with an activation energy of 50.7 and 18.1 kJ mol^{-1} when the catalyst concentration was 5 and 8%, respectively.

Table 2 Chemical compositions of lignocellulosic biomass in Malaysia[379]

Wood/fibre	Polysaccharides (wt%)	Lignin (wt%)
Oil palm fronds[380]	86.5–83.5	14.8–20.5
EPFB[381,382]	82.4	17.6–25[382]
Oil palm fibres[383]	59.6	28.5
Oil palm shells[384]	43.5	50.7
Oil palm trunks[385]	75.6	17.1
Coconut husk *Cocosnucifera* L. (fibre)	50.9[386]	32.8[387]

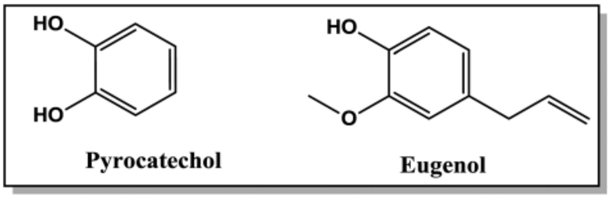


Fig. 12 Structures of phenols extracted from palm oil.

Organosolv methods give rise to lower molecular weight lignins that are soluble in most organic solvents[403] and the presence of phenolic hydroxyl groups and oxidized groups favour their incorporation into polymer formulations and their chemical modification.[404] Among organosolv pulping methods, EFB was subjected to pulping with organic solvents with a high boiling temperature (ethylene glycol, diethylene glycol, ethanolamine and diethanolamine), showing the pulps from amines to have better properties than the ones from glycols.

Delignification of OPF black liquor using kraft, soda and organosolv pulping processes showed the presence of H : G : S ratio as 21 : 6 : 51, 30 : 21 : 49 and 10 : 23 : 67, respectively. It was found that OPF lignin obtained by alkaline pulping method (kraft and soda) had higher phenolic OH, thermal stability and molecular weight than that obtained by the organosolv method.[405] The presence of G-type unit in OPF lignin structure with a free C5 position could give potentially highly active sites for polymerization processes such as in phenol–formaldehyde condensation reactions. While S-type unit (C3 and C5 positions are linked to methoxy group) tends to show a low reactivity toward formaldehyde. Besides, a higher amount of phenolic hydroxyl in the OPF lignin structure can activate the free ring positions. Thus, it promotes better non-covalent interactions with formaldehyde to form a stiffer lignin–phenol–formaldehyde (LPF) macromolecular resin.

Palm oil mill effluents are also found to be a good source for water-soluble phenolics which can be separated by simple separation techniques[142] in combination with, for example, centrifugation and membrane filtration technologies.

The advantages of supercritical solvents in liquefaction processes are extraction of liquid products from waste at low temperature and faster conversion rates of the order of seconds (at 380 °C and 100 MPa for 8 s).[406] Liquefaction of palm waste with Sc-H_2O[407] or sub/supercritical methanol, ethanol, acetone and 1,4-dioxane[408] showed promising results. The treatment of palm oil waste with supercritical solvents showed that the water-insoluble portion on further fractionation into methanol-insoluble residue was mainly composed of lignin (>84 wt%) and phenolic hydroxyl contents.[406,407]

Lignin[409] or substituted phenols obtained from palm waste are structurally characterized by FTIR,[399] ^{1}H-NMR[397] and ^{13}C-NMR spectroscopy, and analytical pyrolysis GC-MS spectrometry.[399] The two-dimensional GC-ToF-MS chemical characterization of bio-oils[410] indicated that the major classes of components are ketones, cyclopentenones, furanones, furans, phenols, benzenediols, methoxyphenols, dimethoxyphenols and sugars. In addition, esters, aldehydes and pyridines were also found for samples obtained from EPFB. The high quantity of phenol in the bio-oil of EPFB is of interest because phenol isolated from the bio-oil could provide an alternative to the phenol obtained from petroleum.

2.5 Coconut shell tar (CST)

Materials based on the coconut tree form a major renewable resource of the tropical regions of the world. Coconut shells are produced as waste of about 4.2 million tons per year. Destructive distillation of coconut shells gives coconut shell char, which is used as filler in plastics and for the development of activated carbon. CST is a by-product obtained during the distillation process and has been considered as a waste so far. The CST is a tarry oil, dark brown in colour with a characteristic unpleasant empyreumatic odor. Except for some identification of the components, not much work has been reported so far in the literature.

Distillation of CST[153] was performed at atmospheric pressure, unlike CNSL, and fractions were collected at 100 °C (water, 22%), 103–105 °C (crotonaldehyde, 3%), and 118–120 °C (acetic acid, 11%). The residue was treated with 3% sodium hydroxide for 2 h and neutralized with glacial acetic acid. It was dissolved in acetone and filtered to remove free carbon. The filtrate, after the removal of acetone, was used for polymerization. It is reported to contain many monomers, the major one being phenolic in nature (~45%).

Green coconut husk, an abundant agro-industrial residue in Brazil, is a potential source of FA, from which vanillin is produced *via* microbial fermentation.[401] It was found that coconut husk is a very rich source for 4-hydroxybenzoic acid (13 mg g^{-1}) on alkaline treatment.[411] Coconut husk has a maximum percent of lignin content of nearly 33% (Table 2) among naturally occurring plant material and therefore is a valuable source for generation of phenolic compounds. However, its exploration is not much reported in the literature and therefore it needs to be researched.

3. Modifications of naturally occurring phenols

The functionalities present in agro-waste such as lignin, cardanol, tannin, palm oil and CST offer a wide variety of structural modifications to synthesize new bio-based renewable structures. The functionalities vary from phenolic –OH to aromatic rings, aliphatic side chains (saturated or unsaturated bonds), carboxylic groups, carbonyl groups *etc.* which could be either used as such or further chemically transformed. These chemicals may then act as monomers or oligomers or intermediates which could be further explored for a range of polymers. Modifications of such naturally occurring phenolic compounds can be classified into three categories; namely, reaction due to (i) phenolic hydroxyl group, (ii) aryl group and (iii) side chains, which are each described below.

3.1 Reaction due to –OH group

The phenolic hydroxyl group can react with different structural modifiers and lead to different molecules *via* nucleophilic substitution (S_NAr/S_N) or condensation reaction. A generalized scheme for the possible modifications of –OH groups in naturally occurring phenolic compounds is shown in Fig. 13. The structure of monomer can be tailored by using various electrophilic centres with different substitution groups attached, which could be further altered by using additional polymerisable sites to affect the curing process.

Cardanol or other renewable phenolics are modified to various new chemical structures[42] which find applications as surfactants, glycolipids, and polymers derived from cardanol, and they can subsequently self-assembly into functional soft materials such as 4-aminodiphenyl ether,[412] 4-nitro-3′-pentadecyldiphenyl ether,[413] 3,5-dinitro-*N*-(4-(3-pentadecylphenoxy)phenyl)benzamide,[413] cardanol glycolipids (GlyLip),[414,415] polyethoxylates,[58,416] acrylate/methacrylates,[417,418] epoxide,[419] phosphorylation,[420] chloroformate[421] *etc.* Cardanol-based surfactants showed biodegradable properties comparable to or better than commercially available petro-based nonylphenol polyethoxylates.[58,416] The formation of a new synthetic structure, which can be used as such or modified further, imparts new characteristics to the monomer. Acryloylation,[417,421] epoxidation[419] and phosphorylation[420] of cardanol were also reported as some synthetic procedures of structural modification. However, cardanol, being less reactive, undergoes epoxidation to a lesser extent than phenol or bisphenol-A. Although cardanol epoxides do not form cross-linked networks due to being

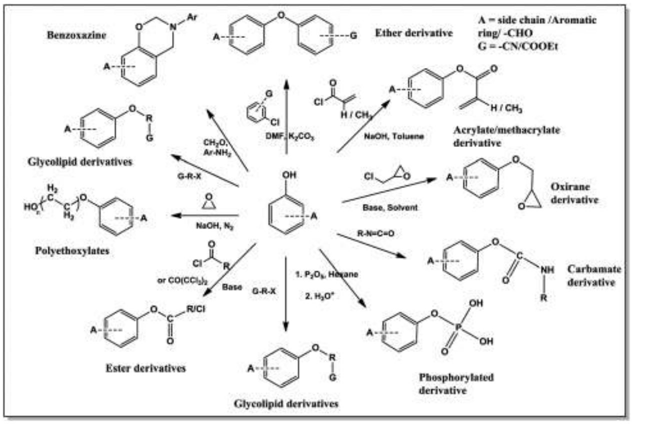


Fig. 13 Molecular flexibility provided by hydroxyl group modification.

mono-functional, they are found to be effective in producing relatively flexible systems when reactively blended with commercial diglycidyl ether of bisphenol-A (DGEBA). Phosphorylation[420] of phenolic hydroxyl group introduces heteroatom in the phenolic monomer, which can impart flame retardant properties. However, in the case of cardanol, simultaneous oligomerization is noticed and this could be accounted for by a carbonium ion-initiated mechanism of oligomerization of long alkylene side chain due to the acidic nature. The phosphorylated monomer is highly reactive with aldehydes, amines, and isocyanates. In addition, the presence of a double bond opens up further modification possibilities.

The reactivity of Sarkanda grass lignin for epoxidation with epichlorohydrin was found to be higher than that of wheat straw and Protobind 1000 lignin.[422] Lignin hydroxyl groups can be modified to epoxy followed by treatment with diamine leading to amination.[423] Lignin undergoes structural modification on reaction with carboxylic acids, carboxylic acid halides, or anhydrides.[424]

Mannich-like condensation reaction of phenolic –OH group with formaldehyde and an amine[425,426] forms new bicyclic heterocycle benzoxazine (Bz) monomers (Fig. 14). The structure of a Bz monomer can be tailored by using various phenols and amines with different substituents attached, which could be further altered by using additional polymerisable sites to effect the curing process.

Renewable benzoxazine monomers based on reaction of formaldehyde with phenolic –OH from renewable sources such as cardanol, syringol, lignin[427] and ammonia[13] or amine (aniline[428] or diamines[429] and further higher functionality amines[430]) led to a new class of renewable monomers which undergoes ring opening polymerisation (ROP) to form sustainable polymers.

3.2 Reaction due to aryl group

Electrophilic aromatic substitution reaction modifies the aryl group present in cardanol, lignophenol, tannin, palm oil and CST. Generalized reaction pathways possible for such structural modifications are shown in Fig. 15.

The main reaction studied for lignophenol,[423,431] cardanol,[420,432] EPFB[433,434] and CST[435] is the condensation of the phenolic compound with formaldehyde. This resulted in formation of water-soluble methylol derivatives of phenols (resoles) or relatively high molecular mass novolac resins. Modification of lignin prior to resin synthesis has typically been performed by reacting lignin with phenol in the presence of organic solvents such as methanol or ethanol. This process is called phenolysis. Initially, lignin was allowed to react with phenol before undergoing a condensation reaction with formaldehyde. Lignin was added to a mixture of phenol dissolved in ethanol, such that the lignin–phenol weight ratio was varied and known. Phenolysis of the lignin was carried out at 70 °C for a few hours. Organosolv Alcell lignin was also used as a replacement for phenol in PF resins.[436]

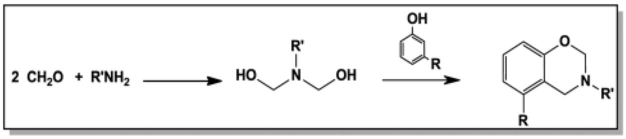


Fig. 14 Synthesis of 3,4-dihydro-2*H*-1,3-benzoxazines.

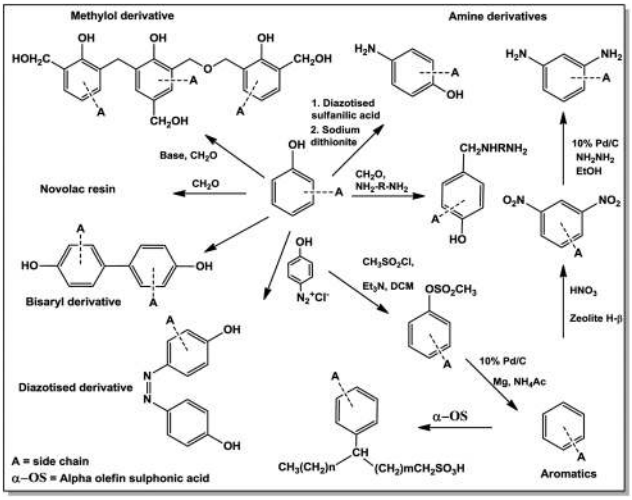


Fig. 15 Molecular flexibility due to aromatic ring modification.

Besides reactions of cardanol–formaldehyde (CF) resins there are several other electrophilic reactions of cardanol also reported such as diazotization of cardanol with different aromatic amines[437,438] and electrophilic substitution of nitro group in benzene ring.[412,439]

Aryl coupling to form bisaryl derivatives leads to a different set of monomers due to addition of functionality,[440] from a monophenol to diphenol. Electropolymerisation of vanillin and eugenol to form polyvanillin[441] and polyeugenol[442] is also gaining importance for completely green polymers. Sulfonation of phenols extracted from the pyrolysis oil of palm shells using simultaneous sulfonation alkylation process in the presence of alpha-olefin sulfonic acid may find applications in the production of surfactants in oil fields.[28]

3.3 Reaction due to side chain

Depending on the source of phenolic compound (*i.e.* cardanol, palm oil, lignophenols) the side group may be alkyl (–CH_3, $C_{15}H_{31}$), alkylene (–$C_{15}H_{29}$, –$C_{15}H_{27}$, $C_{15}H_{25}$, –CH=CH–COOH), ether (–OCH_3), aldehyde group, carboxylic group *etc.* The cardanol double bond may be epoxidised[443] or undergo olefin metathesis reaction[444] the product of which may act as a modified monomer for the formation of a different set of polymers. The modification of alkylene side chain by ozonisation[445] has been carried out to introduce alcohol, aldehyde, carboxylic, *etc.*, functionalities (Fig. 16).

Ruthenium-catalyzed olefin metathesis has been successfully applied to the synthesis of biscardanol derivatives and cardanol-based porphyrins using a Grubbs catalyst.[446,447]

Cardanol and its derivatives were used as precursors for the synthesis of fulleropyrrolidines, which could be used in medicinal chemistry, pharmaceuticals and photovoltaic applications.[40]

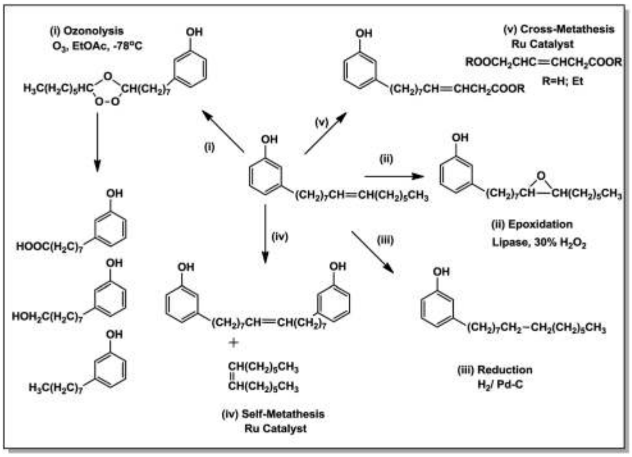


Fig. 16 Chemical modification reactions of alkyl/alkylene chain to form intermediates.

4. Polymers derived from naturally occurring phenolic derivatives

Amongst the various phenolic monomers, cardanol has dual phenolic and alkenyl side chain functionality, which makes it an ideal natural raw material for the synthesis of water-resistant resins and polymers. The polymers obtained from the phenolic monomers either crude or modified are shown in Fig. 17.

Besides these general modifications, certain specialised naturally occurring phenolic biopolymers are designed to have a different set of specialised properties (as elaborated on in Section 4.5).

4.1 Addition polymers

4.1.1 Carbocationic polymerisation. Cardanol undergoes polymerisation through the side chain double bonds of alkenyl group either by heat (180 °C) or using cationic initiators such as diethylsulfate–sulfuric acid/phosphoric acid,[448] $BF_3 \cdot OEt_2$[449,450] *etc.* to form polycardanol (Fig. 18).

The acid-assisted oligomerization is a slow process resulting in an average molecular weight (1200 to 11 507) increase only by 46% when heated at 140 °C for 40 h. The low molecular weight of polymers could be accounted for as due to the bulky nature of the side chain and presence of 1,2-disubstitution at the double bond. Steric hindrances may also restrict the molecular weight attainable in oligomerization. The formation of low molecular weight species could also be because of chain transfer to monomers. The presence of double bonds in alkylene side chain in cardanol may also yield oligomers *via* carbocationic polymerization (Fig. 19).[448]

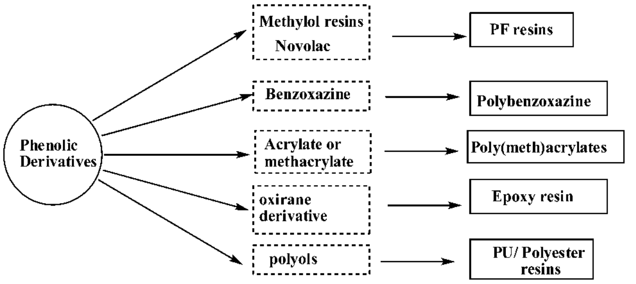


Fig. 17 Scheme depicting polymers obtained from naturally occurring phenolic monomers.

Free radical initiators such as benzoyl peroxide (BPO) or 2,2′-azobisisobutyronitrile (AIBN) do not initiate polymerization or cross-linking to form polycardanol. The phenolic moiety of cardanol, because of its antioxidant nature, can act as a radical scavenger, preventing polymerisation.

Bulk polymerization[451] of cardanol is facilitated by <5 wt% of a cationic initiator consisting of a strong acid, a Lewis acid and a Lewis acid complex, and the obtained cardanol polymer has a number average molecular weight of 10 000–100 000. Tyman has reported oligomerization of CNSL through unsaturated side chains during the distillation process.[452]

4.1.2 Oxidative polymerisation. Oxidative polymerisation of cardanol both in solution and bulk (r.t./80 °C) is catalyzed by metal complexes such as complex of iron with *N*,*N*′-ethylenebis (salicylideneamine) (Fe-salen) and hydrogen peroxide[453] or enzymes such as soybean/fungal peroxidise[454–456] to give a soluble polymer with a number average molecular weight of 2×10^3 to 6×10^3 (polydispersity index of 2–3) in good yield (Fig. 20).

The phenolic moiety was polymerized and the carbon–carbon unsaturated group in the side chain of cardanol

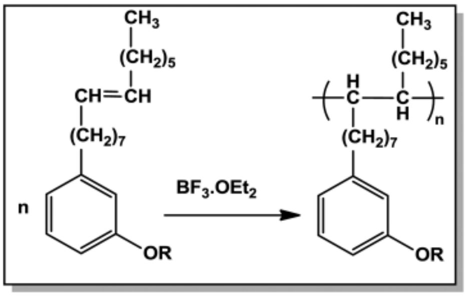


Fig. 18 Carbocationic polymerization of cardanol.

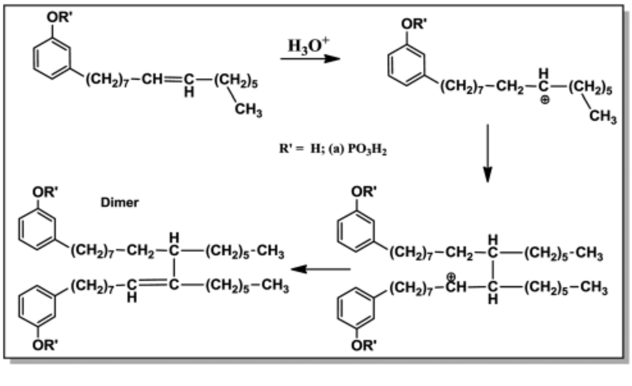


Fig. 19 Low molecular weight species generation *via* carbocationic mechanism.

remained unaffected during the polymerization. The polymer was subjected to hardening by cobalt naphthenate[453] catalyst or thermal treatment or methyl ethyl ketone peroxide to give a cross-linked film (artificial urushi)[457] with high hardness and gloss surface. The alkenyl side chain was modified by epoxidation[456] using *C. antarctica* lipase assisted catalysis in the presence of acetic acid and hydrogen peroxide to introduce epoxy functionalities in polycardanol followed by curing with phenalkamine at 150 °C.

