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Tannin as a renewable raw material for adhesive applications: a review

Fossil fuel depletion by the proliferating population catalysed the research and development of bio-derived compounds. Tannin being an abundant biomaterial, with complex phenolic structure, offers the possibilities of tailor-made modifications. To unveil the complexities and to accelerate the momentum for commercialization, the article highlights overall aspects of tannin as a sustainable and cost effective advanced engineering material. Recent advancements in the extraction of tannin, with its potential ability for chemical modification, has also been highlighted and compared with hydrocarbon-derived counterparts. This article provides a complete database on tannin as a candidate for the circular economy, thereby fuelling a sustainable growth.

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Tannin as a renewable raw material for adhesive applications: a review

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Considering the limits of petrochemical availability and their toxicity, there has been rapid development and innovation in the field of alternatives for petrochemical adhesives. The carcinogenicity of formaldehyde has reduced the demand for formaldehyde-based wood adhesives, which has resulted in the development of adhesives based on renewable resources. This review article summarizes various works published on bio-derived adhesives focusing on tannin. Increasingly acknowledged renewability, sustainability, lower cost, and chemical modification opportunities make tannin a credible precursor for developing competent bio-based adhesives. Henceforth, the chemistry of tannin, its usefulness, possible chemical modification, and compatibility in an attempt to synthesize bio-based adhesives is also being highlighted and compared with its hydrocarbon-derived counterparts. In addition to this, categories of tannin, and techniques available for their extraction along with their pluses and misuses, have also been explained. Moreover, this review includes a detailed discussion on tannin as a raw material for preparing epoxy, polyurethane, polyethyleneimine, and furfuryl-based adhesives. It is expected that by exploring further possibilities of chemical modification, tannin can be a potential candidate that can compete with the petrochemical-based adhesives, thereby paving the way for the advancement of bio-adhesives.

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Introduction

The proliferation of the human population has led to developments in the infrastructure sector resulting in demand for wood-based products such as fiberboards, particleboards, wood panels, oriented strand boards, plywood, laminates, *etc.* The usage of wood products is inevitable in the construction sector. A variety of wood products are being used in both indoor and outdoor applications. Furthermore, the furniture manufacturing industries are also massive consumers of wood products. To ensure the strength and better performance of various wood products, the joining of wood samples plays a significant role. Wood adhesives provide durable and strong bonds between

different wooden parts and offer thermal and moisture resistance.¹ Conventional wood adhesives are formaldehyde-based systems functioning as binders. Major adhesives based on formaldehyde include phenol–formaldehyde (PF), urea–formaldehyde (UF), and melamine–formaldehyde (MF).¹ Formaldehyde-based adhesives were mostly available separately as resins and hardeners in a powder form.² In addition, the durability, robust bond formation, moisture resistance, low cost, and gap-filling property of formaldehyde-based adhesives revolutionized the wood adhesive industries. However, health hazards associated with formaldehyde and its identification as a potential carcinogen with negative environmental impacts led to the exploration of environment-friendly alternative wood adhesives.^{3,4} Among different alternatives, water-based adhesives are used to consolidate wood (or wood panels or wood veneers),^{5–7} where water acts as a solvent, thereby reducing the dependency on harmful and toxic organic solvents. To further mitigate the usage of petrochemical-based adhesives, bio-materials incorporating wood adhesives have gained significant attention in recent years. The world's most prevalent biopolymers have been explored for their use in wood adhesives, including cellulose^{8,9} derived as a residue or in several other forms such as carboxymethyl cellulose (CMC),^{10,11} microfibrillated cellulose,¹² chemically modified nanocellulose,¹³ cellulose nanofibrils,¹⁴ or microcrystalline cellulose;¹⁵ starch^{16–18} or

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blends prepared in various ratios using starch and co-ingredients such as polyvinyl alcohol,^{19,20} silica nanoparticles,²¹ silane coupling agent,²² or sodium dodecyl sulphate,²³ lignin^{24,25} or tailor-made resins like lignin-epoxy from biomass²⁶ and lignin-polyurethane²⁷ in an attempt to give an alternative to formaldehyde; similarly, soy proteins²⁸ or their chemical modifications²⁹ for enhanced end properties and thus performance. With increasingly acknowledged credibility of these naturally available polymers in terms of abundant supply, cost, and ease of functionalization,^{30,31} lately the research focus has shifted from finding suitable raw-materials to developing competent bio-derived adhesives compared to their hydrocarbon-based counterparts.^{32,33} Therefore, with the objective of developing next-generation sustainable adhesives, while hunting for similar suitable materials, which are capable of meeting today's (environmental and health) regulations and exceeding (or meeting) the performance bar set by their hydrocarbon-derived counterparts is critical. With that in mind, tannin is one such material with similar potential and has been thoroughly investigated^{34,35} especially to develop sustainable and competent bio-based wood adhesives.

Tannin

As its generic name, tannin is a highly water-soluble substance, astringent in its aqueous solution, and has the feature of tanning leather. Chemically, tannin is a conjunction of complex organic compounds, with a phenolic structure.³⁶ Primarily tannin can be classified into hydrolyzable and condensed tannin. Fig. 1 shows the basic classification of tannins. Hydrolyzable tannin results in a mixture of gallic acid, ellagic acid, and digallic acid on heating with dilute acid. These consist of ester linkages formed between benzoic acid and sugars. Also, they possess lower nucleophilicity with lower phenolic content.