Enzyme-catalyzed oxidative polymerization of phenols leads to formation of polyphenols which are attractive due to their high thermal stability. Besides this advantage, they are considered as alternative resins to phenol formaldehyde due to the absence of toxic formaldehyde. Enzyme-catalyzed oxidative polymerization may not be suitable for phenolic monomers with longer alkylene chain due to their low solubility in aqueous polymerizing medium. Fe-salen can be used as an alternative to assist such polymerization.[63]

Peroxidase-catalyzed polymerization of phenols is a popular method to give phenolic polymers, lignocresol, which was prepared by lignin and *p*-cresol, in methanol–phosphate buffer solution system to give cross-linked polymers.[458,459]

Lignin-based macromonomers such as lignocatechol and lignourushiol undergo catalytic polymerisation using oxidoreductase laccase. The polymer formed showed high thermal stability due to formation of a highly cross-linked network. The polymers had an affinity for bovine serum albumin and glucoamylase.[460]

4.1.3 Poly(cardanyl acrylate). A linear organic solvent-soluble polymer, poly(cardanyl acrylate) (poly(CA)), was obtained by solution[417] polymerization of cardanyl acrylate (CA) using a free radical initiator (0.8% AIBN/BPO) (Fig. 21).

Poly(CA) undergoes cross-linking on exposure to air (or UV light) on removal of solvent to give an insoluble infusible transparent film. However, in bulk and suspension (2 wt% PVA)[461] polymerization of CA, the polymer undergoes *in situ* cross-linking in the absence of any cross-linking agent. Copolymer beads of methyl methacrylate (MMA) and styrene with CA were prepared by suspension polymerization using free radical initiators and studied by SEM and optical micrograph images. A copolymer of CA (0.05–0.08 mole fraction) with MMA in bulk at 80 °C using 2% BPO as an initiator resulted in significant improvement in the thermal stability of poly(methyl methacrylate) (PMMA).[462] This was accounted for as due to the participation of olefinic double bonds of alkyl group in cardanol in copolymerization, thereby making the side chain less flexible and more stable.

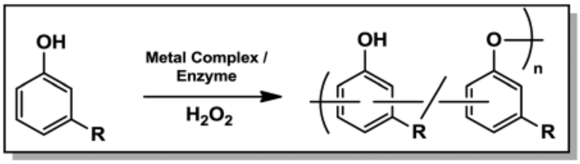


Fig. 20 Oxidative polymerization of cardanol.

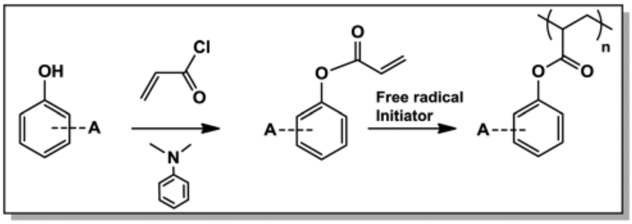


Fig. 21 Polymerization of cardanyl acrylate.

Auto-oxidation (cross-linking) of poly(CA) produced various free radicals which were used as a tool to reduce metal salts to prepare and stabilize gold and silver nanoparticles *in situ*. This sustainable approach avoided the use of external hazardous reducing and stabilizing agents.[463]

4.2 Condensation polymerisation

4.2.1 Phenolic resins. Phenolic resins are well-known examples of commercially exploited condensation polymers formed by electrophilic substitution reaction of phenolic derivatives and aldehydic compounds. The reaction is initiated with acid and basic catalysts such as NH_4OH, NaOH, oxalic acid, or H_2SO_4. The condensation of phenol and formaldehyde resulted in formation of water-soluble methylol derivatives of phenols (resoles) or relatively high molecular mass novolac resins. Phenolic resins prepared from cardanol either alone or in combination with other phenols, and HCHO have been known since 1968. CF resins have the usual characteristics of PF resins but a much better flexibility. However, the disadvantages of CF resins as compared to phenolic resins are lower tensile strength and thermal stability.[464] This may be attributed to C-15 side chain which imparts steric hindrance and reduction in intermolecular interactions. An optimum percentage replacement of phenol by cardanol is required, which possibly can achieve some specific properties and overcome some disadvantages of pure phenolic resins. Phenolic resins (resoles) containing cardanol (<15 wt%) have distinctly improved chemical resistance and mechanical properties (tensile, flexural, and Izod impact strengths) compared to neat PF resin.[465]

The cardanol-based resins were found to be more heat and oil reactive than resins obtained from the usual *p*-substituted phenols such as *p*-*tert*-butylphenol, *p*-*tert*-amylphenol, and *p*-phenylphenol, possibly due to side chain unsaturation and the trifunctional nature of the resins.[466] Varnishes prepared from the cardanol resin compared favourably with similar products derived from other alkyl phenols.

Misra *et al.*[467] reported on the kinetics of the formaldehyde condensation and cardanol by determining the concentration of formaldehyde present in the reaction mixture with time. A theoretical model based on RSM[468] was found to be in good agreement with experimental data between the process variables, and the extent of conversion was established for different types of cardanol–phenol formaldehyde (CPF) (novolac) resins.

Swain *et al.*[469,470] have reported the synthesis and characterization, and thermal, ion-exchange, bactericidal and fungicidal properties of resins based on hydroxyl aromatic compounds, formaldehyde/furfural and substituted aromatic compounds in the presence of acids and bases as catalysts. They found the copolymer of cardanol/*p*-hydroxyacetophenone/formaldehyde to be more thermally stable. In analogy to cardanol, furfural is also obtained from renewable resources such as vegetable waste like cane sugar, bagasse, rice hulls, maize cobs, and other such cellulosic waste materials.

Modification of insulating enamel varnish based on poly(vinyl formal) with CPF resins was found to improve physico-mechanical properties, heat resistance and electrical properties of the insulating enamel varnish for copper wires.[471]

Thermal characterization of cyanate esters derived from CPF novolac resins and the corresponding cured phenolic-triazine networks indicated a detrimental effect of cardanol on the thermal stability and char residue of the resins.[472] The effect on the structure and properties of CNSL-novolac resins prepared using succinic acid as catalyst has also been reported.

Flame-retardant polymers based on cardanol modified with hetero-atoms such as phosphorus (MCPAF) and bromine (BrMCPAF) followed by polymerization with formaldehyde have been reported (Fig. 22).[420,432] Thermal stability of MCPAF resin was found to be higher than that of CF resins above 500 °C. Char yields and limiting oxygen index values of resin based on MCPAF are 21 and 27 while in the case of BrMCPAF resins higher values (27 and 49, respectively) were observed.

Applications of reinforced composites of epoxy-modified CF resin (~40% of cardanol by weight) using surface-treated natural fibres such as short ramie, flax, hemp, and jute with higher renewable content were also explored.[473] Pressure sensing materials have been prepared by *in situ* blending of CF with polyaniline (PANI) doped with H_2SO_4 and cast into polypropylene cups.[474] Condensation of diazotized cardanol with formaldehyde yielded diazotized CF resin.[475] CNSL- and cresol-based novolac copolymers showed usefulness as photoresists for microlithography applications.[476]

Lignin and phenol can undergo hydroxymethylation to form LPF copolymer in the presence of NaOH and excess of formaldehyde.[477,478] DSC scan of LPF resoles showed onset of curing (T_o) at 150–175 °C, which is typical of the conventional phenolic resole resins. A secondary peak at 135–145 °C was observed which could be due to the exothermic reactions between the free formaldehyde with phenol or lignin to form methylol phenols. The replacement ratio of phenol with lignin should be less than 50 wt% due to the mainly lower thermal stability of such resins. However, properties can be improved by purifying the lignin feedstock before the resin synthesis.[479] The lower values of decomposition temperature obtained for the LPF resin with respect of the PF resin also support this explanation, since the thermal stability of a resin is increased as the degree of branching and molecular weight of the resin increases.[480]

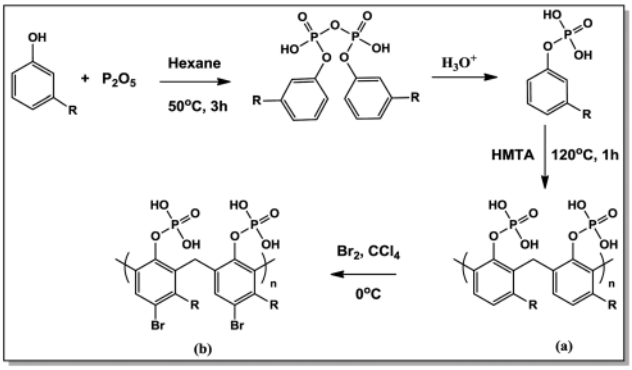


Fig. 22 Preparation of (a) MCPAF and (b) BrMCPAF.[204]

Lignin-based novolac phenolic prepolymers with 25–45 wt% replacement of phenol from different origins (kraft pine, soda/anthraquinone flax, and sulfonated SKL) showed lower T_o and gelation time but with a higher volumetric shrinkage than reference PF resin.[475] Ligno-*p*-cresol with reactive sites on the C1-cresolic and the terminal phenolic units was hydroxymethylated (HM) to give network polymers by heating. On the other hand, ligno-2,4-dimethylphenol, with reactive sites only on the terminal phenolic units, gave linear-type polymers. The polymerisation of lignophenols could be controlled by mixing with HM-ligno-*p*-cresol and HM-ligno-2,4-dimethylphenol. Recyclable composites[481] with high dimensional stability were prepared by the combination of cellulose and HM-lignophenols (HM-LPs). Under alkaline conditions, the resulting polymers were depolymerised and re-separated effectively to small fragments (lignophenols and cellulose) by the switching function (nucleophilic attack of C1-phenolic nuclei to C2).

Lignophenolic thermosets obtained from lignophenol extracted from sugarcane bagasse have similar Izod impact strength as phenolic thermoset.[482] Sisal fiber natural biocomposites based on lignophenolic resin showed good adhesive properties. Phenol extracted from black liquor of oil palm EFB replaced commercial phenol (1 : 1) to form LPF resin. In comparison to PF resin, LPF resin showed a higher bonding strength and lower kinematic viscosity over 21 days' storage time.[433] Enrichment and polymerization of the phenolic components of CST led to a 2.4-fold higher lap shear strength than PF resin.[435] This showed the possibility of lignin utilisation and successful replacement of 50% petro-based phenol for adhesive applications. The good adhesion properties are attributed to the presence of higher hydroxyl to methoxy group ratio[483,484] and lower molecular weight of resin which seeps easily into the pores of the binding substrate to form better cross-linked channels. LPF resins which have either high viscosity due to their high molecular weight or lower thermal stability are not suitable for adhesives for coating wood, and the hot-pressed composites require both high temperature and longer processing time.[485,486] Laccase-modified lignin also showed better adhesion properties than unmodified LPF resin.[487] A 30% replacement of phenol with oxidatively degraded lignosulfonate in phenolic resole-based foams gave properties similar to those traditional foams.[488]

CTs are more suitable than HTs for use in manufacturing a phenolic-type polymeric matrix, due to the presence of phenolic rings with a larger number of free aromatic positions and activating hydroxyl groups to facilitate electrophilic attack,[489] thereby exhibiting a potential for use in the reaction with formaldehyde.[490] However, tannins are large rigid aromatic structures with restricted rotation around their backbone bonds[491] and therefore they require high temperature for curing reactions with formaldehyde. As a result, resins become rapidly immobilized due to premature gelation, while not being further extended due to the restricted backbone mobility and multiple reaction sites. This leads to brittle materials with less stability and short shelf-life making them unsuitable for industrial applications. This behaviour can be explained on the basis of two steps, namely, methylolation and condensation, leading to the formation of tannin–formaldehyde resins.[492] The reactivity of tannins can be enhanced by acid hydrolysis which opens up the heterocyclic ring of polyflavonoids, with the formation of carbocation intermediates.[493] Also, improvement in the performance of a tannin-based adhesive is observed by subjecting tannin extracts to acetic anhydride and subsequent alkaline treatment.[308] Monomeric phenols such as pyrogallol derived from HTs may also act as a phenol substitute in PF resin.[494] The need to explore tannins as alternative phenolic feedstock also stems from the fact that formaldehyde-based resins, despite their superior bonding properties and low costs, are associated with health hazards. Tannins can partially be substituted in industrial PF adhesives, due to their use leading to reduced gel time and pressing time.[495–497] Tannin-based rigid foams are also an important class of compounds by virtue of their numerous applications such as floral foams, ion adsorption, packaging, crash protection or insulation material with superior properties like their great thermal and fire resistance, good mechanical resistance under compression, lower cost and ease of preparation along with an important advantage of being sourced from inexpensive and renewable, environmentally friendly raw materials.[498,499] Recent studies on tannin-based foams formulated without formaldehyde and very volatile blowing agents[500] and by addition of small percentage of multiwall carbon nanotubes have focussed on enhancing the environmental relevance and mechanical properties of these foams.[501,502]

4.2.2 Benzoxazines. Benzoxazines (Bz)[425] are a class of phenolic compounds which have better thermal properties and flame retardancy than phenolics. They provide huge potential for exploration due to their better mechanical performance and molecular design flexibility for advanced composites. They undergo ROP[503–506] accounting for nearly zero shrinkage in cured products (Fig. 23).

The phenolic component was varied from cardanol[13,429,507,508] to cardbisphenol[509] to lignin-derived compounds such as guaiacol, FA, coumaric acid, phloretic acid *etc.* and amines were also varied from petro-based monomers such as monoamine (aniline), diamines (4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenylsulfone) *etc.* and higher functionality amines[430] to sustainable amines such as furfurylamine and stearylamine[510] to lower the curing temperature and enhance thermal stability.

Polybenzoxazines based on cardanol were investigated both as resins for making composites[13,428] and as reactive diluents (liquid monomers) for the solventless synthesis[428] of higher viscosity monomers. Biobased Bz monomers showed very high T_o which is lowered either by adding catalysts or curing promoter (methyl *p*-toluenesulfonate)[511] or by incorporating certain monomers having acid functionalities.[512]

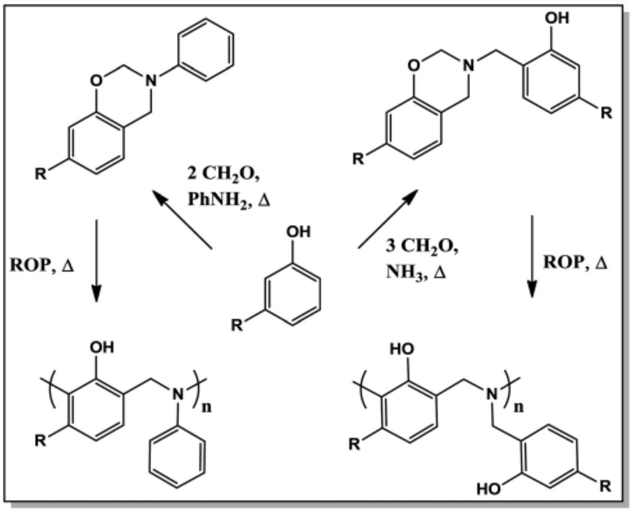


Fig. 23 Synthesis of cardanol-based benzoxazines and polymers by heat-assisted ring-opening polymerisation.

Polybenzoxazines based on esters of ferulic, coumaric, and phloretic acids showed superior T_g values than those prepared with unsubstituted monofuctional benzoxazine.[513]

Cardanol-based polybenzoxazines were explored as composites,[514] coatings,[509] binders and adhesives.[515] They showed good mechanical properties, decreased water absorbability, increased resistivity and dielectric strength, decreased dielectric loss and dielectric constant and exhibited high resistance to both corrosion and organic solvents.

Formation of benzoxazine from the reaction of hydroxyl groups of condensation polymer of phenol or cardanol with furfural showed T_o of 198 and 225 °C and 5% weight loss temperature ($T_{5\%}$) of 432 and 383 °C, respectively.[516]

Cardanol is not the only material used for Bz monomer synthesis. There are other reports where different renewable sources were also utilised for the formation of PBz. Urushiol, a natural product, reacted with monamine, aniline, to form benzoxazine which showed a T_o of 210 °C and temperatures corresponding to $T_{5\%}$ and $T_{10\%}$ weight loss are 325 °C and 357 °C, respectively.[517] Blends of urushiol benzoxazine based on diamines such as DDM and 3,3′-phenylmethanebis (3,4-dihydro-2*H*-1,3-benzoxazine) have lower curing temperature of 180 °C.[518] The lower T_o of the latter Bz monomer structure could be due to formation of bis-oxazine over mono-oxazine in the former. Another renewable source-based Bz monomer of a methylester of renewable diphenolic acid showed a T_o of 220 °C, T_g of 303 °C and $T_{10\%}$ of 386 °C.[519]

4.2.3 Epoxy resins. Epoxies derived from vegetable oils have been studied extensively for several interesting properties,[520,521] but a lack of aromatic structure results in poor thermal and mechanical resistance thereby limiting their industrial applicability. This has paved the way for the exploration of bio-based epoxy polymers with a high aromatic density[522] obtained by the epoxidation of natural phenolic compounds such as cardanol, tannins,[523] and other phenols which have either double bonds or hydroxyl groups and which can undergo epoxidation (Fig. 14 and 17).

Epoxide-containing polycardanol[58] was enzymatically synthesized using two different enzymes: lipase and peroxidase. Curing using either phenalkamine or thermal treatment resulted in transparent polymeric films with a high-gloss surface and higher pencil scratch hardness as compared with polycardanol.

Bisphenol-A based epoxy resin having 20 mol% of cardanol epoxide cured by a polyamine hardener exhibited reduced tensile, impact and compressive strengths.[524] However, the resin showed considerable improvement in elongation-at-break without much decrease in energy absorption.

An epoxy–cardanol resin developed using epichlorohydrin, bisphenol-A and cardanol and hardened with an aromatic polyamine adduct was a better binder for paints and showed better mechanical and anticorrosive properties as compared to epoxy resin.[419]

Cationic photo-polymerization conversion of epoxidised cardanol (CE) containing 10 wt% CE and 5 wt% hydroxy-functional reactive diluents as a function of relative humidity was determined for thin-film materials. CE imparted balanced physiochemical properties to the cationic UV-curable materials thereby showing a great potential as a reactive ingredient in cationic UV-curable materials.[525]

Blends of epoxy with CF and PF resole resins were prepared and it was found that an increase in energy absorption and elongation at break reached a maximum at 60% cardanol content in cardanol–phenol-modified resin as compared to unmodified epoxy resin.[526]

A nanocomposite obtained by *in situ* polymerization of a blend of nanoclay (6 wt%), cardanol-modified resole (15 wt%) and epoxy and polyamide as hardener showed improvement in mechanical properties of the glass-fiber-reinforced epoxy-composite system.[527]

Cardanol epoxidised benzoxazine (CBO) resin displayed a T_g of 76.6 °C whereas the CEO gave a value of 29.5 °C. A maximum T_g of 82.1 °C was observed for a composition of 70–30 where the epoxy content is 70%.[443] Cardanol benzoxazine with two double bonds in its alkylene side chain and CEO monomer have T_o of 225 and 93 °C, respectively, and $T_{5\%}$ of 347 and 305 °C, respectively.

Eugenol epoxy and bisphenol-A type epoxy have similar reactivity, dynamic mechanical properties and thermal stability.[528] This means there is a good possibility of replacement of non-renewable phenol with renewable phenol in polymers.

Lignin epoxidized with epichlorohydrin and cured with 1-(2-cyanoethyl)-2-ethyl-4-methylimidazole showed 70% of the flexural strength of the petroleum-based epoxy resin.[529] Lignin epoxy resins[530,531] were synthesized and characterized. The final properties of the resin depend upon the physical and chemical properties of the lignin, which, in turn, depend upon sources and method of purification, therefore leading to different sets of thermal, structural and chemical properties.