Whereas the condensed tannin upon polymerization results in water-insoluble phlobaphene,³⁷ extracts of chestnut, myrobolans (*Terminalia* and *Phyllanthus*), and dividivi (*Caesalpinacaria*) contain hydrolyzable tannin. On the other side, condensed tannin is present in decent concentrations in the bark and wood of various trees.³⁸ The presence of free hydroxyl groups enables the ease of accessibility as well as the feasibility for modification, hence facilitating chemical modification on tannin.³⁹ Chemical modifications engineer tannin as a potential candidate for the functional adhesive category.⁴⁰



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The introduction of tannin as a renewable material has opened up new avenues in various applications published in several reviews and book chapters from the early 1980s.^{41–44} Tannin is widely reported as a precursor for wood adhesives and waste-water treatment, bio-sorbent, and green raw material for the food and pharmaceutical industries. In addition its antioxidant and antimicrobial properties were also revealed in various reports.^{45–48} Furthermore, bio-foams derived from tannin have also gained much interest.⁴⁹ Koopmann and

colleagues⁵⁰ reviewed the interaction of tannin with ceramic and polymeric materials, extending their applications. Considering the adhesion properties, major developments were reported from the second half of 2010.^{51–57} The most recent detailed review on tannin was published in 2021, which was focused on the developments of tannin and lignin-based polyurethane resins and their applications.⁵⁴ This study summarized various classes of polyurethanes and the importance of non-isocyanate polyurethane resins in multiple applications



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with a detailed synthesis mechanism.⁵⁴ Although multiple reviews^{41–49} are available on tannin as an adhesive, comprehensive reviews discussing the structure–property relationship, benefits that tannin-derived adhesives are capable of offering beyond its renewability, or molecular structures, in particular, having the potential to provide new functionalities with a view on physico-chemical analysis remain scant.

Moreover, recent advancements in tannin extraction and purification protocols, which are catalyzing tannin's industrial viability, have not been reviewed yet. Also, an exclusive review on tannin with detailed discussion on various chemical modifications of tannin and tannin blended adhesives still remains lacking. As tannin-based adhesives are free from formaldehyde emission, and also tannin forms are employed as a precursor for isocyanate-free polyurethanes and bio-derived epoxy resins,

and as a source of natural phenolics, updating such a material to industrial level applications is unequivocally important. Being an updated exclusive review on tannin for adhesive applications, this manuscript is addressing the aforementioned gaps. In particular, as the advancement in environmentally benign and bio-derived adhesives has been booming in the past few decades, the same is being reflected in tannin-based adhesives as well.

Hence with this aim, this review paper is an overview of various works reported on tannin as a potential candidate for developing bio-derived wood adhesives. The article sheds light on multiple related topics, including the methodologies reported for extracting tannin and its classification, followed by a detailed discussion of their pluses and minuses. Increasingly acknowledged renewability, sustainability, lower cost, and chemical



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Mrudul V. Supekar graduated with First Rank in her MS degree (MSc) in Applied Chemistry from Mahatma Gandhi University, Kerala, 2015, and was the recipient of an Aspire fellowship (2014–15), Ministry of Higher Education, Govt. of Kerala. Currently Mrudul Supekar is a joint full-time research scholar at Department of Polymer Science and Rubber Technology and Department of Applied Chemistry, Cochin University of Science and Technology (CUSAT), India. After

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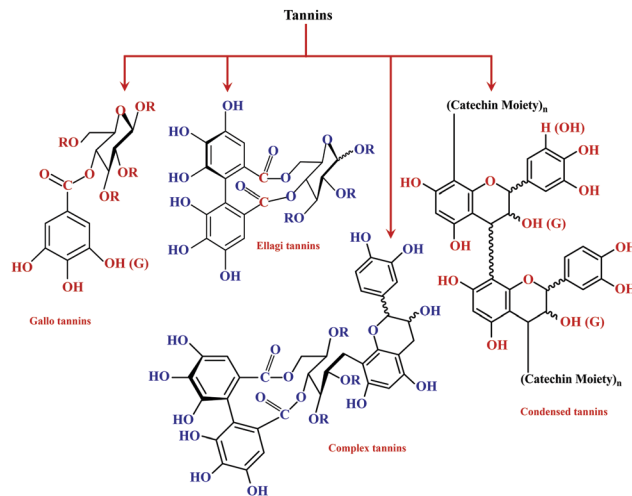


Fig. 1 Types of tannin (hydrolyzable and condensed tannin) and their chemical structure.

modification opportunities make tannin a credible precursor for developing competent bio-based adhesives. Henceforth, the chemistry of tannin, its usefulness, possible chemical modification, and compatibility in an attempt to synthesize bio-based adhesive is also being highlighted and compared with their hydrocarbon-derived counterparts. Moreover, the paper includes detailed studies on the binding properties of tannin and its function as a reactive polymer with other binders such as epoxy, polyurethane, polyethylenimine, and furfuryl-alcohol, in an effort to develop bio-derived adhesive systems. This work, therefore, aims to provide a complete database on tannin, showcasing the potential applications as a reactive bio-derived material for adhesive applications.

Chemistry of tannin

Among hydrolyzable and condensing units, condensed tannin shows reduction in the formaldehyde emission level, due to its higher reactivity with formaldehyde and the presence of catechol groups. Hence, condensed tannin serves as one of the most explored wood adhesive precursors in the global community with an increased market value, compared to hydrolysable tannin.⁵⁵ Furthermore, the presence of flavonoid units in the condensed tannin helps in catalysing the

lightweight charge storage solutions, including high-temperature supercapacitors and batteries. Prof. Prasanth has published many research papers in high-impact factor journals, and a number of books/book chapters, and has more than 7000 citation and h-index of 50 plus. He sits on the editorial board of SCI journals as an Editor or Editorial Advisory Board member of SCI international journals including *Journal of Materials Research*, *Nanofabrication*, *Biomaterials and Polymers Horizon* and *Frontiers of Materials* etc. Prof. Prasanth is a book series editor for Springer Nature, Elsevier, Taylor and Francis, CRC Press etc. Apart from science and technology, Prof. Prasanth is a poet, activist and a columnist in online portals and printed media.



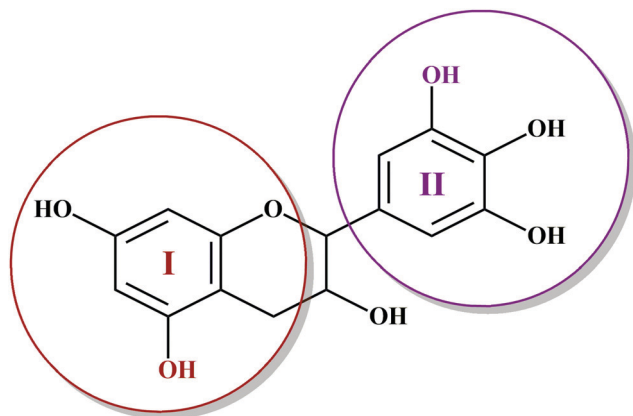


Fig. 2 Condensed tannin structure comprising the I-ring (includes resorcinol and phloroglucinol) and II-ring (includes pyrogallol and catechol).

polymerization reaction. The flavonoid groups are affiliated with their precursors, for example, flavanes-3,4-diols, and flavanes-3-ol.^{58,59} Every flavonoid unit consists of two categories of phenolic nuclei, namely, the 'I' ring and 'II' ring, as shown in Fig. 2. The 'I' ring of condensed tannin comprises phloroglucinol and resorcinol, whereas the 'II' ring incorporates catechol and pyrogallol. As tannin is a conjunction of complex organic compounds, the 'I' rings of different tannins hold different chemical structures, with those extracted from sources like wattle/mimosa, douglasfir, quebracho, and spruce incorporating resorcinol, while that from pine contains phloroglucinol.⁶⁰

According to the resorcinol 'I' ring and pyrogallol II-ring, the main polyphenolic pattern is portrayed through flavonoid analogues (Unit-A from Fig. 3). The structure of this entity



Fig. 3 The condensed tannin units, where the 'A' unit contains 70% tannin and comprises a resorcinol 'I' ring and pyrogallol 'II' ring; the 'B' unit includes 25% tannin with a resorcinol 'I' ring and catechol 'II' ring; the remaining 5% is a mixture of phloroglucinol–pyrogallol (shown by 'C' unit) and phloroglucinol–catechol flavonoids (indicated by 'D' unit), and units 'E' and 'F' are non-tannin compounds.



Fig. 4 Schematic illustration of the different extraction methods. The raw material is subjected to various extraction methods to obtain a polyphenolic extract as the product: solvent extraction (solid–liquid extraction-SLE), extraction at high temperature and pressure (pressurized liquid extraction-PLE), acoustic cavitation phenomenon (ultrasonic-assisted extraction-UAE), microwave energy (microwave assisted extraction-MAE), and supercritical fluid (super critical extraction-SCE).

accounts for about 70% of tannin. The B-unit in condensed tannin accounts for 25%, with a resorcinol 'I' ring and catechol 'II' ring (Unit-B from Fig. 3). The remaining 5% is a combination of phloroglucinol–pyrogallol, and phloroglucinol–catechol flavonoids represented in the 'C' and 'D' units of Fig. 3.⁶¹ These four units/models constitute an average of 65 to 80% of mimosa bark extract. The rest of the constituents are non-tannins, hydrocolloid gums, simple carbohydrates, and nitrogen-based compounds like amino acids and imino acids. Simultaneously, pectin and gums are the crucial constituents of tannin and have a notable effect on the extract's viscosity. They are found to be effective even with concentrations of as low as 4 to 6%.⁶² These non-tannin constituents are found to be responsible for weakening wood products and may also lead to decreased moisture resistance.⁶³ Pine-based tannin primarily confers two models: the first is unit-E, *i.e.*, phloroglucinol 'I' ring and catechol 'II' ring structures, and the other one is unit 'F', *i.e.*, phloroglucinol I-ring and phenol II-ring, represented in Fig. 3.