Catechin-based epoxy monomer can replace up to 50% of DGEBA usage in epoxy resin formulation resulting in a decrease in swelling percentage suggesting the formation of a higher cross-linked network. However, no effect on T_g was observed with 50% replacement.[532] Glycidylation of green tea extract catechin with epichlorohydrin yields epoxy pre-polymers (Fig. 24). Further cross-linking with isophorone diamine (IPD) results in formation of an aromatic biobased cross-linked polymer which exhibited a 3- to 5-fold higher cross-link density and a higher char yield than the commercial epoxy DER352.[533]

Allylation of gallic acid followed by epoxidation yielded a tetra-epoxy monomer which also showed curing characteristics comparable to those of DGEBA with IPD.[534] Epoxy thermosets based on gallic acid and gallotannins have also been synthesised.[535]

4.2.4 Polyesters. Polyester obtained by reaction of diazotised cardanol and *p*-aminobenzoic acid showed liquid crystalline behavior.[536] Similarly, a copolymer based on oxidized cardanol, *i.e.* 8-(3-hydroxyphenyl)octanoic acid, and *p*-hydroxybenzoic acid showed a thermotropic liquid-crystalline behaviour.

A copolyester was synthesized by solution polycondensation of terephthaloyl chloride with 4-[(4-hydroxy-2-pentadecenylphenyl)diazenyl]phenol (HPPDP) and 1,4-butanediol.[537] The polymer showed short-range crystallinity as indicated by melting temperatures (63 and 127 °C) in DSC scan but no crystallinity was observed using wide-angle X-ray diffraction (WAXS).

Lignins can undergo polyesterification reaction when they have a sufficient and an appropriate number of hydroxyl groups present, as observed in the case of wheat lignins.[538] Biodegradable polyester (Biopol D 400P) films containing plasticizers (5–10%) and hydroxyl group-protected lignophenol exhibited tensile strengths better than those of Biopol films without the plasticizer.[539] Lignophenols or their carboxymethylated derivatives are chemically modified with polyalkylene glycol diglycidyl ether to form a cross-linked hydrogel network[540] which showed nearly tens to thousand times higher water absorption as compared to their dry weights.

4.2.5 Polyurethanes. Polyurethanes have been synthesized using hydroxyalkylated CF resins/commercial polyol (polypropylene glycol-2000, PPG-2000) and diphenylmethane diisocyanate (MDI). Polyurethane prepared using a higher mole ratio of cardanol–formaldehyde of hydroxyalkylated CF resin is found to possess better thermal and mechanical properties than the polyurethane prepared from a lower mole ratio.[541]

Polyurethane based on high-ortho novolac CF polyol resin and PPG-2000 condensed with MDI showed lower tensile and tear strength. This could be due to low molecular weight between the cross-links and higher cross-link density. However, a 75% increase in elongation at break was observed due to the flexibility of the chain introduced by the polyol.[542]

Polyurethanes based on HPPDP were prepared by treatment with MDI in *N*,*N*′-dimethylformamide as solvent at 80–90 °C (Fig. 25). The HPPDP was obtained from diazotized cardanol and a polyether prepared by condensing cardanol with epichlorohydrin and polymerizing through ROP.[438] WAXS study of the polyurethane showed a broad amorphous halo indicative of absence of crystallinity in the polymer, which has been explained as due to strong hydrogen bonding in the hard phase. This suggests sustainable polyurethanes can be explored for nonlinear optical applications.[437]

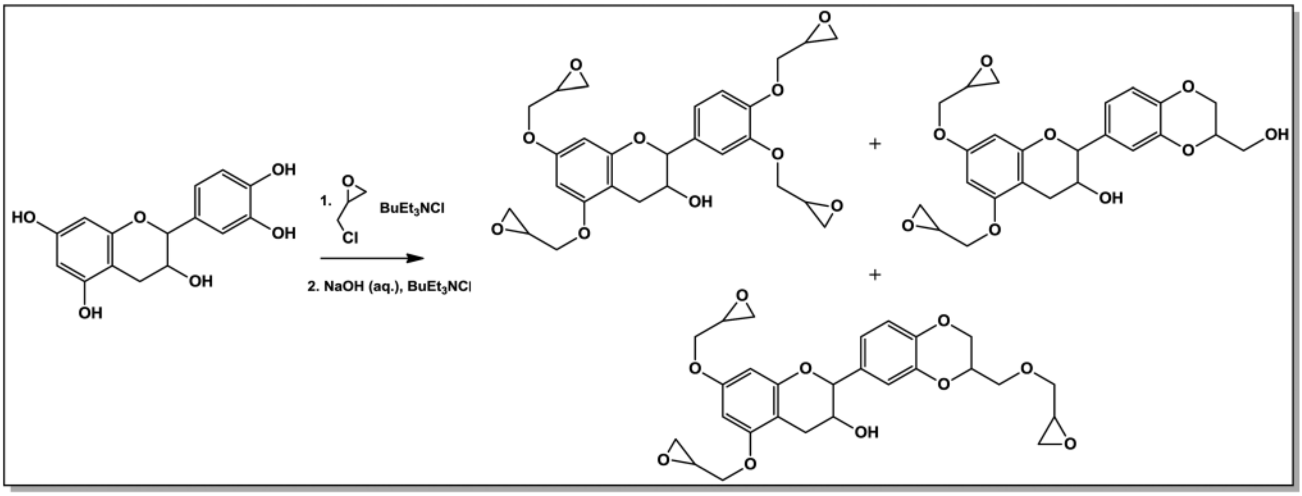


Fig. 24 Epoxidation of catechin to form epoxy monomers.

Double bonds present in side chain of cardanol in cardanol-glycol-based polyurethane (CGPU) films[543] were cross-linked on treatment with cobalt octoate due to autooxidation polymerisation mechanism. The increase of molecular weight of glycols leads to a decrease of cardanol content in CGPUs and hence to a decrease in cross-linking density of the films, which strongly affects T_g and swelling behaviour. A Co^{2+} catalysed and uncatalysed CGPU film showed a T_g of 15–40 °C and −30 to 15 °C respectively.

Polyurethane prepared by reaction of cardanol polyols (diol and triols), Fig. 26, with MDI at 1/1 NCO/OH using dibutyltin dilaurate as catalyst showed a linear increase in T_g with an increase in the hydroxyl value of the polyol and higher thermal stability in comparison to PPG-based polyurethanes.[544]

Solvent-induced self-assembly was observed in cardanol–urethane methacrylate comb polymers based on isophorone diisocyanate. They exhibited three-dimensional honeycomb morphology in chloroform, whereas in tetrahydrofuran, they formed spheres and tubes.[545]

Polyurethane formed by reaction of prepolymer based on demethylated lignin with toluene-2,4-diisocyanate and polyethylene glycol led to a 6.5-fold increase in modulus.[546] Electrospun kraft lignin materials showed moisture-responsive reversible shape change behaviour and this is attributed to both the chemical structure and physical properties of lignin fractions.[547] Polyurethane foams based on sodium ligninosulfonate and ethylene glycol/diethylene glycol/triethylene glycol/polyethylene glycol were synthesized. The T_g was found to be in the range of 37 to 117 °C and was dependent upon the mixing rate and molecular mass of glycols.[548] The hydroxyl groups of lignin can be utilized to replace petroleum-based polyol in polyurethane.[549–552] It was observed that 25–30% w/w replacement of polyol with hardwood ethanol organosolv lignin or 19–23% w/w HKL can lead to similar properties as a polyol-based polyurethane foam.[553,554]

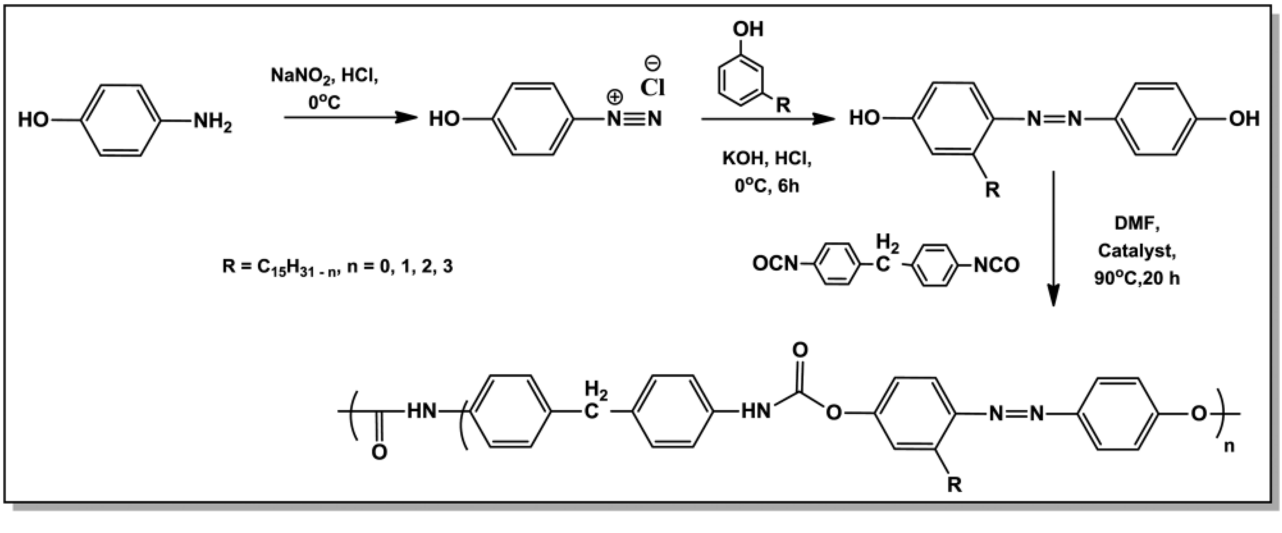


Fig. 25 Polyurethane resin based on diazotized cardanol.

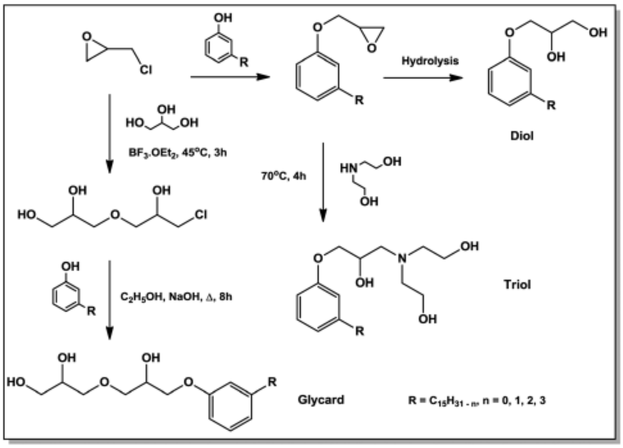


Fig. 26 Preparation of cardanol polyols.[544]

4.3 IPNs

Semi-interpenetrating polymer networks (semi-IPNs) have been reported in the literature of phenolic resins mainly with vinylic polymers such as PMMA[555] and polyurethanes.[556–559]

CF-PMMA showed an unusual increase in T_g of CF from 128 to 144 °C suggesting thereby restrictions in the segmental motion of the CF phase obtained by mixing with another rigid polymer such as PMMA.[555]

Semi-IPNs have also been prepared from castor-oil-based polyurethane with acetylated and phosphorylated cardanol derivatives.[556] CF-substituted aromatic compound-copolymerized resins with castor oil polyurethane semi-IPNs using ethylene glycol dimethacrylate as a cross-linker showed a higher thermal stability.[557] The WAXS analysis of semi-IPNs prepared by condensing CF novolac resins and polyurethanes prepared from castor oil and diisocyanates of varying NCO/OH ratio has also been investigated.[558]

Semi-IPNs were synthesized by reacting castor oil-based polyurethanes and a cardanol- and furfural-based phenolic resin. The semi-IPN containing 75% cardanol–furfural resin was stable up to very high temperatures, due to formation of a highly cross-linked network. The degradation mechanism of these semi-IPNs was suggested based on the kinetic parameters evaluated from computer simulations of TGA data.[559]

4.4 Rubber

Rubber can be physically or chemically modified with phenols obtained from renewable resources. CNSL has been used as an additive that improves the moisture resistance of rubber to explore its usage for electrical insulation. The phosphorylated derivative of cardanol (Anorin-38)[560–571] is found to behave as a multifunctional additive when physically/chemically added to rubber during compounding. However, physical blending of cardanol or its derivatives is usually associated with incompatibility of the additive with the rubber resulting in poor and complex mixing, handling problems, being time consuming and costly, and leaching problems during storage and use. In order to improve the compatibility, natural and synthetic rubber were chemically grafted[572] with cardanol (Fig. 27) or its phosphorylated derivative in both solid state and solution, in the presence of a free radical initiator. Importantly, such rubber variants have high plasticity (57–59), lower Mooney and melt viscosities or viscosity (35–43), and better cure properties, as compared to conventional virgin or plasticized natural rubber (NR). Moreover, upon vulcanization, the grafted rubber mentioned above is found to have superior tensile properties, better ageing resistance and higher flame retardancy.

CF and cardanol glycidyl ether have been synthesized for reinforcing NR, a blend of NR and styrene–butadiene rubber (SBR), and nitrile–butadiene rubber (NBR).[573] In comparison to novolac CF resin, resolic CF acts as both a reinforcing agent and a cross-linking agent for NBR due to reaction of the methylol groups of CF with the nitrile groups of NBR.

Adhesive properties of blends of PF/CF copolymer resin with polychloroprene rubber were studied using different substrates. A 80 : 20 phenol : cardanol ratio was found to be optimum for shear strength of aluminum–aluminum bonds, while a 60 : 40 ratio was the best for peel properties.[574] For SBR–SBR and SBR–Al bonds, a 60 : 40 ratio is optimum for both peel as well as shear strength. The copolymer based on phenol, cardanol and formaldehyde is a better choice for the resin than either of the individual condensation products of phenol or cardanol with formaldehyde. The addition of 3-aminopropyltriethoxysilane[575] to the adhesive formulation improves the bond strength of metal-to-metal specimens.

4.5 Miscellaneous

Several other renewable source phenolic monomers derived from agro waste have arisen recently showing a variety of applications with promising commercial viability.

Vanillin-based polymers such as vinyl ester resins,[418] vanillin–chitosan hybrid,[576–578] neat-[440,579] or chitosan–vanillin Schiff-base biopolymers[580] may find applications in metal ion removal. Polymers formed by methacrylation of hydroxyl functionality or to a carbonate ester[421] have been explored for molecular imprinting applications. Poly(dihydroferulic acid) may act as a substitute for poly(ethylene terephthalate) formed by reaction of vanillin and acetic anhydride which is then subjected to the Perkin reaction followed by hydrogenation to afford acetyldihydroferulic acid (Fig. 28).[581]

Lignin undergoes esterification to produce thermoplastics with flexural properties comparable to those of common plastics such as polypropylene and poly(ethylene terephthalate).[582,583] A cross-linked polymer network based on lignin and a highly branched poly(ester-amine) obtained by melt

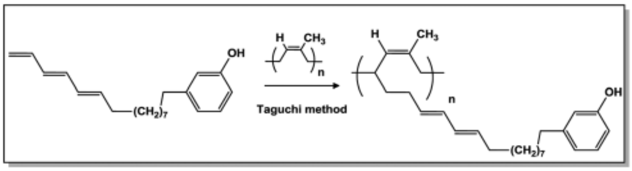


Fig. 27 Chemically grafting natural rubber with cardanol triene.[572]

polycondensation of 1,1,1-triethanolamine and adipic acid showed similar tensile strength, flexibility and elongation at break as commercial polymers.[584]

ATRP and click chemistry have been used to develop lignin-based hybrid copolymers with lignin centre and poly(*n*-butyl acrylate) or polystyrene grafts using "graft from" and "graft onto" methods. While in the former method ATRP was employed to polymerize vinyl monomers from a lignin-based macroinitiator, backbone lignin was linked to polystyrene graft *via* click chemistry in the latter case. Hence, the obtained lignin-based graft copolymers are expected to show high flexibility in processing as thermoplastic polymers.[585]

Lignin-*g*-polyNIPAM (*N*-isopropylacrylamide) copolymers prepared *via* atom transfer radical polymerization (ATRP) showed thermoresponsive and ionic responsive characters.[586] The graft copolymer showed a lower critical solution temperature at 32 °C (Fig. 29).[587] Lignin-containing poly(BMA) graft copolymers formed by reaction of acryloyl-modified lignin-based macromonomer with butyl methacrylate (BMA) showed higher thermal stability and also an increased glass transition temperature compared to poly(BMA) due to the presence of bulky aromatic group of lignin.[588] Grafting polymerization of lactide onto lignin utilizes more aliphatic than phenolic hydroxyl groups. These polymers besides being green also show the possibility of usage as dispersion modifiers in polylactide-based materials.[589]

Vinyl acetate has also been grafted on lignin using potassium persulfate as an initiator and ammonium iron(II) sulfate as a catalyst in aqueous reaction medium paving the way for value-added greener products.[590]

Studies carried out to understand the influence of lignin on the grafting mechanism of lignosulfonate with acrylic acid (AA) indicate the dependence of product yield, monomer conversion and grafting efficiency on phenolic group content.[591]

The graft copolymerization of eucalyptus lignosulfonate calcium from hardwood and AA using Fenton agent as a co-initiator also confirmed the involvement of the phenolic group in the grafting reaction as an active centre.[592]

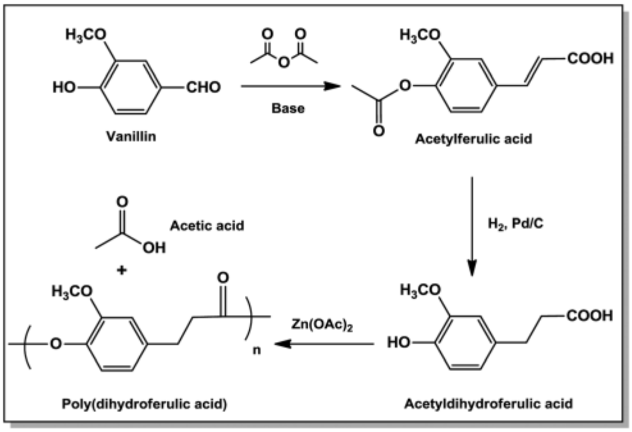


Fig. 28 Synthesis of biorenewable polyester from vanillin and acetic anhydride.[581]

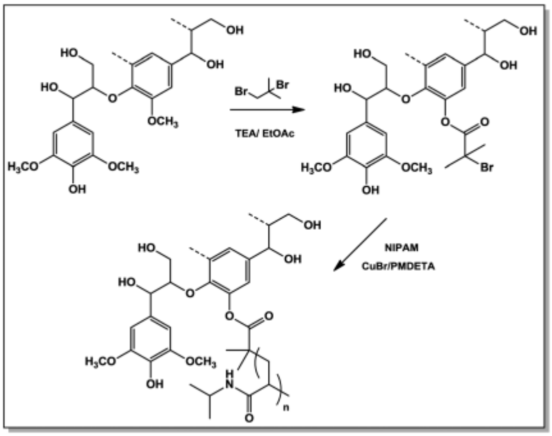


Fig. 29 Synthesis of lignin-*g*-polyNIPAM copolymers.