Extraction of tannin

Tannins are phenolic compounds with a substantial and natural abundance with complex aromatic and heterocyclic ring structures.⁵¹ A wide variety of tannins (approximately 8000 variants) have been explored so far. The majority of these are found in plant cells in bound or free forms. It is possible to distinguish terrestrial plant tannins into four types, namely ellagitannins, gallotannins, complex tannin, and proanthocyanidins (condensed tannin).⁵¹ Plant-derived tannins include oligomers or phloroglucinol polymers, which have been identified as 'phlorotannins.' The percentage of tannin extracted principally relies on the plant species, its habitat, harvest time, and extraction techniques.⁶⁴ Owing to their eco-friendliness and vast applications, tannins have recently gained considerable interest. In the current scenario,



tannins are widely explored in various sectors like food, ink, adhesives, beverages, medicine processing, pigments, tanning industries, water purification, plastic resins, and surface coatings.⁵¹ These compounds have also been widely explored as precipitating agents or complexing agents where the performance of the same is governed based on its concentration.⁶⁵ However, owing to its heterogeneous nature, the extraction is still the principal bottleneck for their recovery. Therefore, effective utilization and recovery of tannin are important for exploring the uniqueness of the material for various applications. Hence, considering the importance of tannin extraction and processing techniques, a detailed discussion based on work carried out over the last 20 years is summarized. An overview of various extraction methods of tannin is shown in Fig. 4.

Advanced extraction methods of tannin

Conventionally, tannins are extracted from various sources using mechanical processes such as milling and grinding. Tannin sources such as barks, wood chips, saw dust, leaves, shoots, *etc.*, are typically ground to a particle size ranging from 0.5 μm to 0.5–5 mm.³⁷ Extraction proceeds faster with smaller particles of the source material. The yield of tannin varies from 6–43%, depending on the source, method of extraction, type of solvent used, time and temperature of the extraction process.⁵¹ Water or aqueous solutions of sodium salts, such as sodium carbonate/bicarbonate, sodium sulphite/bisulphite or aqueous NaOH solution are the widely reported solvents for the extraction.⁵¹ Moreover, various solvent mixtures are also used for the extraction and purification of tannin. Solvent mixtures such as acetone/water, acetone/ethanol, methanol/water, or organic solvents such as *N,N*-dimethylammonium, *N',N'*-dimethylcarbamate *etc.*, under stirring and refluxing have been reported from early times.³⁷ Advancement in technology has reflected its impact on the extraction process as well, hence newer extraction methods were explored. This section aims to explain the evolution of the current methods for tannin extraction. A comprehensive analysis has been carried out between various techniques. Each method's key strengths and drawbacks are discussed in detail. This provides a cleaner and more productive development of tannins.

Solid-liquid extraction (SLE)

In the solid-liquid extraction (SLE) method, tannin extraction is solely based on the interaction between the raw material and a solvent. The solvent penetrates the feedstock's cell wall, leading to the dissolution of the tannin, followed by separation.⁶⁶ SLE is one of the most straightforward and traditional techniques used to isolate tannins. Several forms of solvents, such as aqueous solutions, organic solvents, and ionic liquids, are widely explored. Extraction processes utilizing aqueous and organic solvents, and Soxhlet apparatus are widely used.^{67,68} However, other methods, such as infusion or maceration, are also used and documented in the literature.⁶⁸ Water-based extraction can be carried out under refluxing or by simple maceration. It is typically performed on wood bark on an industrial scale by percolation or open diffusion.⁶⁹ Seppeler

and colleagues performed a purification of industrial tannin, employing the SLE method.⁶⁹ Investigators used black wattle tannin extract purification followed by vacuum filtration, recovery of the extract, drying in a rotary evaporator, and pulverization. Mass spectroscopy analysis and gel permeation chromatography (GPC) showed that the extract is a complex polyphenolic compound with high molecular weight, insoluble compounds. It contains flavonoids, proteins, phenolic substituents, and aliphatic chains. Analysis showed the existence of chemical bonds between polyphenolic molecules and carbohydrates. Moreover, the sample contains constituents which are insoluble in acetone, which have antioxidant properties. Extraction involving ionic liquids is another option focused on substituting these modern liquids for conventional solvents, which are considered to have exceptional properties such as high thermal stability, negligible vapor pressure, and dissolution of a wide variety of plant compounds.⁷⁰

To conclude, it can be observed that simplicity, productivity, and reduced cost are the key benefits of this system. In hot water extraction, it is also necessary to highlight the method that is capable of commercialization at the industrial level, particularly wood bark extraction.^{71,72} Major disadvantages of this process are longer extraction time ranging from hours to days, as well as the surplus usage of solvents. Utilizing ionic liquids (ILs), which exhibit unique properties favorable for the extraction, could mitigate these disadvantages.⁷³ Nonetheless, the higher cost of these solvents coupled with the difficulty of recovering the ILs continues to impede their use.

Supercritical fluid extraction (SCE)

Supercritical fluid extraction (SCE) is based on a critical point, described by a maximum pressure and temperature at which the pristine material may exist in a liquid-vapor equilibrium.⁷⁴ Above this point, the properties of the fluid are exchanged between the liquid as well as the gaseous state, such as the standard weight of liquids including the gas-penetration power.⁷⁵ Carbon dioxide (CO_2) is the most employed solvent in the majority of SCE because of its favorable characteristics such as lower critical point (temperature of 31 $^\circ\text{C}$ and a pressure of 7.28 MPa), non-corrosive nature, non-flammability, non-toxicity, and ease of availability.^{76,77} For the favorable extraction of tannins, the addition of polar co-solvents (*e.g.*, ethanol, methanol, or aqueous mixtures) enhances CO_2 solvation to tannins and thereby augments the extraction rates.^{78,79}

A major advantage of the SCE extraction method includes the utilization of non-toxic solvents like CO_2 that can be easily removed by generating an oxygen-free environment and preventing further oxidation reactions. On the other hand, the method requires high pressure for extraction (the major drawback), creating a huge investment cost.⁸⁰ Another major hitch of this method is the non-polar nature of CO_2 , which considerably reduces tannin extraction owing to the polar nature of the components; hence the efficient extraction of tannin using SCE requires the incorporation of co-solvents like methanol, ethanol, acetone, or water.



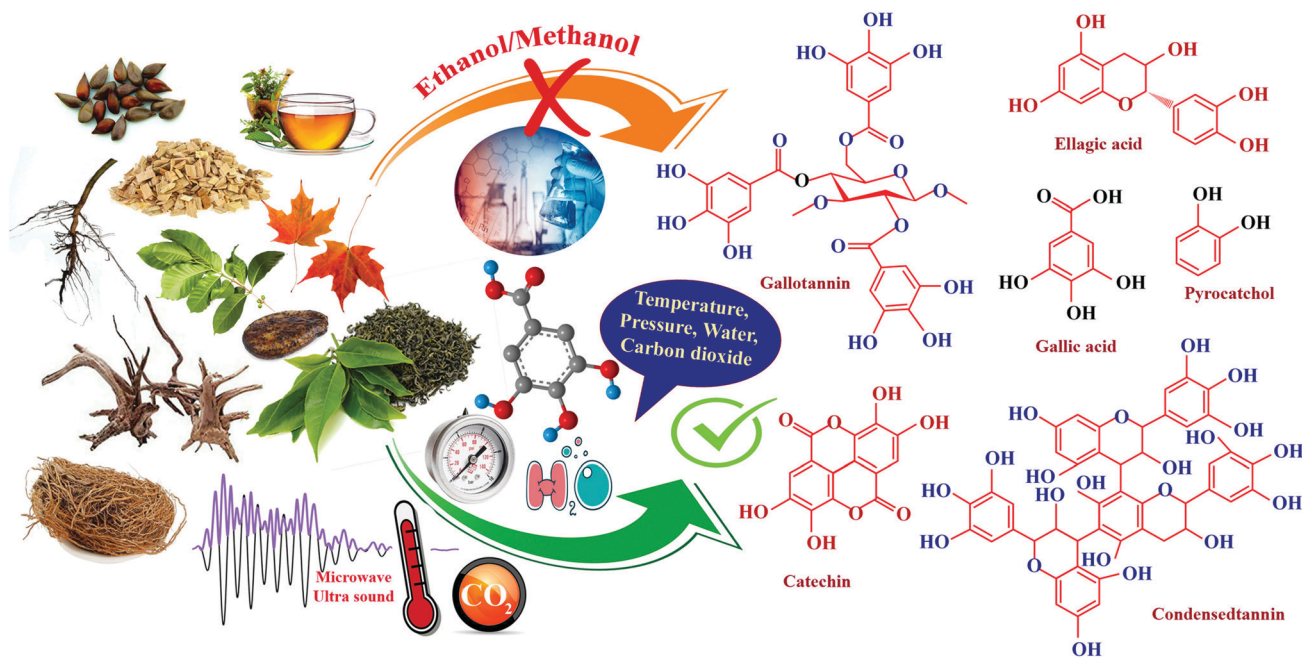


Fig. 6 Schematic illustration of the extraction of tannin from various renewable resources by different methods leading to the extraction of the major chemical components of tannin such as ellagic acid, gallic acid, pyrocatechol, catechin, etc.

Table 1 Limitations of tannin-adhesive resin and their respective causes

Limitations of tannin-adhesive resin	Causes
Poor strength of resin and poor water resistance	Presence of non-tannin components (like sugars and gums).
Highly viscous	High molecular weight of tannin extract. Presence of hydrogen bonding and electrostatic interaction between gum–gum, tannin–gum, and tannin–tannin
Low-grade strength	Phenolic substituents in tannin with hydroxyl groups makes tannins highly reactive.
Bad adhesion	Short pot life with lower crosslinking, due to the tannin/formaldehyde condensate.
Brittleness	
Unserviceable shelf and pot lives	
Large pressing time	
Short assembly time	
Uneconomic conditions of application	

raw materials emit formaldehyde, a volatile and carcinogenic material.⁹⁰ Equating the growing concerns over volatile organic solvents and the limited availability of fossil fuels, approaches to develop alternatives have received much appreciation.⁹¹

As tannin is unique in its composition and abundantly available, the development of value-added products offers a sustainable alternative. It is emerging as a green substitute for the wood adhesives, produced from petroleum-based resources, specifically phenol and resorcinol.^{92,93} There have been a number of works reported on tannin-based adhesives for particleboard, plywood, and laminated products from the group of Pizzi.^{35,94–96} Tannin can be classified as hydrolyzable tannin, and condensed tannin.