Acetone-fractionated SKL with protected phenolic hydroxyl groups has been utilised for the synthesis of poly(arylene ether) sulfones, demonstrating the use of technical kraft lignin as a phenolic precursor for the creation of heat-stable thermoplastic materials.[593] Lignin exhibits strong ultraviolet (UV) absorbing properties which were explored by the copolymerization of acryloyl chloride-modified biobutanol lignin with *n*-butyl acrylate and MMA by free-radical polymerization to yield potential UV-absorbent films.[594] Utility of lignin as a biomaterial is hampered due to its non-uniform structure and low thermal stability. Application of low-dosage of γ-irradiation has come up as a promising technique to modify lignin's thermal properties and to attach requisite functional groups onto it.[595]

The graft copolymerization of lignin and 1-ethenylbenzene co-initiated by lignin, calcium chloride, and hydrogen peroxide in dimethyl sulfoxide solution led to a change in the surface properties of lignin from hydrophilic to hydrophobic. Thermoplastic material hence obtained showed biodegradability where rate of degradation was found to increase with an increase in lignin content of the copolymer sample.[596]

Star-shaped polymers (SPCs) containing PEG with cardanol side groups synthesized by ATRP undergo self-cross-linking reaction between unsaturated hydrocarbon chains of cardanol moieties upon UV irradiation, imparting water-insoluble properties to the SPCs thereby having antifoulant applications.[597] Cardanol has also been used to prepare a trithiocarbonate RAFT agent and a reactive anionic surfactant, which were combined to prepare a cardanol–PMMA polymer resulting in high-stability latex.[598]

5. Properties of polymers derived from naturally occurring phenolic derivatives

5.1 Thermal stability

CNSL showed a higher thermal stability when heated for a longer duration at 140 °C due to thermal oligomerisation.[599]

The thermal stability of CF resins is lower than that of PF resins due to the presence of *m*-alkylene side chains. The poorer thermal stability of the CPF and CF resins cannot be explained only by the low temperature stability of the alkyl group of cardanol but is also caused by the negative influence of the long alkyl chain (because of its steric effect) on the cross-linking of the resins. Therefore, the addition of CF resins to PF resins results in a decrease in thermal stability of the blends. A cardanol content less than 15 wt% in CPF resins does not seriously affect the thermostability of the resin blend at temperatures below 400 °C, which is of most practical importance.[465]

The thermal stability of CF resin is found to be less than that of cardanol–furfural-hydroxy compound-based resin and can be explained on the basis that the furfural moiety in the resin backbone imparts a higher stability than the methylene bridge present in CF resin.[469]

CF resin containing boron–nitrogen co-ordinate bond (CFBN) has higher thermal stability than CF resin. The temperature of maximum rate of weight loss was 394 °C in CF resins but it increased to 437 °C in CFBN.[600]

Our group has studied thermal behaviour of benzoxazine monomer blends based on cardanol (Bz-c), bisphenol-A (Bz-A), and *p*-hydroxybenzoic acid (Bz-pA). The curing characteristics [onset of curing (T_o), peak curing temperature (T_p) and heat of curing (ΔH)] and thermal properties [$T_{5\%}$, $T_{10\%}$ and char yield (Y_c)] of monomer blends Bz-C–Bz-A with and without Bz-pA was studied by DSC analysis (Table 3). The T_o of Bz-C reduced from 242 to 211 °C by addition of Bz-A (1 : 3 ratio). Addition of Bz-pA further reduced the onset temperature of curing. The catalytic effect of carboxyl acid in the opening of the benzoxazine ring is well documented in the literature.[601–603] Incorporation of Bz-pA, however, lowers the thermal stability of the tri-copolymer due to decarboxylation of carboxylic group. Neat cardanol-based polymer (PBz-C) and copolymers were found to be more thermally stable and flexible than neat bisphenol-A based benzoxazine polymer (PBz-A). This behaviour is different from CF resins, where incorporation of cardanol resulted in lowering of thermal stability of the resin.

Tannin-based foams also exhibit physical properties which are on a par with those of existing commercial phenolic foams. Of note is their property of fire resistance, which is even better than that of other phenolic foams, as the latter have ignition time of around 2 min when submitted to a heat flux as high as 50 kW m^{-2}. The released heat, 12 kW m^{-2}, is much lower than that required for burning them under the same radiant energy. Therefore, tannin foams are slowly consumed without flame if the heat flux is maintained and spontaneously self-extinguish as soon as the heat source is removed.[604]

5.2 Chemical resistance

Chemical resistance of samples was determined after immersing cured PF/CF samples in standard reagents such as water, acid, alkali, organic solvent for 7 days. Phenolic resole resins based on phenol and cardanol (<15%) showed higher chemical resistance than the PF resins.[465] In general a 20 wt% of phenol replacement by cardanol in CPF resins showed no weight loss indicating the samples were well cured. It was also found that, with an increase in cardanol content in the resin, a reduction of the weight gain in aqueous solvents took place. This is largely due to the fact that the cardanol molecule contains a long alkyl group which is hydrophobic in nature. However, in acetone, weight gain is more in CF and is accounted for by less cross-linking for steric reasons of long alkyl chain and hence favouring higher reagent absorption.

Anticorrosive properties of epoxy–cardanol resin-based paints are superior to those of the paints formulated with the unmodified epoxy resin.[419]

5.3 Mechanical properties

With an increase in cardanol content in PF resin from 0 to 15 wt %, an increase of the flexural, tensile and Izod impact strength and a decrease in tensile modulus were observed. The alkyl group of cardanol plays the role of an intramolecular plasticizer and, hence, the resins become more flexible and more elastic. The lower tensile strength of CF resins compared to PF resins may be understood on the basis of the structure of the C-15 side chain imparting steric hindrance and reduction in intermolecular interactions. Neat CF resin has low tensile strength and modulus and high flexural strength. However, no effect was observed on compressive strength with increase in cardanol content. A cardanol–phenol (15/85 w/w) material was found to have a good chemical resistance as well as mechanical properties, and the thermal stability up to 250 °C still remains on the level of a phenolic resin and suitable for commercial use.[465]

Table 3 Results of DSC analysis of blends of benzoxazine monomers (Bz-C, Bz-A and Bz-pA, static air, heating rate 10 °C min^{-1})

Designation	T_o (°C)	T_p (°C)	ΔH (J g^{-1})	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield (%) at 800 °C
Bz-C	242	263	71	398	430, 467	12
Bz-C–Bz-A (3 : 1)	235	255	74	394	430, 465	14
Bz-C–Bz-A–Bz-pA (3 : 1 : 0.1)	201	235	129	346	421	10
Bz-C–Bz-A (1 : 1)	233	250	114	379	430, 456	17
Bz-C–Bz-A–Bz-pA (1 : 1 : 0.1)	174	216	157	258	346	15
Bz-C : Bz-A (1 : 3)	211	231	223	377	447	20
Bz-C–Bz-A–Bz-pA (1 : 3 : 0.15)	436	483	200	277	343	26
Bz-C–Bz-A–Bz-pA (1 : 5.67 : 0.57)	161	209	190	288	339	29
Bz-A	187	219	64.8	274	310, 450	39

Interpenetration of CF with PMMA improved the mechanical properties only marginally.[558]

A replacement of phenol by lignin (40% w/w) extracted from sugarcane bagasse by the organosolv process was used as a partial substitute in the preparation of resole-type lignophenolic matrixes. A reinforced carbon material obtained by a controlled pyrolysis of lignophenolic matrix/sugarcane bagasse showed a flexural strength as high as 21 MPa and flexural modulus in the range of 11–13 GPa.[605] Also short bagasse fiber composites with resole phenolic matrixes prepared by partial substitution of phenol (40 w/w) with lignin were reported.[606] An improvement in the impact strength was observed as a result of the use of sugarcane bagasse. The inner part of the fractured samples was analyzed by SEM, and the results indicated adhesion between fibers and matrix, because the fibers are not set free, suggesting they suffered a break during the impact test. The results as a whole showed that it is feasible to replace some phenol by lignin in phenolic matrices without the loss of mechanical properties.

Phenolic closed-cell foams based on neat phenolic and partial substitution of phenol with lignin showed similar thermal conductivity while analysis of mechanical properties showed that the partial replacement of phenol by lignin was extremely advantageous, because it increases the compression strength and puts the lignophenolic foam in the structural foam class.[141]

Plywood samples glued with organosolv LPF and degraded organosolv LPF adhesives with a phenol replacement ratio up to 75 wt% showed higher dry and wet tensile strengths than those glued with PF adhesives.[171,607] The reason may be because of the higher phenolic content of organosolv and degraded lignin.

Phenol substituted with 50 wt% lignin showed comparable adhesive strength.[608,609] The tensile strengths of dry plywood samples bonded with bio-oil PF resole resin adhesives were comparable to that of the conventional pure PF resin adhesive.[610] Resin formulation of conventional PF when substituted with 30% of bagasse lignin PF as wood adhesive gave tensile strength of 1.2 and 1.8 MPa respectively.[611]

5.4 Conductivity

Conductive composites based on LPs and PANI (emeraldine salts) showed conductivities in the range of 4.6×10^{-6} to 1.0×10^{-7} S cm^{-1} which is sufficient for removal of static electricity and also enables resistance against rust.[612] A dependence on the nature of the wood from where LPs are extracted and grafted and the nature of the monophenol dictates the conductivity values.

Composites of lignin-based polymers and their derivatives were also used as photosensitizers for nano-porous TiO_2 electrodes.[613] This is probably due to higher absorbance of lignophenol/TiO_2 electrodes in the region of $\lambda = 400–600$ nm leading to η of 0.48% under 100.3 mW cm^{-2} of visible light irradiation. Dye-sensitized solar cells using porous TiO_2 with lignophenols have shown stable and higher light–electricity conversions, $\eta =$ 3.3%. The photo-electricity conversions could be caused by both complexation of phenolic hydroxyl groups with Ti^{4+} and stacking of 1,1-bis(aryl)propane units of LPs onto the higher surface area provided by porous titanium dioxide nanoparticles.

5.5 Biodegradability

The main attraction for replacement of petro-based phenol with bio-based phenols such as cardanol, lignin, and the lignin derived lower molecular weight phenols in polymers is to explore the possibility of bio-degradation of polymers upon completion of their usage. It was found that degradation of lignin-based polymers, namely lignocatechol and lignocresol, occurred in the presence of peroxidise and laccase enzymes. The degree of degradation was found to be lower in case of *Rhus vernicifera* laccase compared to peroxidase, which might be because of the low activity of laccase on the lignin moieties in lignophenols.[614] White rot fungus was found to degrade styrene graft lignin copolymer samples and the rate of degradation was found to increase with increase in lignin content.[615]

Distilled CNSL has been shown to be biodegradable when tested using OECD Method 301D (96% degradation after 28 days) in a GLP study.[616]

Tannic acid (TA) or tannin is a biocompatible and biodegradable polyphenol due to the presence of a glucose core linked with phenolic moieties. A biodegradable miscible blend of poly(butylene adipate-*co*-butylene terephthalate)[617,618] or poly(ε-caprolactone) (PCL) with TA was prepared. The blends in acid showed miscibility due to hydrogen bonding between phenolic hydroxyl in TA and carbonyl groups of the polymer. PCL and TA were found to be miscible as indicated by the single T_g value and depression of equilibrium melting point of PCL in the blends.[619]

6. Conclusions and future challenges

In the past decade, naturally occurring phenolic derivatives have arisen as attractive precursors for developing new materials from renewable bio-sources for use in eco-friendly processes. Resins have been prepared utilising either the whole liquid product or a phenolics-enriched fraction obtained after fractional condensation or further processing, such as solvent extraction or use of greener extraction methods.

However, to date, none of the phenolic production and fractionation techniques has been utilized to allow substitution of 100% of the phenol content of the resin without impacting its effectiveness compared to commercial formulations based on petroleum-derived phenol. The variable nature of the percentage of phenolic compounds in terms of purity from different batches of crops from one season to another and geographical influence does not allow the reproducibility of phenolic compounds and hence the resulting polymers. Therefore, the direction that needs to be explored should be oriented towards complete replacement of petro-based phenolics with bio-based ones in the face of an urgent petroleum crisis. In addition, there is a necessity for materials showing enhanced applicability and improved performance. It is a beginning of the era of such a step which requires further exploration of natural phenolic sources aimed at their enhanced utilization.

Notes and references

1 P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538.
2 F. W. Lichtenthaler and S. Peters, *C. R. Chim.*, 2004, **7**, 65.
3 B. Lochab, I. K. Varma and J. Bijwe, *Adv. Mater. Phys. Chem.*, 2012, **2**, 221.
4 R. Mülhaupt, *Macromol. Chem. Phys.*, 2013, **214**, 159.
5 J. M. Kawser and A. F. Nash, *J. Oil Palm Res.*, 2000, **12**, 86.
6 H. Kozlowska, D. A. Rotkiewicz, R. Zadernowski and F. W. Sosulski, *J. Am. Oil Chem. Soc.*, 1983, **60**, 1119.
7 L. Zahradníková, Š. Schmidt, Z. Sékelyová and S. Sekretár, *Czech J. Food Sci.*, 2008, **26**, 58.
8 D. Wasserman and C. R. Dawson, *Ind. Eng. Chem.*, 1945, **37**, 396.
9 E. R. Leal, R. R. Vaquez and T. Galindo, *J. Wood Chem. Technol.*, 1994, **14**, 369.
10 P. Lauri, P. Havlík, G. Kindermann, N. Forsell, H. Böttcher and M. Obersteiner, *Energy Policy*, 2014, **66**, 19.
11 http://www.cashewindia.org/index.php.
12 W. F. Symes and C. R. Dawson, *Nature*, 1953, **171**, 841.
13 E. Calo, A. Maffezzoli, G. Mele, F. Martina, S. E. Mazzetto, A. Tarzia and C. Stifani, *Green Chem.*, 2007, **9**, 754.
14 M. Himejima and I. Kubo, *J. Agric. Food Chem.*, 1991, **39**, 418.
15 I. Kubo, M. Ochi, P. C. Vieira and S. Komatsu, *J. Agric. Food Chem.*, 1993, **41**, 1012.
16 I. Kubo, I. K. Hori and Y. Yokokawa, *J. Nat. Prod.*, 1994, **57**, 545.
17 D. Secci, S. Carradori, B. Bizzarri, A. Bolasco, P. Ballario, Z. Patramani, P. Fragapane, S. Vernarecci, C. Canzonetta and P. Filetici, *Bioorg. Med. Chem.*, 2014, **22**, 1680.
18 M.-K. Kim, D.-H. Lee, S. Lee, E.-J. Kim and J.-H. Chung, *J. Dermatol. Sci.*, 2014, **73**, 169.
19 I. Kubo, N. Masuoka, T. J. Ha and K. Tsujimoto, *Food Chem.*, 2006, **99**, 555.
20 A. Velmurugan and M. Loganathan, *J. Eng. Tech.*, 2011, **58**, 889.
21 C. Sze Ki Lin, L. A. Pfaltzgraff, L. Herrero-Davila, E. B. Mubofu, S. Abderrahim, J. H. Clark, A. A. Koutinas, N. Kopsahelis, K. Stamatelatou, F. Dickson, S. Thankappan, Z. Mohamed, R. Brocklesby and R. Luque, *Energy Environ. Sci.*, 2013, **6**, 426.
22 A. Contantinescu and J. Reyes, US 8349924 B2coatings, 2013.
23 S. Li, X. Yang, K. Huang, M. Li and J. Xia, *Prog. Org. Coat.*, 2014, **77**, 388.
24 M. Kathalewar, A. Sabnis and D. D'Melo, *Prog. Org. Coat.*, 2014, **77**, 616.
25 F. Jaillet, E. Darroman, A. Ratsimihety, R. Auvergne, B. Boutevin and S. Caillol, *Eur. J. Lipid Sci. Technol.*, 2014, **116**, 63.
26 A. Pizzi, *Rev. Adhes. Adhes.*, 2013, **1**, 88.
27 S. Suwanprasop, T. Nhujak, S. Roengsumran and A. Petsom, *Ind. Eng. Chem. Res.*, 2004, **43**, 4973.
28 M. Awang and G.-M. Seng, *ChemSusChem*, 2008, **1**, 210.
29 H. Y. Xiao, M. W. Zhi, J. Fei, H. H. Li and H. Z. Yong, *Appl. Mech. Mater.*, 2013, **483**, 83.
30 P. Verge, T. Fouquet, C. Barrère, V. Toniazzo, D. Ruch and J. A. S. Bomfim, *Compos. Sci. Technol.*, 2013, **79**, 126.
31 P. Saini and M. Arora, *J. Mater. Chem. A*, 2013, **1**, 8926.
32 P. De Maria, P. Fillippone, A. Fontana, C. Gasbarri, G. Siani and D. Velluto, *Colloids Surf., B*, 2005, **40**, 11.
33 R. A. Garcia, S. P. Pantazatos, D. P. Pantazatos and R. C. MacDonald, *Biochim. Biophys. Acta*, 2001, **1511**, 270.
34 B. Thiele, V. Heinke, E. Kleist and K. Guenther, *Environ. Sci. Technol.*, 2004, **38**, 3405.
35 A. Soares, B. Guieysse, B. Jefferson, E. Cartmell and J. N. Lester, *Environ. Int.*, 2008, **34**, 1033.
36 D. Lomonaco, F. J. N. Maia and S. E. Mazzetto, *J. Therm. Anal. Calorim.*, 2013, **111**, 619.
37 P. Kasemsiri, S. Hiziroglu and S. Rimdusit, *Thermochim. Acta*, 2011, **520**, 84.
38 M. D. Besteti, F. G. Souza Jr, D. M. G. Freire and J. C. Pinto, *Polym. Eng. Sci.*, 2014, **54**, 1222.
39 K. Huang, Y. Zhang, M. Li, J. Lian, X. Yang and J. Xi, *Prog. Org. Coat.*, 2012, **74**, 240.
40 G. Vasapollo, G. Mele and R. D. Sole, *Molecules*, 2011, **16**, 6871.
41 G. Mele, J. Li, E. Margapoti, F. Martina and G. Vasapollo, *Catal. Today*, 2009, **140**, 37.
42 V. S. Balachandran, S. R. Jadhav, P. K. Vemula and G. John, *Chem. Soc. Rev.*, 2013, **42**, 427.
43 P. K. Vemula and G. John, *Acc. Chem. Res.*, 2008, **41**, 769.
44 P. Das and A. Ganesh, *Biomass Bioenergy*, 2003, **25**, 113.
45 R. Li, Y. Shen, X. Zhang, M. Ma, B. Chen and T. A. van Beek, *J. Nat. Prod.*, 2014, **77**, 571.
46 http://www.epa.gov/HPV/pubs/summaries/casntliq/c13793rt.pdf.
47 K. S. Nagabhushana and B. Ravindranath, *J. Agric. Food Chem.*, 1995, **43**, 2381.
48 J. H. P. Tyman, R. A. Johnson, M. Muir and R. Rokhgar, *J. Am. Oil Chem. Soc.*, 1989, **66**, 553.
49 J. H. P. Tyman, Synthetic and Natural Phenols Studies, in *Organic Chemistry*, Elsevier, Amsterdam, 1998, p. 518.
50 M. O. Edoga, L. Fadipe and R. N. Edoga, *Leonardo Electron. J. Pract. Technol.*, 2006, **9**, 107.
51 P. S. Kumar, N. A. Kumar, R. Sivakumar and C. Kaushik, *J. Mater. Sci.*, 2009, **44**, 5894, DOI: 10.1007/s10853-009-3834-8.
52 P. Das, T. Sreelatha and A. Ganesh, *Biomass Bioenergy*, 2004, **27**, 265.
53 S. V. Shobha and B. Ravindranath, *J. Agric. Food Chem.*, 1991, **39**, 2214.
54 A. Ganesh, R. Patel and S. Bandyopadhyay, *Bioresour. Technol.*, 2006, **97**, 847.
55 R. N. Patel, S. Bandyopadhyay and A. Ganesh, *Energy*, 2011, **36**, 1535.
56 W. B. Setianto, S. Yoshikawa, R. L. Smith Jr, H. Inomata, L. J. Florusse and C. J. Peters, *J. Supercrit. Fluids*, 2009, **48**, 203.
57 R. Paramashivappa, P. P. Kumar, J. Vithayathil and A. S. Rao, *J. Agric. Food Chem.*, 2001, **49**, 2548.