Hydrolyzable tannin has limited applications in the wood industry because of its low reactivity with formaldehyde, which can be ascribed to its simple phenolic structure, as shown in Fig. 1. Apart from the phenolic structures of tannin, commercial

extracts consist of sugars and gums hence making the tannin extract impure.⁵¹

Sugars and gums are unitedly known as non-tannin components, usually 20–30% in black wattle and hardwood-based tannin, whereas pine obtained tannin has non-tannin components as high as 40–50%.⁹⁷ As non-tannin components do not take part in the synthesis of the resin adhesive, they reduce the actual solid content, therefore hampering the final properties of the resin.⁹⁸ Non-tannin constituents are responsible for the weaker strength of the resin and accountable for the poor moisture resistance of the adhesives. In addition to that, an un-modified tannin-based adhesive is unfit for wood products having high requirements. Table 1 summarises the limitations and respective causes of tannin as an adhesive material. In the current scenario, these disadvantages are the most significant obstacle limiting the productive and global development of tannin as a bio-derived alternative. Hence to unveil the



limitations and to reveal the ease of resin formation, a better insight into structure–property relations of tannin needs utmost interest. As tannin has complex phenolic groups, exhibiting excellent physico-chemical properties, with easiness-to-use compared to conventional phenolic resin, it can function as a potential candidate for greener adhesives.⁹⁹ Furthermore, the chemical composition of tannin allows possibilities for further chemical modification.¹⁰⁰

Chemical modification of tannin

The resemblance of tannin and similarity in the reactivity with formaldehyde-based systems, such as conventional phenol resorcinol formaldehyde, makes tannin a potential substituent for petrochemical based resins.⁹⁰ Although tannins have limitations as listed in Table 1, wood adhesives based on condensed tannin have been extensively studied. Moreover, hydrolysable tannin has limited reaction with formaldehyde.⁵⁴

In addition, linking units between hydrolysable tannin groups are highly susceptible to moisture, whereas condensed tannin is found to be highly immune to moisture.¹⁰¹ Several attempts have been made to improve the properties of tannin, blending tannin with polymers or copolymerizing or used as additives to the main resin *etc.*^{35,95,96} The polyphenolic structure of tannin can be engineered through various chemical modifications, such as acylation, esterification, methylation, etherification *etc.*³⁶ Two primary approaches through which condensed tannin can be used to manufacture adhesives are auto-condensation and poly-condensation reactions.

Co-polymerization of tannin with synthetic adhesives is also possible and the reason behind this is often,

- to suppress the emission of formaldehyde from synthetic resin (when a small percentage of tannin is added) or.
- to make the tannin-based adhesive immune to moisture (when a small percentage of synthetic resins are added). A simple addition of a small percentage (~10 to 30%) of polymeric 4,4'-diphenylmethane diisocyanate (pMDI) into mimosa

Table 2 Applications of tannin-based adhesives for consolidation of various wood products with significant outcomes

No.	Resin + hardener	Application	Outcomes	Ref.
1	<i>Wattle tannin</i> + HCHO (modified by different bridging agent)	Exterior plywood	A marketable adhesive in South Africa (SA)	98
2	<i>Wattle tannin</i> + resorcinol–HCHO	Glulam and finger joints	A marketable adhesive in SA (South Africa)	104
3	<i>Mimosa tannin</i> + methylol–urea	Particleboard (for exterior and semi exterior application)	Inexpensive Tannin adhesives. methylol–ureas can be effectively used as hardeners.	105
4	<i>Larix tannin</i> (60%) + phenol–formaldehyde	Plywood (for general and construction application)	The obtained resin had much better properties than pure phenol–formaldehyde	106
5	<i>Quebracho tannin</i> + furfuryl alcohol	Hardboard	Results were similar to that of phenol–formaldehyde	107
6	Phenol–formaldehyde + <i>pinus oocarpa tannin</i> (10%)	Plywood	Modulus of rupture and modulus of elasticity remains constant, except for similar modulus of elasticity.	108
7	<i>Wattle tannin</i> + polyvinyl acetate (20%)	Bonding fancy veneers to plywood	The bonding strength of tannin-based adhesives is improved using 20% polyvinyl acetate	109
8	Phenol–formaldehyde (80%) + corn starch (15%) + <i>quebracho tannin</i> (5%)	Plywood (for exterior use)	Improved mechanical properties than plywood panels made out of commercial phenol–formaldehyde	110
9	Corn–starch + <i>wattle tannin</i> + formaldehyde	Plywood (for interior use)	Outstanding mechanical properties, similar to phenol–formaldehyde	111
10	Phenol–formaldehyde + <i>Eucalyptus tannin</i> (10–15%)	Cellulose fibre composite sheets	Improved mechanical properties against the panel using pure phenol–formaldehyde.	112
11	<i>Mimosa tannin</i> (50%) + <i>lignin</i> (50%)	Particleboard (for interior use)	Exterior grade panels can be made out of tannin alone.	113
12	<i>Grape tannin</i> (60%) + <i>lignin</i> (40%)	Particleboard (for interior use)	Tannin molecules, responsible for a higher density, crosslinking, and increased strength	114
13	<i>Mimosa tannin</i> /formaldehyde (60%) + <i>lignin</i> (40%)	Particleboard	Meet all the requirements for internal bonding specified by European standards.	115
14	<i>Pine tannin</i>	Particleboard and medium density fibreboard	It has the potential to become an industrial adhesive.	95
15	Furfuryl alcohol (54%) + <i>Quebracho tannin</i> (45%) + <i>para</i> -toluene sulfonic acid (0.9%)	Composite with vegetal fibers reinforcement	Outstanding mechanical properties and fast curing	116
16	Melamine–formaldehyde/phenol–formaldehyde + tannin (20%)	Plywood	The reaction between Tannin and formaldehyde leads to cross-linking of the adhesive system and resulted in the reinforced melamine–formaldehyde and Phenol–formaldehyde	117
17	<i>Mimosa/Pine tannin</i> – Furfuryl Alcohol (50%)	Particleboard	Capable of meeting European standards at pH = 10	118
18	<i>Pine tannin</i> + Phenol–Formaldehyde /urea formaldehyde/polymeric isocyanate	Interior and exterior plywood	Adding 20 to 35% of synthetic adhesive encouraged tannin adhesive.	94
19	<i>Lignin polyol–tannin</i> + polyethylenimine (PEI)	plywood	PEI brings greater tensile strength, heat and moisture-resistance	119
20	<i>Tannin</i> + PVA + boric acid	Hardwood and softwood	Free hydroxyl groups of PVA and tannin serve as cross-linking sites that enhance thermal, mechanical, and performance properties. An improved hydrophobicity was noticed.	120





Fig. 9 Reaction of bio-hardener hydrolysis and the crosslinking of tannins with 2-hydroxy-5-hydroxymethyl furan, resulting in 2,5-dihydroxymethyl furan.

chemical additives.¹²⁶ The as-prepared adhesive showed non-toxic behaviour, as it consisted of natural renewable ingredients; in the combination, about 30% of the tannin is mixed with 13% of the EPL. Among the tested samples, about 44 out of 100 samples passed the criteria of EN 314 class-1,¹²⁶ confirming the pertinence for indoor bonding applications. Fig. 10 represents the reaction involved, where the adhesive showed excellent water resistance and bonding strength. The reaction follows a Michael addition-type plausible mechanism, where gallic acid oxidises to a diketone molecule.¹²⁶

Auto-condensation reaction without hardeners

'Auto-condensation' terminology applies to the opening of the pyran rings under acidic as well as alkaline conditions without using an external hardener.¹²⁷ This is a unique chemical

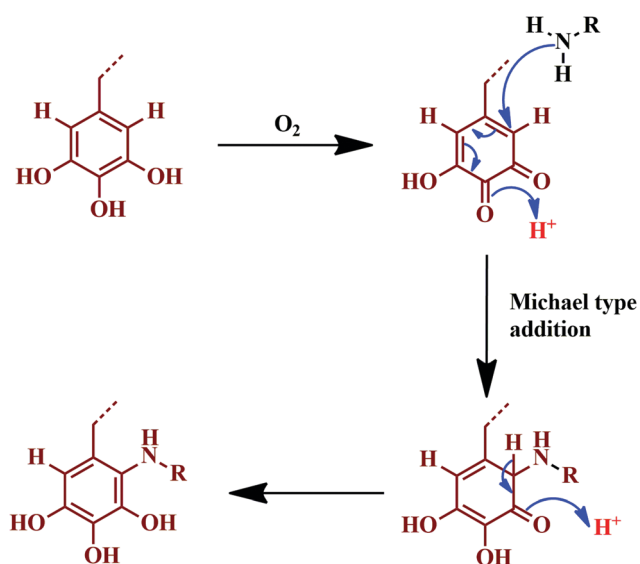


Fig. 10 Michael addition-type plausible reaction mechanism, where gallic acid is oxidised to a diketone.



Fig. 11 Mechanism of auto-condensation of tannin molecules.

property of tannin, as it induces self-polymerization to obtain a crosslinked polyphenolic network.⁶⁵ The rates of auto-condensation reaction of tannins depend on the source of extraction and its chemical composition. 'Quebracho' and 'mimosa' tannins are slower-natured, whereas 'pecan nut' and 'pine' are comparatively faster, considering the auto-condensation.¹²⁸ For faster-natured tannins, rapid self-polymerization is just a contact away with the lignocellulose surface.¹²⁷ Contrarily, the slower-nature took more time, resulting in poor internal strength of the bonded wood panel due to its sluggish rate of hardening.¹²⁹ The polyflavonoid tannin adhesives undergo auto-condensation, which can be physically observed by the increase in viscosity without aldehydes or dialdehydes.^{65,127} Under acidic or alkaline conditions, the chain opening of the flavonoid units occurs on the O1-C2 bonds followed by condensation at C2 with the free sites of flavonoid at C6/C8 with different tannin molecules.¹³⁰ The chemical reaction of auto-condensation is shown in Fig. 11.

It is reported that the auto-condensation of different tannins can be swayed by weak Lewis acids, like boric acid, silicates, aluminium chloride, and silica.¹³¹ Lewis-acid catalyses auto-condensation of tannin, thus rectifying the problems associated with the slower reaction of tannins. Moreover, the Lewis-acid based auto-condensation system demonstrates a reduction in pressing time and pressing temperature and offers stronger internal bonds.^{127,132} A recent study reported the usage of quebracho tannin adhesive (of 50% water solution), and (2 to 4%) boric acid, for the preparation of a poplar plywood (populus deltoids) panel.¹³³ The prepared plywood panels met the bonding requirements of the relevant standard; also, the panel showed enhanced biological resistance due to the biocide nature of boric acid.¹³³ The tannins, which are hardened by the auto-condensation technique, induced either by Lewis-acid or



lingo-cellulosic substrate, solely resulted in bonds of interior grade quality.⁵⁴

Tannin epoxy-based adhesives

Epoxy resin is the most popular and highly demanding commercial thermosetting polymer, which has been extensively used in various fields such as coatings,^{134–138} adhesives,^{139–142} and advanced composites^{143–148} due to its unique chemical resistance, excellent adhesion, and mechanical properties.^{149,150} However, petrochemical based epoxy resins are not environmentally benign. Based on recent European directives, especially the EU's 2015 Circular Economy Strategy, the industrial approach and research directions are now focused on reducing waste and lowering pollutant volume.¹⁵¹ Moreover, realising the toxicity of petrochemical compounds to both humans and the environment, many petrochemical-based substances are identified as carcinogens.