58 J. H. P. Tyman and I. E. Bruce, *J. Surfactants Deterg.*, 2003, **6**, 291.
59 T. Gandhi, M. Patel and B. K. Dholakiya, *J. Nat. Prod. Plant Resour.*, 2012, **2**, 135.
60 S. Sato, W. B. de Almeida, A. F. Filho and R. C. Bueno, US 7825284 B2, 2010.
61 S. K. Pathak and B. S. Rao, *J. Appl. Polym. Sci.*, 2006, **102**, 4741.
62 P. P. Kumar, R. Paramashivappa, P. J. Vithayathil, P. V. S. Rao and A. S. Rao, *J. Agric. Food Chem.*, 2002, **50**, 4705.
63 R. Ikeda, H. Tanaka, H. Uayama and S. Kobayashi, *Macromol. Rapid Commun.*, 2000, **21**, 496.
64 W. Boerjan, *Curr. Opin. Biotechnol.*, 2005, **16**, 159.
65 W. Boerjan, J. Ralph and M. Baucher, *Annu. Rev. Plant Biol.*, 2003, **54**, 519.
66 M. Kleinert and T. Barth, *Chem. Eng. Technol.*, 2008, **31**, 736.
67 O. Kazuhide, M. Xin, U. Mitsuo, T. Seiichi and A. Tadafumi, *J. Phys.: Condens. Matter*, 2004, **6**, 1325.
68 Y. Akao, N. Seki, Y. Nakagawa, H. Yi, K. Matsumoto, Y. Ito, K. Ito, M. Funaoka, W. Maruyama, M. Naoia and Y. Nozawa, *Bioorg. Med. Chem.*, 2004, **12**, 4791.
69 E. Dorrestijn, L. J. J. Laarhoven, I. W. C. E. Arends and P. Mulder, *J. Anal. Appl. Pyrolysis*, 2000, **54**, 153.
70 R. Vanholme, B. Demedts, K. Morreel, J. Ralph and W. Boerjan, *Plant Physiol.*, 2010, **153**, 895.
71 J. J. Stewart, T. Akiyama, C. Chapple, J. Ralph and S. D. Mansfield, *Plant Physiol.*, 2009, **150**, 621.
72 M. P. Pandey and C. S. Kim, Lignin, *Chem. Eng. Technol.*, 2011, **34**, 29.
73 A. Effendi, H. Gerhauser and A. V. Bridgwater, *Renewable Sustainable Energy Rev.*, 2008, **12**, 2092.
74 Q. Bu, H. Lei, A. H. Zacher, L. Wang, S. Ren, J. Liang, Y. Wei, Y. Liu, J. Tang, Q. Zhang and R. Ruan, *Bioresour. Technol.*, 2012, **124**, 470.
75 F. Xu, R.-C. Sun, J.-X. Sun, C.-F. Liu, B.-H. He and J.-S. Fan, *Anal. Chim. Acta*, 2005, **552**, 207.
76 M. Baucher, C. Halpin, M. Conil-Petit and W. Boerjan, *Crit. Rev. Biochem. Mol. Biol.*, 2003, **38**, 305.
77 H. Rabemanolontsoa and S. Saka, *RSC Adv.*, 2013, **3**, 3946.
78 B. A. Simmons, D. Logue and J. Ralph, *Curr. Opin. Plant Biol.*, 2010, **13**, 313.
79 T.-F. Yeh, H.-M. Chang and J. F. Kadla, *J. Agric. Food Chem.*, 2004, **52**, 1435.
80 K. Iiyama and A. F. A. Wallis, *Wood Sci. Technol.*, 1988, **22**, 271.
81 N. Brosse, R. El Hage, M. Chaouch, M. Petrissans, S. Dumarcay and P. Gerardin, *Polym. Degrad. Stab.*, 2010, **95**, 1721.
82 A. Bismarck, S. Mishra and T. Lampke, *Biopolym. Biocomp.*, ed. A. K. Mohanty, M. Misra and L. T. Drzal, CRC Press, Taylor and Francis, NW, FL, 2005, ch. 2, p. 37.
83 R. S. Fukushima and R. D. Hatfield, *J. Agric. Food Chem.*, 2004, **52**, 3713.
84 A.-C. Albertsson, U. Edlund and I. K. Varma, Synthesis, chemistry and properties of hemicelluloses, in *Biopolymers – new materials for sustainable films and coatings*, ed. D. Plackett, Wiley, UK, 2011, ch. 7, pp. 133–150.
85 L. Wati, S. Kumari and B. S. Kundu, *Indian J. Microbiol.*, 2007, **47**, 26.
86 R. Nordin, C. M. S. Said and H. Ismail, *Solid State Sci. Technol.*, 2007, **15**, 83.
87 A. Pandey, C. R. Soccola, P. Nigam and V. T. Soccol, *Bioresour. Technol.*, 2000, **74**, 69.
88 K. V. Sarkanen and H. L. Hergert, Classification and distribution, in *Lignins: occurrence, formation structure and reactions*, ed. K. V. Sarkanen and C. H. Ludwig, Wiley-Interscience, New York, 1971, pp. 43–94.
89 M. Asmadi, H. Kawamoto and S. Saka, Green Energy and Technology, in *Zero-Carbon Energy Kyoto 2010: Proceedings of the Second International Symposium of Global COE Program "Energy Science in the Age of Global Warming—Toward CO_2 Zero-emission Energy System"*, ed. T. Yao, Springer, Tokyo, 2011, pp. 129–135.
90 R. Sun, J. M. Lawther and W. B. Banks, *Ind. Crops Prod.*, 1997, **6**, 1.
91 A. U. Buranov and G. Mazza, *Ind. Crops Prod.*, 2008, **28**, 237.
92 Y. Barrière, C. Riboulet, V. Méchin, S. Maltese, M. Pichon and A. Cardinal, *Genes, Genomes and Genomics*, 2007, **1**, 133.
93 G. de Carvalho, J. A. Pimenta, W. N. dos Santos and E. Frollini, *Polym.-Plast. Technol. Eng.*, 2003, **42**, 605.
94 M. Brebu and C. Vasile, *Cellul. Chem. Technol.*, 2010, **44**, 353.
95 R. D. Hatfield and J. M. Marita, *Phytochem. Rev.*, 2010, **9**, 35.
96 D. J. Nowakowski, A. V. Bridgwater, D. C. Elliott, D. Meier and P. de Wild, *J. Anal. Appl. Pyrolysis*, 2010, **88**, 53.
97 E. Adler, *Wood Sci. Technol.*, 1977, **11**, 169.
98 R. B. Santos, E. A. Capanema, M. Y. Balakshin, H.-M. Chang and H. Jameel, *J. Agric. Food Chem.*, 2012, **60**, 4923.
99 T. E. Timell, *Adv. Carbohydr. Chem.*, 1965, **19**, 409.
100 M. Galbe and G. Zacchi, *Appl. Microbiol. Biotechnol.*, 2002, **59**, 618.
101 N. Phaiboonsilpa and S. Saka, Green Energy and Technology, in *Zero-Carbon Energy Kyoto 2010: Proceedings of the Second International Symposium of Global COE Program "Energy Science in the Age of Global Warming—Toward CO_2 Zero-emission Energy System"*, ed. T. Yao, Springer, Tokyo, 2011, pp. 142–146.
102 M. Asmadi, H. Kawamoto and S. Saka, *J. Wood Sci.*, 2010, **56**, 319.
103 D. Fengel and G. Wegener, Polyoses (Hemicelluloses), in *Wood—chemistry, ultrastructure, reactions*, Walter de Gruyter, Berlin and New York, 1989, pp. 109–111.
104 M. Fidalgo, M. Terron, A. Martinez, A. Gonzalez, F. Gonzalez-vila and G. Galletti, *J. Agric. Food Chem.*, 1993, **41**, 1621.
105 A. Scalbert, B. Monties, J. Lallemand, E. Guittet and C. Rolando, *Phytochemistry*, 1985, **24**, 1359.
106 S. H. Ghaffar and M. Fan, *Int. J. Adhes. Adhes.*, 2014, **48**, 92.
107 D. S. Himmelsbach, Structure of forage cell walls, in *Forage cell wall structure and digestibility*, ed. H. Jung, D. Buxton, R. Hartfield and J. Ralph, American Society of Agronomy, Madison, WI, 1993, pp.271–283.

108 M. Bunzel, J. Ralph, J. M. Marita, R. D. Hatfield and H. Steinhart, *J. Sci. Food Agric.*, 2001, **81**, 653.

109 T. B. T. Lam, K. Iiyama and B. A. Stone, *Phytochemistry*, 1992, **31**, 1179.

110 T. B. T. Lam, K. Kadoya and K. Iiyama, *Phytochemistry*, 2001, **57**, 987.

111 J. H. Grabber, J. Ralph and R. D. Hatfield, *J. Agric. Food Chem.*, 2000, **48**, 6106.

112 R. C. Sun, X. F. Sun and S. H. Zhang, *J. Agric. Food Chem.*, 2001, **49**, 5122.

113 R. C. Sun, X. F. Sun, S. Q. Wang, W. Zhu and X. Y. Wang, *Ind. Crops Prod.*, 2002, **15**, 179.

114 A. Geng, F. Xin and J.-Y. Ip, *Bioresour. Technol.*, 2012, **104**, 715.

115 M. G. Jackson, *Anim. Feed Sci. Technol.*, 1977, **2**, 105.

116 K. Ryan, Comparison between utilization of cellulose for paper from wood and straw, in *New approaches to research on cereal carbohydrates*, ed. R. Hill and L. MunckL, Elsevier, Amsterdam, 1985, pp.323–7.

117 M. G. Alriols, A. Tejado, M. Blanco, I. Mondragon and J. Labidi, *Chem. Eng. J.*, 2009, **148**, 106.

118 M. Camciuc, M. Deplagne, G. Vilarem and A. Gaset, *Ind. Crops Prod.*, 1998, **7**, 257.

119 L. Serrano, F. Marín, A. Gonzalo and J. Labidi, *Ind. Crops Prod.*, 2012, **40**, 110.

120 S. Kubo and J. F. Kadla, *Biomacromolecules*, 2005, **6**, 2815.

121 S. Singh, P. Varanasi, P. Singh, P. D. Adams, M. Auer and B. A. Simmons, *Biomass Bioenergy*, 2013, **54**, 276.

122 H.-T. Chang, T.-F. Yeh and S.-T. Chang, *Polym. Degrad. Stab.*, 2002, **77**, 129.

123 A. Degryse and L. Sonnenberg, *Proceedings of the 1999 National Conference on Undergraduate Research*, Rochester, NY, April 1999.

124 B. Sedai, C. Díaz-Urrutia, R. T. Baker, R. Wu, L. A. P. Silks and S. K. Hanson, *ACS Catal.*, 2011, **1**, 794.

125 M.-L. Mattinen, P. Maijala, P. Nousiainenc, A. Smeds, J. Kontro, J. Sipilä, T. Tamminen, S. Willförd and L. Viikari, *J. Mol. Catal. B: Enzym.*, 2011, **72**, 122.

126 H. Lange, S. Decina and C. Crestini, *Eur. Polym. J.*, 2013, **49**, 1151.

127 C. Xu, H. Su and D. Cang, *BioResources*, 2008, **3**, 363.

128 Q. Bu, H. Lei, S. J. Ren, L. Wang, Q. Zhang, J. Tang and R. Ruan, *Bioresour. Technol.*, 2012, **108**, 274.

129 F. B. Phillip, A. C. Buchanan and A. M. Elizabeth, *Energy Fuels*, 2000, **14**, 1314.

130 G. Jiang, D. J. Nowakowski and A. V. Bridgwater, *Thermochim. Acta*, 2010, **498**, 61.

131 G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044.

132 A. V. Bridgwater and G. V. C. Peacocke, *Renewable Sustainable Energy Rev.*, 2000, **4**, 1.

133 T. P. Vispute, H. Zhang, A. Sanna, R. Xiao and G. W. Huber, *Science*, 2010, **330**, 1222.

134 A. Gani and I. Naruse, *Renewable Energy*, 2007, **32**, 649.

135 B. G. Diehl, N. R. Brown, C. W. Frantz, M. R. Lumadue and F. Cannon, *Carbon*, 2013, **60**, 531.

136 J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552.

137 T. Yoshikawa, S. Shinohara, T. Yagi, N. Ryumon, Y. Nakasaka, T. Tago and T. Masuda, *Appl. Catal., B*, 2014, **146**, 289.

138 X. Pan, J. F. Kadla, K. Ehara, N. Gilkes and J. N. Saddler, *J. Agric. Food Chem.*, 2006, **54**, 5806.

139 V. N. Bui, D. Laurenti, P. Delichère and C. Geantet, *Appl. Catal., B*, 2011, **101**, 246.

140 H. Kobayashi, H. Ohta and A. Fukuoka, *Catal. Sci. Technol.*, 2012, **2**, 869.

141 D. Areskogh, J. Li, G. Gellerstedt and G. Henriksson, *Biomacromolecules*, 2010, **11**, 904.

142 T. Yoshikawa, T. Yagi, S. Shinohara, T. Fukunaga, Y. Nakasaka, T. Tago and T. Masuda, *Fuel Process. Technol.*, 2013, **108**, 69.

143 C. A. Mullen and A. A. Boateng, *Fuel Process. Technol.*, 2010, **91**, 1446.

144 R. K. Sharma and N. N. Bakhshi, *Fuel Process. Technol.*, 1993, **35**, 201.

145 P. de Wild, R. Van der Laan, A. Kloekhorst and H. J. Heeres, *Environ. Prog. Sustainable Energy*, 2009, **28**, 461.

146 R. W. Thring, S. P. R. Katikaneni and N. N. Bakhshi, *Fuel Process. Technol.*, 2000, **62**, 17.

147 M. A. Jackson, D. L. Compton and A. A. Boateng, *J. Anal. Appl. Pyrolysis*, 2009, **85**, 226.

148 D. K. Shen, S. Gu, K. H. Luo, S. R. Wang and M. X. Fang, *Bioresour. Technol.*, 2010, **101**, 6136.

149 Y. Zhao, L. Deng, B. Liao, Y. Fu and Q. X. Guo, *Energy Fuels*, 2010, **24**, 5735.

150 D. J. Mihalcik, C. A. Mullen and A. A. Boateng, *J. Anal. Appl. Pyrolysis*, 2011, **92**, 224.

151 T. Dickerson and J. Soria, *Energies*, 2013, **6**, 514.

152 Z. Ma, E. Troussard and J. A. van Bokhoven, *Appl. Catal., A*, 2012, **423-424**, 130.

153 V. N. Bui, D. Laurenti, P. Afanasiev and C. Geantet, *Appl. Catal., B*, 2011, **101**, 239.

154 J. C. del Río, F. Martín and F. J. González-Vila, *TrAC, Trends Anal. Chem.*, 1996, **15**, 70.

155 J. M. Challinor, *J. Anal. Appl. Pyrolysis*, 1995, **35**, 93.

156 D. J. Clifford, D. M. Carson, D. E. MacKinney, J. M. Bortiatynski and P. G. Hatcher, *Org. Geochem.*, 1995, **23**, 169.

157 J. C. del Río, F. J. González-Vila and T. Verdejo, *J. Anal. Appl. Pyrolysis*, 1995, **35**, 1.

158 J. C. del Río, D. E. McKinney, H. Knicker, M. A. Nanny, R. D. Minard and P. G. Hatcher, *J. Chromatogr. A*, 1998, **823**, 433.

159 K. Kuroda, N. Nishimura, A. Izumi and D. R. Dimmel, *J. Agric. Food Chem.*, 2002, **50**, 1022.

160 A.-C. Chen, H. Pakdel and C. Roy, *Bioresour. Technol.*, 2001, **79**, 277.

161 K. Kuroda, T. Ashitani and K. Fujita, *J. Anal. Appl. Pyrolysis*, 2010, **89**, 233.

162 T. Persson, H. Krawczyk, A. K. Nordin and A. S. Jonsson, *Bioresour. Technol.*, 2010, **101**, 3884.

163 M. G. Alriols, A. García, R. Llano-ponte and J. Labidi, *Chem. Eng. J.*, 2010, **157**, 113.

164 H. Hatakeyama, Y. Tsujimoto, M. J. Zarubin, S. M. Krutov and T. Hatakeyama, *J. Therm. Anal. Calorim.*, 2010, **101**, 289.

165 N. Sun, H. Rodríguez, M. Rahman and R. D. Rogers, *Chem. Commun.*, 2011, **47**, 1405.

166 V. Chaturvedi and P. Verma, *3 Biotech*, 2013, **3**, 415.

167 M. S. Wahyudiono and M. Goto, *J. Mater. Cycles Waste Manage.*, 2011, **13**, 68.

168 W. M. Sasaki and M. Goto, *Chem. Eng. Process.*, 2008, **47**, 1609.

169 W. M. Sasaki and M. Goto, *Fuel*, 2009, **88**, 1656.

170 P. T. Patil, U. Armbruster, M. Richter and A. Martin, *Energy Fuels*, 2011, **25**, 4713.

171 S. Cheng, Z. Yuan, M. Leitch, M. Anderson and C. Xu, *Ind. Crops Prod.*, 2013, **44**, 315.

172 S. Zhu, Y. Wu, Q. Chen, Z. Yu, C. Wang, S. Jin, Y. Ding and G. Wu, *Green Chem.*, 2006, **8**, 325.

173 K. Stärk, N. Taccardi, A. Bösmann and P. Wasserscheid, *ChemSusChem*, 2010, **3**, 719.

174 X.-D. Hou, N. Li and M.-H. Zong, *Biotechnol. Bioeng.*, 2013, **110**, 1895.

175 G. Cheng, M. S. Kent, L. He, P. Varanasi, D. Dibble, R. Arora, K. Deng, K. Hong, Y. B. Melnichenko, B. A. Simmons and S. Singh, *Langmuir*, 2012, **28**, 11850.

176 S. Martins, S. I. Mussatto, G. M. Avila, J. Montañez-Saenz, C. N. Aguilar and J. A. Teixeira, *Biotechnol. Adv.*, 2011, **29**, 365.

177 S. K. Ang, E. M. Shaza, Y. Adibah, A. A. Suraini and M. S. Madihah, *Process Biochem.*, 2013, **48**, 1293.

178 E. Uzan, P. Nousiainen, V. Balland, J. Sipila, F. Piumi, D. Navarro, M. Asther, E. Record and A. Lomascolo, *J. Appl. Microbiol.*, 2010, **108**, 2199.

179 R. Singh, J. C. Grigg, W. Qin, J. F. Kadla, M. E. P. Murphy and L. D. Eltis, *ACS Chem. Biol.*, 2013, **8**, 700.

180 M. Ahmad, C. R. Taylor, D. Pink, K. Burton, D. Eastwood, G. R. Bending and T. D. H. Bugg, *Mol. BioSyst.*, 2010, **6**, 815.

181 U. Tuor, K. Winterhalter and A. Fiechter, *J. Biotechnol.*, 1995, **41**, 1.

182 J. M. Coyne, V. K. Gupta, A. O'Donovon and M. G. Tuohy, *Biofuel Technol.*, 2013, 121.

183 E. Masai, Y. Katayama and M. Fukuda, *Biosci., Biotechnol., Biochem.*, 2007, **71**, 1.

184 W. Zimmermann, *J. Biotechnol.*, 1990, **13**, 119.

185 M. Ramachandra, D. L. Crawford and G. Hertel, *Appl. Environ. Microbiol.*, 1988, **54**, 3057.

186 J. Michel, M. Jourdes, A. L. Floch, T. Giordanengo, N. Mourey and P.-L. Teissedre, *J. Agric. Food Chem.*, 2013, **61**, 11109.

187 I. Jarauta, J. Cacho and V. Ferreira, *J. Agric. Food Chem.*, 2005, **53**, 4166.

188 R. Hatfield and R. S. Fukushima, *Crop Sci.*, 2005, **45**, 832.

189 J. Rodrigues, O. Faix and H. Pereira, *Holzforschung*, 1998, **52**, 46.

190 K. K. Pandey and A. J. Pitman, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 2340.

191 F. S. Poke and C. A. Raymond, *J. Wood Chem. Technol.*, 2006, **26**, 187.

192 T.-F. Yeh, T. Yamada, E. Capanema, H.-M. Chang, V. Chiang and J. F. Kadla, *J. Agric. Food Chem.*, 2005, **53**, 3328.

193 J. Mao, K. M. Holtman, J. T. Scott, J. F. Kadla and K. Schmidt-Rohr, *J. Agric. Food Chem.*, 2006, **54**, 9677.

194 S. Y. Lin and C. W. Dence, *Methods in lignin chemistry*, ed. C. W. Dence, Springer-Verlag, Heidelberg, Germany, 1992, p. 33.

195 C. Lapierre, B. Pollet and C. Rolando, *Res. Chem. Intermed.*, 1995, **21**, 397.

196 C. Puentes, M. Norambuena, R. T. Mendonça, J. P. Elissetche and J. Freer, *Wood Res.*, **127**(57), 91.

197 K. Kaiser and R. Benner, *Anal. Chem.*, 2012, **84**, 459.

198 J. I. Hedges and J. R. Ertel, *Anal. Chem.*, 1982, **54**, 174.

199 I. Kögel and R. Bochter, *Soil Biol. Biochem.*, 1985, **17**, 637.

200 M. A. Goni and S. Montgomery, *Anal. Chem.*, 2000, **72**, 3116.

201 B. J. Dalzell, T. R. Filley and J. M. J. Harbor, *J. Geophys. Res.: Biogeosci.*, 2005, **110**, GO2011, DOI: 10.1029/2005jg000043.

202 Z. Strassberger, A. H. Alberts, M. J. Louwerse, S. Tanase and G. Rothenberg, *Green Chem.*, 2013, **15**, 768.

203 J. Nakayama and A. Miyake, *J. Therm. Anal. Calorim.*, 2012, **110**, 321.

204 P. Louchouarn, R. M. W. Amon, S. Duan, C. Pondell, S. M. Seward and N. White, *Mar. Chem.*, 2010, **118**, 85.

205 K. M. Holtman, H.-M. Chang, H. Jameel and J. F. Kadla, *J. Agric. Food Chem.*, 2003, **51**, 3535.

206 F. Lu and J. Ralph, *J. Agric. Food Chem.*, 1992, **45**, 2590.

207 A. R. Robinson and S. D. Mansfield, *Plant J.*, 2009, **58**, 706.

208 K. K. Pandey, *J. Appl. Polym. Sci.*, 1999, **71**, 1969.

209 K. V. Sarkanen, H.-M. Chang and G. G. Allan, *Tappi J.*, 1967, **50**, 587.

210 P. A. Evans, *Spectrochim. Acta*, 1991, **47**, 1441.

211 K. V. Sarkanen, H.-M. Chang and B. Ericsson, *Tappi J.*, 1967, **50**, 572.

212 J. Zeng, G. L. Helms, X. Gao and S. Chen, *J. Agric. Food Chem.*, 2013, **61**, 10848.

213 J. C. del Río, J. Rencoret, P. Prinsen, A. T. Martínez, J. Ralph and A. Gutiérrez, *J. Agric. Food Chem.*, 2012, **60**, 5922.

214 M. Sette, R. Wechselberger and C. Crestini, *Chem.–Eur. J.*, 2011, **17**, 9529.

215 J.-L. Wen, S.-L. Sun, B.-L. Xue and R.-C. Sun, *Materials*, 2013, **6**, 359.

216 K. M. Holtman, N. Chen, M. A. Chappell, J. F. Kadla, L. Xu and J. Mao, *J. Agric. Food Chem.*, 2010, **58**, 9882.

217 T.-Q. Yuan, S.-N. Sun, F. Xu and R.-C. Sun, *J. Agric. Food Chem.*, 2011, **59**, 10604.

218 G. Hawkes, C. Smith, J. Utley, R. Vargas and H. Viertler, *Holzforschung*, 1993, **47**, 302.

219 K. M. Holtman, H.-M. Chang and J. F. Kadla, *J. Agric. Food Chem.*, 2004, **52**, 720.

220 E. A. Capanema, M. Y. Balakshin and J. F. Kadla, *J. Agric. Food Chem.*, 2004, **52**, 1850.

221 D.-Y. Min, S. W. Smith, H.-M. Chang and H. Jameel, *BioResources*, 2013, **8**, 1790.

222 D. J. Yelle, P. Kaparaju, C. G. Hunt, K. Hirth, H. Kim, J. Ralph and C. Felby, *BioEnergy Res.*, 2013, **6**, 211.

223 D. Y. Min, H. Jameel, H.-M. Chang, L. Lucia, Z. G. Wanga and Y. C. Jina, *RSC Adv.*, 2014, **4**, 10845.
224 T. I. Eglinton, B. C. Benitez-Nelson, A. Pearson, A. P. McNichol, J. E. Bauer and E. R. M. Druffel, *Science*, 1997, **277**, 796.
225 A. E. Ingalls, E. E. Ellis, G. M. Santos, K. E. McDuffee, L. Truxal, R. G. Keil and E. R. M. Druffel, *Anal. Chem.*, 2010, **82**, 8931.
226 J. Nakashima, F. Chen, L. Jackson, G. Shadle and R. A. Dixon, *New Phytol.*, 2008, **179**, 738.
227 K. Ruel, J. B. -Sierra, M. M. Derikvand, B. Pollet, J. Thévenin, C. Lapierre, L. Jouanin and J. P. Joseleau, *New Phytol.*, 2009, **184**, 99.
228 Y. Matsushita, K. Ioka, K. Saito, R. Takama, D. Aoki and K. Fukushima, *Holzforschung*, 2012, **67**, 365.
229 K. Saito, T. Kato, H. Takamori, T. Kishimoto and K. Fukushima, *Biomacromolecules*, 2005, **6**, 2688.
230 M. D'Auria, L. Emanuele and R. Racioppi, *Lett. Org. Chem.*, 2011, **8**, 436.
231 M. D'Auria, L. Emanuele and R. Racioppi, *Nat. Prod. Res.*, 2012, **26**, 1368.
232 K. L. Takahashi, J. Zhou, O. Kostko, A. Golan, S. R. Leone and M. Ahmed, *J. Phys. Chem. A*, 2011, **115**, 3279.
233 J. H. Banoub, B. Benjelloun-Mlayah, F. Ziarelli, N. Joly and M. Delmas, *Rapid Commun. Mass Spectrom.*, 2007, **21**, 2867.
234 B. W. Penning, R. W. Sykes, N. C. Babcock, C. K. Dugard, J. F. Klimek, D. Gamblin, M. Davis, T. R. Filley, N. S. Mosier, C. F. Weil, M. C. McCann and N. C. Carpita, *BioEnergy Res.*, DOI: 10.1007/s12155-014-9410-3.
235 F. Shadkami, B. B. Sithole and R. Helleur, *Org. Geochem.*, 2010, **41**, 586.
236 J. C. del Río, A. Gutiérrez, I. M. Rodríguez, D. Ibarra and Á. T. Martínez, *J. Anal. Appl. Pyrolysis*, 2007, **79**, 39.
237 C. Saiz-Jimenez and J. W. de Leeuw, *Org. Geochem.*, 1986, **10**, 869.
238 A. Awal and M. Sain, *J. Appl. Polym. Sci.*, 2011, **122**, 956.
239 K. David and A. J. Ragauskas, *Energy Environ. Sci.*, 2010, **3**, 1182.
240 P. Sannigrahi, A. J. Ragauskas and G. A. Tuskan, *Biofuels, Bioprod. Biorefin.*, 2010, **4**, 209.
241 R. P. Anex, A. Aden, F. K. Kazi, J. Fortman, R. M. Swanson and M. M. Wright, *Fuel*, 2010, **89**, 29.
242 M. M. Wright, Y. Román-Leshkov and W. H. Green, *Biofuels, Bioprod. Biorefin.*, 2012, **6**, 503.
243 S. Jones, J. Holladay, C. Valkenburg, D. Stevens, C. Walton, C. Kinchin, D. Elliott and S. Czernik, *PNNL*, 2009, 18284.
244 G. Gellerstedt and G. Henriksson, *Monomers, Polymers and Composites from Renewable Resources*, ed. M. Belgacem and A. Gandini, Elsevier, Amsterdam, 2008, pp. 201–224.
245 D. Kubĭcka, I. Kubĭckova and J. Čejka, *Catal. Rev.: Sci. Eng.*, 2013, **55**, 1.
246 M. J. Climent, A. Corma and S. Iborra, *Green Chem.*, 2011, **13**, 520.
247 http://www.ecs.umass.edu/biofuels/roadmap.htm.
248 C. Wu, Z. Wang, J. Huang and P. T. Williams, *Fuel*, 2013, **106**, 697.
249 D. A. Hazlebeck and E. Cajone, US 20120077234 A1, 2012.
250 J. A. Geboers, S. Van de Vyver, R. Ooms, B. Op de Beeck, P. A. Jacobs and B. F. Sels, *Catal. Sci. Technol.*, 2011, **1**, 714.
251 A. K. Deepa and P. L. Dhepe, *RSC Adv.*, 2014, **4**, 12625.
252 M. Kleinert and T. Barth, *Energy Fuels*, 2008, **22**, 1371.
253 P. de Wild, H. Reith and E. Heeres, *Biofuels*, 2011, **2**, 185.
254 H. Ben and A. J. Ragauskas, *Energy Fuels*, 2011, **25**, 2322.
255 M. Kosa, H. Ben, H. Theliander and A. J. Ragauskas, *Green Chem.*, 2011, **13**, 3196.
256 H. Ben and A. J. Ragauskas, *Energy Fuels*, 2011, **25**, 5791.
257 H. Ben and A. J. Ragauskas, *Prepr. Symp.–Am. Chem. Soc., Div. Fuel Chem.*, 2012, **57**, 140.
258 W. Mu, H. Ben, A. Ragauskas and Y. Deng, *BioEnergy Res.*, 2013, **6**, 1183.
259 R. French and S. Czernik, *Fuel Process. Technol.*, 2010, **91**, 25.
260 H. Ben and A. J. Ragauskas, *Energy Fuels*, 2011, **25**, 4662.
261 A. Aho, N. Kumar, K. Eranen, T. Salmi, M. Hupa and D. Murzin, *Process Saf. Environ. Prot.*, 2007, **85**, 473.
262 H. Ben and A. J. Ragauskas, *ACS Sustainable Chem. Eng.*, 2013, **1**, 316.
263 M. Zhang and A. Moutsoglou, *Energy Fuels*, 2014, **28**, 1066.
264 H. Benab and A. J. Ragauskas, *RSC Adv.*, 2012, **2**, 12892.
265 S. Czernik and A. V. Bridgwater, *Energy Fuels*, 2004, **18**, 590.
266 P. D. Chantal, S. Kaliaguine and J. L. Grandmaison, *Appl. Catal.*, 1985, **18**, 133.
267 A. G. Gayubo, A. T. Aguayo, A. Atutxa, R. Aguado and J. Bilbao, *Ind. Eng. Chem. Res.*, 2004, **43**, 2610.
268 T. R. Viljava, R. S. Komulainen and A. O. I. Krause, *Catal. Today*, 2000, **60**, 83.
269 E. Furimsky and F. E. Massoth, *Catal. Today*, 1999, **52**, 381.
270 E. Laurent and B. Delmon, *J. Catal.*, 1994, **146**, 281.
271 A. Niquille-Röthlisberger and R. Prins, *J. Catal.*, 2006, **242**, 207.
272 T. Tang, C. Yin, L. Wang, Y. Ji and F.-S. Xiao, *J. Catal.*, 2007, **249**, 111.
273 M. Garcia-Perez, A. Chaala, H. Pakdel and D. Kretschmer, *Biomass Bioenergy*, 2007, **31**, 222.
274 D. Mohan, C. U. Pittman and P. H. Steele, *Energy Fuels*, 2006, **20**, 848.
275 D. Fu, S. Farag, J. Chaouki and P. G. Jessop, *Bioresour. Technol.*, 2014, **154**, 101.
276 K. David, M. Kosa, A. Williams, R. Mayor, M. Realff, J. Muzzy and A. Ragauskas, *Biofuels*, 2010, **1**, 839.
277 P. F. Britt, A. C. Buchanan, M. J. Cooney and E. A. Malcolm, *J. Org. Chem.*, 2000, **65**, 1376.
278 K. Kuroda and A. Nakagawa-izumi, *Org. Geochem.*, 2006, **37**, 665.
279 P. F. Britt, M. K. Kidder and A. C. Buchanan, *Energy Fuels*, 2007, **21**, 3102.
280 H. Kawamoto and S. Saka, *J. Wood Chem. Technol.*, 2007, **27**, 113.
281 H. Kawamoto, S. Horigoshi and S. Saka, *J. Wood Sci.*, 2007, **53**, 168.
282 T. Nakamura, H. Kawamoto and S. Saka, *J. Anal. Appl. Pyrolysis*, 2008, **81**, 173.
283 H. Kawamoto, T. Nakamura and S. Saka, *Holzforschung*, 2008, **62**, 50.

284 H. Kawamoto, M. Ryoritani and S. Saka, *J. Anal. Appl. Pyrolysis*, 2008, **81**, 88.

285 G. Gellerstedt, J. Li, I. Eide, M. Kleinert and T. Barth, *Energy Fuels*, 2008, **22**, 4240.

286 P. F. Britt, A. C. Buchanan and E. A. Malcolm, *Energy Fuels*, 2000, **14**, 1314.

287 C. A. Mullen, G. D. Strahan and A. A. Boateng, *Energy Fuels*, 2009, **23**, 2707.

288 A. Pizzi, Tannins: Major Sources, Properties and Applications, in *Monomers, Polymers and Composites from Renewable Resources*, ed. M. N. Belgacem and A. Gandini, Elsevier, Amsterdam, 2008, ch. 8, pp. 179–199.

289 C. T. Robbins, *Ecology*, 1987, **68**, 98.

290 E. Haslam, *Plant polyphenols: vegetable tannins revisited*, Cambridge University Press, Cambridge, 1989.

291 T. Okuda and H. Ito, *Molecules*, 2011, **16**, 2191.

292 C. Penã, K. De la Caba, A. Eceiza, R. Ruseckaite and I. Mondragon, *Bioresour. Technol.*, 2010, **101**, 6836.

293 E. C. Ramires and E. Frollini, *Composites, Part B*, 2012, **43**, 2851.

294 A. Pizzi, *Wood adhesives – chemistry and technology*, ed. A. Pizzi and M. Dekker, New York, 1983, ch. 4.

295 http://www.users.muohio.edu/hagermae/tannin.pdf.

296 W. Hummer and P. Schreier, *Mol. Nutr. Food Res.*, 2008, **52**, 1381.

297 M. Monagas, J. E. Quintanilla-López, C. Gómez-Cordovésa, B. Bartoloméa and R. Lebrón-Aguilarc, *J. Pharm. Biomed. Anal.*, 2010, **51**, 358.

298 L.-L. Zhang, Y.-M. Lin, H.-C. Zhou, S.-D. Wei and J.-H. Chen, *Molecules*, 2010, **15**, 420.

299 A. Gandini, *Macromolecules*, 2008, **41**, 9491.

300 A. Pizzi, G. Tondi, H. Pasch and A. Celzard, *J. Appl. Polym. Sci.*, 2008, **110**, 1451.

301 H. Pasch, A. Pizzi and K. Rode, *Polymer*, 2001, **42**, 7531.

302 A. Pizzi, *Advanced Wood Adhesives Technology*, Dekker, New York, 1994.

303 M. Karonen, J. Loponen, V. Ossipov and K. Pihlasja, *Anal. Chim. Acta*, 2004, **522**, 105.

304 Y. Lu and Q. Shi, *Holz Roh- Werkst.*, 1995, **53**, 17.

305 E. T. N. Bisanda, W. O. Ogola and J. V. Tesha, *Cem. Concr. Compos.*, 2003, **25**, 593.

306 H. R. E. Kaspar and A. Pizzi, *J. Appl. Polym. Sci.*, 1996, **59**, 1181.

307 A. Nicollin, X. Zhou, A. Pizzi, W. Grigsby, K. Rode and L. Delmotte, *Ind. Crops Prod.*, 2013, **49**, 851.

308 S. Sowunmi, R. O. Ebewele, A. H. Conner and B. H. River, *J. Appl. Polym. Sci.*, 1996, **62**, 577.

309 R. Niemetz and G. G. Gross, *Phytochemistry*, 2005, **66**, 2001.

310 L. Almela, B. Sanchez-Munoz, J. A. Fernandez-Lopez, M. J. Roca and V. Rabe, *J. Chromatogr. A*, 2006, **1120**, 221.

311 C. Bicchi, A. Binello and P. Rubiolo, *Phytochem. Anal.*, 2000, **11**, 236.

312 J. M. Roldan-Gutierrez, J. Ruiz-Jimenez and M. D. Luque de Castro, *Talanta*, 2008, **75**, 1369.

313 M. Kivilompolo and T. Hyotylainen, *J. Chromatogr. A*, 2009, **1216**, 892.

314 E. Ibanez, A. Kubatova, F. J. Senorans, S. Cavero, G. Reglero and S. B. Hawthorne, *J. Agric. Food Chem.*, 2003, **51**, 375.

315 M. Markoma, M. Hasan, W. R. W. Daud, H. Singh and J. M. Jahim, *Sep. Purif. Technol.*, 2007, **52**, 487–496.

316 M. Singh, A. Jha, A. Kumar, N. Hettiarachchy, A. K. Rai and D. Sharma, *J. Food Sci. Technol.*, 2014, DOI: 10.1007/s13197-014-1267-0.

317 H. Purushotham, A. Koshy, V. S. Sundar Rao, P. Latha, M. M. Gurumoorthy, S. Ananthanarayanan, V. Haridoss, K. Venkataboopathy and R. Sundaram, *J. Soc. Leather Technol. Chem.*, 1994, **78**, 178.

318 K. Kemppainen, M. Siikaaho, S. Pattathil, S. Giovando and K. Kruus, *Ind. Crops Prod.*, 2014, **52**, 158.

319 M. C. Vieira, R. C. C. Lelis, B. C. da and G. L. Oliveira, *Floresta e Ambiente*, 2011, **18**, 1.

320 L. Chupin, C. Motillon, F. Charrier-El Bouhtoury, A. Pizzi and B. Charrier, *Ind. Crops Prod.*, 2013, **49**, 897.

321 E. Aspe and K. Fernandez, *Ind. Crops Prod.*, 2011, **34**, 838.

322 G. F. Ferrazzano, I. Amato, A. Ingenito, A. Zarrelli, G. Pinto and A. Pollio, *Molecules*, 2011, **16**, 1486.

323 J. Š. Gajić, Z. Stojanović, A. S. Carretero, D. A. Román, I. Borrás and I. Vasiljević, *J. Food Eng.*, 2013, **119**, 525.

324 L. Ping, A. Pizzi, Z.-D. Guo and N. Brosse, *Ind. Crops Prod.*, 2011, **34**, 907.

325 M. Brahim, F. Gambier and N. Brosse, *Ind. Crops Prod.*, 2014, **52**, 18.

326 Z.-X. Jin, B.-Q. Wang and Z.-J. Chen, *J. Med. Plants Res.*, 2010, **4**, 2229.

327 H. N. Rajha, N. Louka, N. E. Darra, Z. Hobaika, N. Boussetta, E. Vorobiev and R. G. Maroun, *Food Nutr. Sci.*, 2014, **5**, 351.

328 I. T. Karabegović, S. S. Stojičević, D. T. Veličković, N. Č. Nikolić and M. L. Lazić, *Sep. Purif. Technol.*, 2013, **120**, 429.

329 W. Lijun and L. W. Curtis, *Trends Food Sci. Technol.*, 2006, **17**, 300.

330 J. Dong, Y. Liu, Z. Lian and W. Wan, *Ultrason. Sonochem.*, 2010, **17**, 61.

331 M. Vinatoru, *Ultrason. Sonochem.*, 2001, **8**, 303.

332 M. I. S. Melecchi, V. F. Péres, C. Dariva, C. A. Zini, F. C. Abad, M. M. Martinez and E. B. Caramã, *Ultrason. Sonochem.*, 2006, **13**, 242.

333 V. Sivakumara, V. R. Verma, P. G. Rao and G. Swaminathan, *J. Cleaner Prod.*, 2007, **15**, 1813.

334 P. C. Veggi, D. T. Santos, A.-S. Fabiano-Tixier, C. Le Bourvellec, M. A. A. Meireles and F. Chemat, *Food Publ. Health*, 2013, **3**, 119.

335 C. Carrera, A. Ruiz-Rodríguez, M. Palma and C. G. Barroso, *Anal. Chim. Acta*, 2012, **732**, 100.

336 C. J. Sarneckis, R. G. Dambergs, P. Jones, M. Mercurio, M. J. Herderich and P. A. Smith, *Aust. J. Grape Wine Res.*, 2006, **12**, 39.

337 M. D. Mercurio and P. A. Smith, *J. Agric. Food Chem.*, 2008, **56**, 5528.

338 S. A. Chowdhury, R. Vijayaraghavanb and D. R. MacFarlane, *Green Chem.*, 2010, **12**, 1023.

339 N. Sathitsuksanoh, K. M. Holtman, D. J. Yelle, T. Morgan, V. Stavila, J. Pelton, H. Blanch, B. A. Simmons and A. George, *Green Chem.*, 2014, **16**, 1236.

340 C. Lu, H. Wanga, W. Lv, C. Ma, Z. Lou, J. Xie and B. Liu, *Nat. Prod. Res.*, 2012, **26**, 1842.

341 C. Lu, X. Luo, L. Lu, H. Li, X. Chen and Y. Ji, *J. Sep. Sci.*, 2013, **36**, 959.

342 L. Roumeas, C. Aouf, E. Dubreucq and H. Fulcrand, *Green Chem.*, 2013, **15**, 3268.

343 R. Murga, R. Ruiz, S. Beltrán and J. L. Cabezas, *J. Agric. Food Chem.*, 2000, **48**, 3408.

344 E. E. Yilmaz, E. B. Ozvural and H. Vural, *J. Supercrit. Fluids*, 2011, **55**, 924.

345 M. Karamać, *Int. J. Mol. Sci.*, 2009, **10**, 5485.

346 L. Brooks, L. McCloskey, D. McKesson and M. Sylvan, *J. AOAC Int.*, 2008, **91**, 1090.

347 P. Schofield, D. M. Mbugua and A. N. Pell, *Anim. Feed Sci. Technol.*, 2001, **91**, 21.

348 L. M. Magalhães, I. I. Ramos, S. Reis and M. A. Segundo, *Aust. J. Grape Wine Res.*, 2014, **20**, 72.

349 L. M. Magalhães, F. Santos, M. A. Segundo, S. Reis and J. Lima, *Talanta*, 2010, **83**, 441.

350 L. M. Magalhães, L. Barreiros, M. A. Maia, S. Reis and M. A. Segundo, *Talanta*, 2012, **97**, 473.

351 R. Re, N. Pellegrini, A. Proteggente, A. Pannala, M. Yang and C. Rice-Evans, *Free Radical Biol. Med.*, 1999, **26**, 1231.

352 W. Brand-Williams, M. E. Cuvelier and C. Berset, *LWT – Food Sci. Technol.*, 1995, **28**, 25.

353 T. Wang, R. Jonsdottir and G. Olafsdottir, *Food Chem.*, 2009, **116**, 240.

354 R. Horax, N. Hettiarachchy and P. Chen, *J. Agric. Food Chem.*, 2010, **58**, 4428.

355 D. J. Huang, B. X. Ou, M. Hampsch-Woodill, J. A. Flanagan and R. L. Prior, *J. Agric. Food Chem.*, 2002, **50**, 4437.

356 L. Laghi, G. P. Parpinello, D. D. Rio, L. Calani, A. U. Mattioli and A. Versari, *Food Chem.*, 2010, **121**, 783.

357 L. Ping, A. Pizzi, Z.-D. Guo and N. Brosse, *Ind. Crops Prod.*, 2012, **40**, 13.

358 G. Vasquez, S. Freire, J. Gonzalez and G. Antorrena, *Holz Roh- Werkst.*, 2000, **58**, 57.

359 P. J. Hernes and J. I. Hedges, *Anal. Chem.*, 2000, **72**, 5115.

360 W. Xu, K. Chu, H. Li, Y. Zhang, H. Zheng, R. Chen and L. Chen, *Molecules*, 2012, **17**, 14323.

361 P. Navarrete, A. Pizzi, H. Pasch, K. Rode and L. Delmotte, *Ind. Crops Prod.*, 2010, **32**, 105.

362 A. Behrens, N. Maie, H. Knicker and I. Kögel-Knabner, *Phytochemistry*, 2003, **62**, 1159.

363 K. M. Kalili, J. Vestner, M. A. Stander and A. de Villiers, *Anal. Chem.*, 2013, **85**, 9107.

364 P. Comandini, M. J. L. García, E. Francisco, S. Alfonso and T. G. Toschi, *Food Chem.*, 2014, DOI: 10.1016/j.foodchem.2014.02.003.

365 A. Romani, F. Ieri, B. Turchetti, N. Mulinacci, F. F. Vincieri and P. Buzzini, *J. Pharm. Biomed. Anal.*, 2006, **41**, 415.

366 J. T. Pierson, G. R. Monteith, S. J. Roberts-Thomson, R. G. Dietzgen, M. J. Gidley and P. N. Shaw, *Food Chem.*, 2014, **149**, 253.

367 A. Romani, R. Coinu, S. Carta, P. Pinelli, C. Galardi and F. F. Vincieri, *Free Radical Res.*, 2004, **38**, 97.

368 T. B. Machado, I. C. R. Leal, A. C. F. Amaral, H. R. N. dos Santos, M. da Silva and G. R. M. Kuster, *J. Braz. Chem. Soc.*, 2002, **13**, 606.

369 A. Romani, M. Campo and P. Pinelli, *Food Chem.*, 2012, **130**, 214.

370 D. G. Reid, S. L. Bonnet, G. Kemp and J. H. van der Westhuizen, *Phytochemistry*, 2013, **94**, 243.

371 L. L. Zhang and Y. M. Lin, *Molecules*, 2008, **13**, 2986.

372 R. H. Newman and L. J. Porter, Solid state ^{13}C NMR studies on CTs, *Plant polyphenols: synthesis, properties, significance*, ed. W. R. Hemingway and P. E. Laks, Plenum Press, New York, 1992, pp. 339–347.

373 K. Lorenz and C. M. Preston, *J. Environ. Qual.*, 2002, **31**, 431.

374 G. Vázquez, A. Pizzi, M. S. Freire, J. Santos, G. Antorrena and J. González-Álvare, *Wood Sci. Technol.*, 2013, **47**, 523.

375 L. Ping, N. Brosse, L. Chrusciel, P. Navarrete and A. Pizzi, *Ind. Crops Prod.*, 2011, **33**, 253.

376 http://www.fas.usda/oilseeds/current/.

377 C.-S. Goh and K.-T. Lee, *Renewable Sustainable Energy Rev.*, 2011, **15**, 2714.

378 S. S. Hanim, M. A. M. Noor and A. Rosma, *Bioresour. Technol.*, 1234, **102**.

379 W. D. W. Rosli and K. N. Law, *BioResources*, 2011, **6**, 901.

380 W. D. W. Rosli, K. N. Law, Z. Zainuddin and R. Asro, *Bioresour. Technol.*, 2004, **93**, 233.

381 R. C. Sun and J. Tomkinson, *Sep. Purif. Technol.*, 2001, **24**, 529.

382 A. Ferrer, A. Vega, A. Rodríguez and L. Jiménez, *Bioresour. Technol.*, 2013, **132**, 115.

383 K. N. Law, W. D. Wanrosli and A. Ghazali, *BioResources*, 2007, **2**, 351.

384 Y. Koba and A. Ishizaki, *Agric. Biol. Chem.*, 1990, **54**, 1183.

385 T. L. Kelly-Yong, K. T. Lee, A. R. Mohamed and S. Bhatia, *Energy Policy*, 2007, **35**, 5692.

386 J. E. G. van Dam, M. J. A. van den Oever, E. R. P. Keijsers, J. C. van der Putten, C. Anayron, F. Josol and A. Peralta, *Ind. Crops Prod.*, 2006, **24**, 96.

387 H. P. S. A. Khalil, M. S. Alwani and A. K. M. Omar, *BioResources*, 2006, **1**, 220.

388 C. S. Goh, H. T. Tan and K. T. Lee, *Bioresour. Technol.*, 2012, **110**, 662.

389 H. M. Abdullah, M. H. A. Latif and H. G. Attiya, *Int. J. Biol. Macromol.*, 2013, DOI: 10.1016/j.ijbiomac.2013.06.020.

390 S. Shamsudin, M. U. K. Shah, H. Zainudin, S. Abd-Aziz, S. M. M. Kamal, Y. Shirai and M. A. Hassan, *Biomass Bioenergy*, 2012, **36**, 280.

391 F. Hamzah, A. Idris and T. K. Shuan, *Biomass Bioenergy*, 2011, **35**, 1055.

392 C.-S. Goh, K. T. Lee and S. Bhatia, *Bioresour. Technol.*, 2010, **101**, 7362.

393 C.-S. Goh, K.-T. Tan, K. T. Lee and S. Bhatia, *Bioresour. Technol.*, 2009, **101**, 4834.

394 H. T. Tan, K. T. Lee and A. R. Mohamed, *Carbohydr. Polym.*, 2011, **83**, 1862.

395 N. Abdullah, H. Gerhauser and F. Sulaiman, *Fuel*, 2010, **89**, 2166.

396 D. N. Ranong, R. Yuangsawad, T. Tago and T. Masuda, *Korean J. Chem. Eng.*, 2008, **25**, 426.

397 M. E. Borges and L. Díaz, *Renewable Sustainable Energy Rev.*, 2012, **16**, 2839.

398 T. Masuda, Y. Kondo, M. Miwa, T. Shimotori, S. R. Mukai, K. Hashimoto, M. Takano, S. Kawasaki and S. Yoshida, *Chem. Eng. Sci.*, 2001, **56**, 897.

399 F. L. Pua, S. Zakaria, C. H. Chia, S. P. Fan, T. Rosenau and A. P. F. Liebner, *Sains Malays.*, 2013, **42**, 793.

400 L. Wu, M. Arakane, M. Ike, M. Wada, T. Takai, M. Gau and K. Tokuyasu, *Bioresour. Technol.*, 2011, **102**, 4793.

401 A. Ferrer, A. Vega, P. Ligero and A. Rodríguez, *BioResources*, 2011, **6**, 4282.

402 J. Akhtar, S. K. Kuang and N. S. Amin, *Renewable Energy*, 2010, **35**, 1220.

403 M. N. Belgacem, A. Blayo and A. Gandini, *Ind. Crops Prod.*, 2003, **18**, 145.

404 S. Kubo and J. F. Kadla, *Macromolecules*, 2004, **37**, 6904.

405 M. H. Hussin, A. A. Rahim, M. Nasir, M. Ibrahim and N. Brosse, *Ind. Crops Prod.*, 2013, **49**, 23.

406 M. Varman, H. Miyafuji and S. Saka, *J. Wood Sci.*, 2010, **56**, 488.

407 H. Mazaheri, K. T. Lee, S. Bhatia and A. R. Mohamed, *Bioresour. Technol.*, 2010, **101**, 745.

408 H. Mazaheri, K. T. Lee, S. Bhatia and A. R. Mohamed, *Bioresour. Technol.*, 2010, **101**, 7641.

409 S.-N. Sun, M.-F. Li, T.-Q. Yuan, F. Xu and R.-C. Sun, *Ind. Crops Prod.*, 2012, **37**, 51.

410 N. S. Tessarolo, L. R. M. dos Santos, R. S. F. Silva and D. A. Azevedo, *J. Chromatogr. A*, 2013, **1279**, 68.

411 G. Dey, A. Sachan, S. Ghosh and A. Mitra, *Ind. Crops Prod.*, 2003, **8**, 171.

412 S. B. Mhaske, R. V. Bhingarkar, M. B. Sabne, R. Mercier and S. P. Vernekar, *J. Appl. Polym. Sci.*, 2000, **77**, 627.

413 J. S. Mathew, Ph.D. thesis, University of Pune, 2001.

414 G. John, M. Masuda, Y. Okada, K. Yase and T. Shimizu, *Adv. Mater.*, 2001, **13**, 715.

415 H. Yui, Y. Guo, K. Koyama, T. Sawada, G. John, B. Yang, M. Masuda and T. Shimizu, *Langmuir*, 2005, **21**, 721.

416 J. H. P. Tyman and I. E. Bruce, *J. Surfactants Deterg.*, 2004, **7**, 169.

417 G. John and C. S. K. Pillai, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31**, 1069.

418 J. F. Stanzione III, J. M. Sadler, J. J. La Scala, K. H. Renoc and R. P. Wool, *Green Chem.*, 2012, **14**, 2346.

419 L. K. Aggarwal, P. C. Thapliyal and S. R. Karade, *Prog. Org. Coat.*, 2007, **59**, 76.

420 R. Antony and C. K. S. Pillai, *J. Appl. Polym. Sci.*, 1993, **49**, 2129.

421 K. Puzio, R. Delépée, R. Vidal and L. A. Agrofoglio, *Anal. Chim. Acta*, 2013, **790**, 47.

422 H. Pan, G. Sun and T. Zhao, *Int. J. Biol. Macromol.*, 2013, **59**, 221.

423 T. Malutan, R. Nicu and V. I. Popa, *BioResources*, 2008, **3**, 1371.

424 C. H. Hoyt and D. W. Goheen, *Lignins: occurrence, formation, structure and reactions*, Wiley-Interscience, New York, 1971, p. 833.

425 N. N. Ghosh, B. Kiskan and Y. Yagci, *Prog. Polym. Sci.*, 2007, **32**, 1344.

426 C. P. R. Nair, *Prog. Polym. Sci.*, 2004, **29**, 401.

427 E. M. Nour-Eddine, Q. Yuan and F. Huang, *J. Appl. Polym. Sci.*, 2012, **125**, 1773.

428 B. Lochab, I. K. Varma and J. Bijwe, *J. Therm. Anal. Calorim.*, 2010, **102**, 769.

429 T. Agag, S.-Y. An and H. Ishida, *J. Appl. Polym. Sci.*, 2013, **127**, 2710.

430 B. Lochab, S. Shukla and I. K. Varma, *246th ACS Conference*, Indianapolis, 2013.

431 D. Maldas and N. Shiraishi, *Biomass Bioenergy*, 1997, **12**, 273.

432 C. K. S. Pillai, V. S. Prasad, J. D. Sudha, S. C. Bera and A. R. R. Menon, *J. Appl. Polym. Sci.*, 1990, **41**, 2487.

433 M. N. M. Ibrahim, A. M. Ghani and N. Nen, *Malaysian J. Anal. Sci.*, 2007, **11**, 213.

434 A. Ahmadzadeh, S. Zakaria and R. Rashid, *Ind. Crops Prod.*, 2009, **30**, 54.

435 S. Manjula, J. D. Sudha, S. C. Bera and C. K. S. Pillai, *J. Appl. Polym. Sci.*, 1985, **30**, 1767.

436 N. S. Cetin and N. Ozmen, *Int. J. Adhes. Adhes.*, 2002, **22**, 477.

437 H. P. Bhunia, R. N. Jana, A. Basak, S. Lenka and G. B. Nando, *J. Polym. Sci., Part A: Polym. Chem.*, 1998, **36**, 391.

438 H. P. Bhunia, G. B. Nando, T. K. Chaki, A. Basak, S. Lenka and P. L. Nayak, *Eur. Polym. J.*, 1999, **35**, 1381.

439 N. V. Sadavarte, M. R. Halhalli, C. V. Avadhani and P. P. Wadgaonkar, *Eur. Polym. J.*, 2009, **45**, 582.

440 A. S. Amarasekara and A. Razzaq, *ISRN Polym. Sci.*, 2012, **2012**, 1.

441 A. S. Amarasekara, B. Wiredu and A. Razzaq, *Green Chem.*, 2012, **14**, 2395.

442 D. W. Paul, I. Prajapati and M. L. Reed, *Sens. Actuators, B*, 2013, **183**, 129.

443 B. S. Rao and A. Palanisamy, *Eur. Polym. J.*, 2013, **49**, 2365.

444 O. A. Attanasi, G. Mele, P. Filippone, S. E. Mazzetto and G. Vasapollo, *ARKIVOC*, 2009, **8**, 69.

445 M. B. Graham and J. H. P. Tyman, *J. Am. Oil Chem. Soc.*, 2002, **79**, 725.

446 Y.-C. Guo, G. Mele, F. Martina, E. Margapoti, G. Vasapollo and W.-J. Xiao, *J. Organomet. Chem.*, 2006, **691**, 5383.

447 G. Mele, J. Li, E. Margapoti, F. Martina and G. Vasapollo, *Catal. Today*, 2009, **140**, 37.

448 S. Manjula, V. C. Kumar and C. K. S. Pillai, *J. Appl. Polym. Sci.*, 1992, **45**, 309.

449 R. Antony, C. K. S. Pillai and J. Scariah, *J. Appl. Polym. Sci.*, 1990, **41**, 1765.

450 S. Manjula, Ph.D. thesis, Kerala University, 1988.

451 J. S. Choi and J. Y. Park, Repub Korean Kongkae Taeho Kongbo, KR 2003038937 A 20030517, 2003.

452 J. H. P. Tyman, *J. Chromatogr. A*, 1978, **156**, 255.

453 R. Ikeda, H. Tanka, H. Uyama and S. Kobayashi, *Polymer*, 2002, **43**, 3475.

454 Y. H. Kim, K. Won, J. M. Kwon, H. Y. Jeong, S. Y. Park, E. S. An and B. K. Song, *J. Mol. Catal. B: Enzym.*, 2005, **34**, 33.

455 S. Y. Park, Y. H. Kim, K. Wong and B. K. Song, *J. Mol. Catal. B: Enzym.*, 2009, **57**, 312.

456 Y. H. Kim, E. S. An, S. Y. Park and B. K. Song, *J. Mol. Catal. B: Enzym.*, 2007, **45**, 39.

457 T. Tsujimoto, R. Ikeda, H. Uyama and S. Kobayashi, *Macromol. Chem. Phys.*, 2001, **202**, 3420.

458 Z. Xia, T. Yoshida and M. Funaoka, *Biotechnol. Lett.*, 2003, **25**, 9.

459 T. Yoshida, Z. Xia, K. Takeda, T. Katsuta, K. Sugimoto and M. Funaoka, *Polym. Adv. Technol.*, 2005, **16**, 783.

460 T. Yoshida, R. Lu, S. Han, K. Hattori, T. Katsuta, K. Takeda, K. Sugimoto and M. Funaoka, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 824.

461 G. John and C. K. S. Pillai, *Makromol. Chem., Rapid Commun.*, 1992, **13**, 255.

462 S. Aggarwal, V. Choudhary and I. K. Varma, *J. Appl. Polym. Sci.*, 1992, **46**, 1707.

463 P. K. Vemula, K. Douglas, C. Achong, A. Kumar, P. M. Ajayan and G. John, *J. Biobased Mater. Bioenergy*, 2008, **2**, 218.

464 D. O. Connor, *J. Appl. Polym. Sci.*, 1987, **33**, 1933.

465 N. L. Huong, N. H. Nieu and T. T. M. Tan, *Angew. Makromol. Chem.*, 1996, **243**, 77.

466 H. N. Isaiah, H. Dakshinamurty and J. Aggarwal, *PaintMfr.*, 1968, **38**, 29.

467 A. K. Misra and G. N. Pandey, *J. Appl. Polym. Sci.*, 1985, **30**, 979.

468 R. Yadav and D. Srivastava, *Eur. Polym. J.*, 2009, **45**, 946.

469 S. K. Swain, S. Sahoo, D. K. Mohapatra, B. K. Mishra, S. Lenka and P. L. Nayak, *J. Appl. Polym. Sci.*, 1994, **54**, 1413.

470 S. K. Sahoo, S. K. Swain, D. K. Mohapatra, P. L. Nayak and S. Lenka, *Angew. Makromol. Chem.*, 1995, **233**, 1.

471 V. Phien, L. T. Long, N. T. V. Trieu, H. N. Tao and P. T. Hong, *TapChiHoaHoc*, 1993, **31**, 1.

472 C. R. Nair, R. L. Bindu and V. C. Joseph, *J. Polym. Sci.*, 1995, **33**, 621.

473 A. Maffezzoli, E. Calo, S. Zurlo, G. Mele, A. Tarzia and C. Stifani, *Compos. Sci. Technol.*, 2004, **64**, 839.

474 F. G. J. Souza, P. Richa, A. D. Siervo, G. E. Oliveira, C. H. M. Rodrigues, M. Nele and J. C. Pinto, *Macromol. Mater. Eng.*, 2008, **293**, 675.

475 A. Tejado, G. Kortaberria, C. Pena, J. Labidi, J. M. Echeverria and I. Mondragon, *J. Appl. Polym. Sci.*, 2007, **106**, 2313.

476 D. Roy, P. Basu, P. K. Raghunathan and S. V. Eswaran, *J. Appl. Polym. Sci.*, 2003, **89**, 1959.

477 M. V. Alonso, M. Oliet, J. C. Dominguez, E. Rojo and F. Rodriguez, *J. Therm. Anal. Calorim.*, 2011, **105**, 349.

478 M. N. Ibrahim, N. Zakaria, C. S. Sipaut, O. Sulaiman and R. Hashim, *Carbohydr. Polym.*, 2011, **86**, 112.

479 M. Wang, M. Leitch and C. Xu, *Eur. Polym. J.*, 2009, **45**, 3380.

480 J. C. Domínguez, M. Oliet, M. V. Alonso, E. Rojo and F. Rodríguez, *Ind. Crops Prod.*, 2013, **42**, 308.

481 Y. Nagamatsu and M. Funaoka, *Green Chem.*, 2003, **5**, 595.

482 F. D. P. M. Jane and E. Frollini, *Macromol. Mater. Eng.*, 2006, **291**, 405.

483 W. Zhang, Y. Ma, Y. Xu, C. Wang and F. Chu, *Int. J. Adhes. Adhes.*, 2013, **40**, 11.

484 N. E. El Mansouri and J. Salvado, *Ind. Crops Prod.*, 2006, **24**, 8.

485 B. Danielson and R. Simonson, *J. Adhes. Sci. Technol.*, 1998, **12**, 941.

486 M. A. Khan, S. M. Ashraf and V. P. Malhotra, *Int. J. Adhes. Adhes.*, 2004, **24**, 485.

487 X. Jin, Y. Wu and Z. Yu, *Adv. Mater. Res.*, 2011, **236-238**, 1410.

488 L. Hu, Y. Zhou, R. Liu, M. Zhang and X. Yang, *Ind. Crops Prod.*, 2013, **44**, 364.

489 E. Frollini, F. B. Oliveira, E. C. Ramires and V. Barbosa Jr, BRPI0801091, Brazil, 2009.

490 G. Tondi and A. Pizzi, *Ind. Crops Prod.*, 2009, **29**, 356.

491 S. Kim and H. J. Kim, *J. Adhes. Sci. Technol.*, 2003, **17**, 1369.

492 M. Ozacar, C. Soykan and I. A. Sengil, *J. Appl. Polym. Sci.*, 2006, **102**, 786.

493 A. Pizzi, A. Mekleiham and A. Stephanou, *J. Appl. Polym. Sci.*, 1995, **55**, 929.

494 J. M. G. Galvez and B. Riedl, *J. Appl. Polym. Sci.*, 1997, **65**, 399.

495 T. Trosa and A. Pizzi, *Holz Roh- Werkst.*, 2001, **59**, 266.

496 G. Nemli, S. Hiziroglu, M. Usta, Z. Serin, T. Ozdemir and H. Kalaycioglu, *For. Prod. J.*, 2004, **54**, 36.

497 L. Calve, G. C. J. Mwalongo, B. A. Mwingira, B. Riedl and J. A. Shields, *Holzforschung*, 1995, **49**, 259.

498 X. Zhou, A. Pizzi, A. Sauget, A. Nicollin, X. Li, A. Celzard, H. Pasch and K. Rode, *Ind. Crops Prod.*, 2013, **43**, 255.

499 C. Lacoste, M. C. Basso, A. Pizzi, M.-P. Laborie, D. Garcia and A. Celzard, *Ind. Crops Prod.*, 2013, **45**, 401.

500 C. Basso, S. Giovando, A. Pizzi, A. Celzard and V. Fierro, *Ind. Crops Prod.*, 2013, **49**, 17.

501 X. Li, V. K. Srivastava, A. Pizzi, A. Celzard and J. Leban, *Ind. Crops Prod.*, 2013, **43**, 636.

502 A. Szczurek, V. Fierro, A. Pizzi, M. Stauber and A. Celzard, *Ind. Crops Prod.*, 2014, **54**, 40.

503 (*a*) W. J. J. Burke, *J. Am. Chem. Soc.*, 1949, **71**, 609; (*b*) W. J. Burke, J. L. Bishop, E. L. Glennie and W. N. J. Bauer, *J. Org. Chem.*, 1965, **30**, 3423.

504 G. Riess, M. J. Schwob, G. Guth, M. Roche and B. Lande, *Advances in polymer synthesis*, ed. M. B. Culbertson and E. J. Mcgrath, Plenum, New York, 1985, p. 27.

505 J. Dunkers and H. J. Ishida, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 1913.

506 P. Chutayothin and H. Ishida, *Macromolecules*, 2010, **43**, 4562.

507 A. Minigher, E. Benedetti, O. De Giacomo, P. Campaner and V. Aroulmoji, *Nat. Prod. Commun.*, 2009, **4**, 521.

508 B. S. Rao and A. Palamisamy, *React. Funct. Polym.*, 2011, **71**, 148.

509 R. M. Rao, G. S. S. Sampathkumaran and P. S. M. Shirsalkar, *J. Appl. Polym. Sci.*, 1990, **39**, 1993.

510 C.-F. Wang, J.-Q. Sun, X.-D. Liu, A. Sudob and T. Endo, *Green Chem.*, 2012, **14**, 2799.

511 C.-F. Wang, C.-H. Zhao, J.-Q. Sun, S.-Q. Huang, X.-D. Liu and T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 2016.

512 B. Lochab, I. K. Varma and J. Bijwe, *J. Therm. Anal. Calorim.*, 2012, **111**, 1357.

513 M. Comí, G. Lligadas, J. C. Ronda, M. Galià and V. Cádiz, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 4894.

514 Z. Zhu, Faming Zhuanli Shenqing Gongkai Shuomingshu, CN 101177055 A 20080514, 2008.

515 B. Lochab, I. K. Varma and J. Bijwe, *J. Therm. Anal. Calorim.*, 2012, **107**, 661.

516 S. Li, S. Yan, J. Y. Yu and B. Yu, *J. Appl. Polym. Sci.*, 2011, **122**, 2843.

517 H. Xu, Z. Lu and G. Zhang, *RSC Adv.*, 2012, **2**, 2768.

518 H. Xu, Z.-J. Lu and G. Zhang, *RSC Adv.*, 2013, **3**, 3677.

519 C. Zúñiga, G. Lligadas, J. C. Ronda, M. Galià and V. Cádiz, *Polymer*, 2012, **53**, 1617.

520 P. Jiang, M. Chen, Y. Dong, Y. Lu, X. Ye and W. Zhang, *J. Am. Oil Chem. Soc.*, 2010, **87**, 83.

521 M. A. R. Meier, J. O. Metzger and U. S. Schubert, *Chem. Soc. Rev.*, 2007, **36**, 1788.

522 A. Schieber, F. C. Stintzing and R. Carle, *Food Sci. Technol.*, 2001, **12**, 401.

523 B. Boutevin, S. Caillol, C. Burguiere, S. Rapior, H. Fulcrand and H. Nouailhas, WO2010136725A1, 2010.

524 K. P. Unnikrishnan and E. T. Thachil, *Des. Monomers Polym.*, 2008, **11**, 593.

525 Z. Chen, B. J. Chisholm, D. C. Webster, Y. Zhang and S. Patel, *Prog. Org. Coat.*, 2009, **65**, 246.

526 K. P. Unnikrishnan and E. T. Thachil, *Int. J. Polym. Mater.*, 2006, **55**, 323.

527 L. H. Nguyen, D. T. Nguyen, T. La, K. X. Phan, T. T. T. Nguyen and H. N. Nguyen, *J. Appl. Polym. Sci.*, 2007, **103**, 3238.

528 J. Qin, H. Liu, P. Zhang, M. Wolcott and J. Zhang, *Polym. Int.*, 2014, **63**, 760.

529 C. Sasaki, M. Wanaka, H. Takagi, S. Tamura, C. Asada and Y. Nakamura, *Ind. Crops Prod.*, 2013, **43**, 757.

530 T. N. Maznee, T. Ismail, H. A. Hassan, S. Hirose, Y. Taguchi, T. Hatakeyama and H. Hatakeyama, *Polym. Int.*, 2010, **59**, 181.

531 Q. Yin, W. Yang, C. Sun and M. Di, *BioResources*, 2012, **7**, 5737.

532 H. C. Aouf, C. L. Guerneve, S. Caillol, B. Boutevin and H. Fulcrand, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 2261.

533 S. Benyahya, C. Aouf, S. Caillol, B. Boutevin, J. P. Pascault and H. Fulcrand, *Ind. Crops Prod.*, 2014, **53**, 296.

534 C. Aouf, H. Nouailhas, M. Fachee, S. Caillol, B. Boutevine and H. Fulcrand, *Eur. Polym. J.*, 2013, **49**, 1185.

535 C. Aouf, C. L. Guernevé, S. Caillol and H. Fulcrand, *Tetrahedron*, 2013, **69**, 1345.

536 C. K. S. Pillai, *Pure Appl. Chem.*, 1998, **70**, 1249.

537 H. P. Bhunia, A. Basak, T. K. Chakia and G. B. Nando, *Eur. Polym. J.*, 2000, **36**, 1157.

538 F. M. -Rivera, M. Phuong, M. Ye, A. Halasz and J. Hawari, *Ind. Crops Prod.*, 2013, **41**, 356.

539 M. Funaoka, E. Osaki, S. Fujita and K. Shibahara, Jpn. Kokai Tokkyo Koho, JP 2001064494 A 20010313, 2001.

540 N. Seki, K. Ito, T. Hara and M. Funaoka, *Trans. Mater. Res. Soc. Jpn.*, 2004, **29**, 2471.

541 C. V. Mythili, A. M. Retna and S. Gopalakrishnan, *J. Appl. Polym. Sci.*, 2005, **98**, 284.

542 C. V. Mythili, A. M. Retna and S. Gopalakrishnan, *Bull. Mater. Sci.*, 2004, **27**, 235.

543 T. T. M. Tan, *J. Appl. Polym. Sci.*, 1997, **65**, 507.

544 I. S. Kattimuttathu and S. K. Vadi, *Ind. Eng. Chem. Res.*, 2005, **44**, 4504.

545 N. Rekha and S. K. Asha, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 2996.

546 H. Chung and N. R. Washburn, *ACS Appl. Mater. Interfaces*, 2012, **4**, 2840.

547 I. Dallmeyer, S. Chowdhury and J. F. Kadla, *Biomacromolecules*, 2013, **14**, 2354.

548 H. Hatakeyama, A. Hirogaki, H. Matsumura and T. Hatakeyama, *J. Therm. Anal. Calorim.*, 2013, **114**, 1075.

549 C. Ciobanu, M. Ungureanu, L. Ignat, D. Ungureanu and V. I. Popa, *Ind. Crops Prod.*, 2004, **20**, 231.

550 C. A. Cateto, M. F. Barreiro, A. E. Rodrigues and M. N. Belgacem, *Ind. Eng. Chem. Res.*, 2009, **48**, 2583.

551 Y. Li and A. J. Ragauskas, *J. Wood Chem. Technol.*, 2012, **32**, 210.

552 Y. Li and A. J. Ragauskas, *RSC Adv.*, 2012, **2**, 3347.

553 X. Pan and J. N. Saddler, *Biotechnol. Biofuels*, 2013, **6**, 12.

554 N. E. El Masouri, Q. Yuan and F. Huaund, *BioResources*, 2011, **6**, 2647.

555 S. Manjula, C. Pavithran, C. K. S. Pillai and V. G. Kumar, *J. Mater. Sci.*, 1991, **26**, 4001.

556 T. K. Das, D. Das, B. N. Guru, K. N. Das and S. Lenka, *Polym.-Plast. Technol. Eng.*, 1998, **37**, 427.

557 D. K. Mohapatra, D. Das, P. L. Nayak and S. Lenka, *J. Appl. Polym. Sci.*, 1998, **70**, 837.

558 D. K. Mohapatra, P. L. Nayak and S. Lenka, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 3117.

559 D. K. Mishra, B. K. Mishra, S. Lenka and P. L. Nayak, *Polym. Eng. Sci.*, 1996, **36**, 1047.

560 G. B. Nando and T. Vikram, WO 2007060677 20070531, 2005.

561 A. R. R. Menon, C. K. S. Pillai, A. K. Bhattacharya, G. B. Nando and B. R. Gupta, *Kautsch. Gummi Kunstst.*, 2000, **53**, 35.

562 A. R. R. Menon, C. K. S. Pillai and G. B. Nando, *J. Appl. Polym. Sci.*, 1999, **73**, 813.

563 A. R. R. Menon, C. K. S. Pillai and G. B. Nando, *Eur. Polym. J.*, 1998, **34**, 923.

564 A. R. R. Menon, C. K. S. Pillai and G. B. Nando, *Polymer*, 1998, **39**, 4033.

565 A. R. R. Menon, C. K. S. Pillai and G. B. Nando, *J. Appl. Polym. Sci.*, 1998, **68**, 1303.

566 A. R. R. Menon, C. K. S. Pillai and G. B. Nando, *J. Adhes. Sci. Technol.*, 1995, **9**, 443.

567 A. R. R. Menon, C. K. S. Pillai, A. K. Bhattacharya and G. B. Nando, *Polymer Science: Recent Advances*, ed. I. S. Bhardwaj, 1994, vol. 2, p. 657.

568 A. R. R. Menon, C. K. S. Pillai and G. B. Nando, *Kautsch. Gummi Kunstst.*, 1992, **45**, 708.

569 A. R. R. Menon, C. K. S. Pillai and G. B. Nando, *Met., Mater. Processes*, 2001, **13**, 179.

570 A. R. R. Menon, C. K. S. Pillai and G. B. Nando, *J. Appl. Polym. Sci.*, 1994, **51**, 2157.

571 A. R. R. Menon, C. K. S. Pillai and G. B. Nando, *Polym. Degrad. Stab.*, 1996, **52**, 265.

572 S. Mohapatra and G. B. Nando, *Ind. Eng. Chem. Res.*, 2013, **52**, 5951.

573 T. T. Do, V. K. Nguyen, Q. K. Do and V. L. Dang, *J. Macromol. Sci., Part A: Pure Appl.Chem.*, 1996, **33**, 1963.

574 L. A. Varghese and E. T. Thachil, *J. Adhes. Sci. Technol.*, 2004, **18**, 1217.

575 L. A. Varghese and E. T. Thachil, *J. Adhes. Sci. Technol.*, 2004, **18**, 181.

576 E. Renbutsu, S. Okabe, Y. Omura, F. Nakatsubo, S. Minami, H. Saimoto and Y. Shigemasa, *Carbohydr. Polym.*, 2007, **69**, 697.

577 H. Peng, H. Xiong, J. Li, M. Xie, Y. Liu, C. Bai and L. Chen, *Food Chem.*, 2010, **121**, 23.

578 J. F. Stanzione, J. M. Sadler, J. J. La Scala and R. P. Wool, *ChemSusChem*, 2012, **5**, 1291.

579 N. K. Sini, J. Bijwe and I. K. Varma, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 7.

580 L. Marin, I. Stoica, M. Mares, V. Dinu, B. C. Simionescu and M. Barboiu, *J. Mater. Chem. B*, 2013, **1**, 3353.

581 L. Mialon, A. G. Pemba and S. A. Miller, *Green Chem.*, 2010, **12**, 1704.

582 M. M. Campbell and R. R. Sederoff, *Plant Physiol.*, 1996, **11**, 3.

583 S. C. Fox and A. G. McDonald, *BioResources*, 2010, **5**, 990.

584 G. Sivasankarapillai and A. G. McDonald, *Biomass Bioenergy*, 2011, **35**, 919.

585 H. Chung, A. Al-Khouja and N. R. Washburn, *Green Polymer Chemistry: Biocatalysis and Materials II*, ed. H. N. Cheng, R. A. Gross and P. B. Smith, American Chemical Society, Washington, DC, 2013, ch. 25.

586 G. Gao, J. I. Dallmeyer and J. F. Kadla, *Biomacromolecules*, 2012, **13**, 3602.

587 Y.-S. Kim and J. F. Kadla, *Biomacromolecules*, 2010, **11**, 981.

588 X. Liu, J. Wang, J. Yu, M. Zhang, C. Wang, Y. Xu and F. Chu, *Int. J. Biol. Macromol.*, 2013, **60**, 309.

589 Y.-L. Chung, J. V. Olsson, R. J. Li, C. W. Frank, R. M. Waymouth, S. L. Billington and E. S. Sattely, *ACS Sustainable Chem. Eng.*, 2013, **1**, 1231.

590 S. S. Panesar, S. Jacob, M. Misra and A. K. Mohanty, *Ind. Crops Prod.*, 2013, **46**, 191.

591 D.-Z. Ye, L. Jiang, C. Ma, M.-H. Zhang and X. Zhang, *Int. J. Biol. Macromol.*, 2014, **63**, 43.

592 D.-Z. Ye, X.-C. Jiang, C. Xia, L. Liu and X. Zhang, *Carbohydr. Polym.*, 2012, **89**, 876.

593 D. S. Argyropoulos, H. Sadeghifar, C. Cui and S. Sen, *ACS Sustainable Chem. Eng.*, 2014, **2**, 264.

594 X. Liu, J. Wang, S. Li, X. Zhuang, Y. Zu, C. Wang and F. Chu, *Ind. Crops Prod.*, 2014, **52**, 633.

595 A. Ayoub, R. A. Venditti, H. Jameel and H.-M. Chang, *J. Appl. Polym. Sci.*, 2014, **131**, 39743.

596 M.-J. Chen, D. W. Gunnells, D. J. Gardner, O. Milstein, R. Gersonde, H. J. Feine, A. Huttermann, R. Frund, H. D. Ludemann and J. J. Meister, *Macromolecules*, 1996, **29**, 1389.

597 D.-G. Kim, H. Kang, Y.-S. Choi, S. Han and J.-C. Lee, *Polym. Chem.*, 2013, **4**, 5065.

598 C. Cheng, X. Bai, S. Liu, Q. Huang, Y. Tu, H. Wu and X. Wang, *J. Polym. Res.*, 2013, **20**, 197.

599 F. H. A. Rodrigues, J. R. R. Souza, F. C. F. Franca, N. M. P. Ricardo and J. P. A. Feitosa, *e-Polym.*, 2006, **6**, 1027.

600 J. Lin and B. Hu, *Chin. J. Polym. Sci.*, 1998, **16**, 219.

601 R. Andreu, J. A. Reina and J. C. Ronda, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6091.

602 R. Andreu, M. A. Espinosa, M. Galia, V. Cadiz, J. C. Ronda and J. A. Reina, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 1529.

603 M. A. Espinosa, V. Cadiz and M. Galia, *J. Appl. Polym. Sci.*, 2003, **90**, 470.

604 A. Celzard, V. Fierro, G. Amaral-Labat, A. Pizzi and J. Torero, *Polym. Degrad. Stab.*, 2011, **96**, 477.

605 J. M. F. Paiva, W. G. Trindade, E. Frollini and L. C. Pardini, *Polym.-Plast. Technol. Eng.*, 2004, **43**, 1187.

606 J. M. F. Paiva and E. Frollini, *J. Appl. Polym. Sci.*, 2002, **83**, 880.

607 N. S. Etun and N. Yözmen, *Turk. J. Agric. For.*, 2003, **27**, 183.

608 M. A. Khan and S. M. Ashraf, *J. Therm. Anal. Calorim.*, 2007, **89**, 993.

609 A. Moubarikv, A. Pizzi, A. Allal, F. Charrier and B. Charrier, *Ind. Crops Prod.*, 2009, **30**, 188.

610 S. Cheng, I. D'Cruz, Z. Yuan, M. Wang, M. Anderson, M. Leitch and C. Xu, *J. Appl. Polym. Sci.*, 2011, **121**, 2743.

611 A. Moubarika, N. Grimi, N. Boussetta and A. Pizzi, *Ind. Crops Prod.*, 2013, **45**, 296.

612 M. Aoyagi and M. Funaoka, *Trans. Mater. Res. Soc. Jpn.*, 2007, **32**, 1115.

613 M. Aoyagi and M. Funaoka, *Trans. Mater. Res. Soc. Jpn.*, 2006, **31**, 891.

614 Z. Xia, T. Yoshida and M. Funaoka, *Eur. Polym. J.*, 2003, **39**, 909.

615 O. Milstein, R. Gersonde, A. Huttermann, M. J. Chen and J. J. Meister, *Appl. Environ. Microbiol.*, 1992, **58**, 3225.

616 http://www.Cardolite.com.

617 L.-T. Lee, M.-C. Wu and M.-H. Lee, *J. Polym. Res.*, 2013, **20**, 282.

618 M.-T. Weng and Z. Qiu, *Thermochim. Acta*, 2014, **575**, 262.

619 Y. Liang, F. Yang and Z. Qiu, *J. Appl. Polym. Sci.*, 2012, **124**, 4409.