Conventionally, many of these compounds were widely used by plastic industries. Among them, bisphenol-A (BPA) is classified as CMR R3, which is one of the main components of epoxy resins.^{149,150} However, BPA, a primary raw material for the production of commercial epoxy resin, is a petroleum-derived product. Economic, health, and environmental consequences of these materials have inhibited their extensive use industry, which is being converted to a green-labelled industry. The substitution of petroleum-derived chemicals with newer and eco-friendly (preferably bio-derived) polymers has come in first place as far as the most attractive development projects are concerned.^{152,153} Coupled with environmental awareness and primarily food safety and packaging considerations, developments in the exploration of green materials have boomed. As a result, low toxic precursor materials which can synthesize epoxy resin have been extensively explored in the past few years. Bio-derived materials also function as a raw material or as a substitute for the non-biodegradable petroleum-derived product.^{154–156} As green technology has received huge investment, extensive research, regarding chemically modified bio-derived epoxy resin from lignin, tannin, clay material, plant-seed oils, eugenol, vanillin, plant waste filler, cellulosic materials *etc.*, has been reported.^{154–160} Moreover, incorporating natural materials, containing natural-phenolic compounds, in epoxy technology offers comparable properties to synthetic materials. However, the lower value of modulus, mechanical strength, and curing is still a significant challenge with natural-phenolic materials. Tannin is one of the naturally occurring phenolic materials, consisting of amorphous and complex-natured compounds.⁹² As mentioned earlier, the extraction of tannins can be possible from natural products, such as tree barks, plant cell walls, and plant-based by-products.¹⁶¹ For the production of adhesives, partial substitution of phenol with tannins can be a potential step in the manufacturing of epoxy-based adhesive.^{65,99,100} Partial substitution is possible, because of the numerous hydroxyl and phenolic groups present in tannin.^{158–160} Previous studies reported that approximately 90% of phenol could be substituted by tannin in the phenolic resin technologies, particularly by condensed tannin.^{162,163} Among different bio-resources, polyphenolic natured

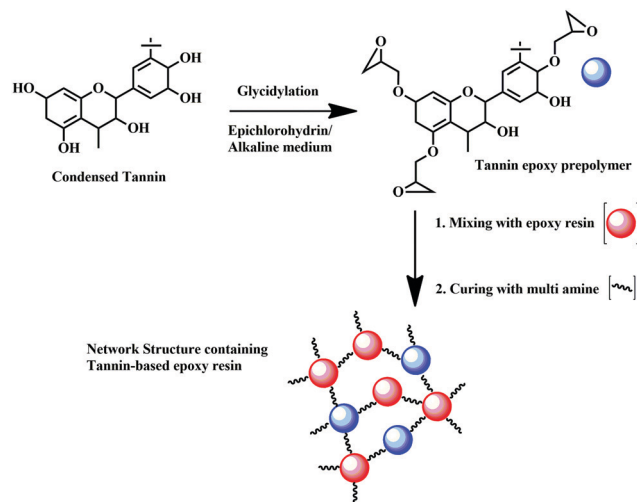


Fig. 12 Preparation of tannin-based epoxy resin by glycidylation reaction of condensed tannin with epichlorohydrin in alkaline medium.

tannins, which are derived from woods, ought to be a multi-functional epoxy hardener.^{149,164} Condensed tannins include recurring flavonoid units; on the other hand, hydrolyzable tannins are saccharides partially or wholly replaced by ellagic or gallic acid. The presence of hydroxyl groups as well as aromatic rings in its structure enables covalent and non-covalent interactions at the cost of the mechanical properties of the epoxy resin. With the tuneful effect these tannin properties bring, one might expect an enhanced flame retardancy and improved mechanical properties of polymeric materials.¹⁶⁵

Towards preparing flame-retardant epoxy resin, the most remarkable renewable hardener is tannic acid (TA), which has applications as an oxygen radical quencher, and charring agent.^{165–167} It reacts with commercial-grade diglycidyl ether of bisphenol-A (DGEBA) to form TA-DGEBA, which acts an effective flame retardant thermoset compound, possessing a limiting oxygen index (LOI) value of 46% more than that of the control sample.¹⁶⁶ Hence, confirming the potential role of TA-based epoxy resins as a flame-retardant polymer. The chemical reaction of TA with epoxy monomer is considered to be the most promising method to synthesize flame-retardant epoxy, which finds application in various fields like aerospace, automobile, construction, *etc.*¹⁶⁶ Eucalyptus tannin can also be considered a promising route for the partial replacement of BPA from commercial-grade epoxy. Bio-derived epoxy resin can also be synthesized by the reaction of condensed tannin with epichlorohydrin, through glycidylation reaction, as shown in Fig. 12.

Tannin also acts as a precursor for bio-derived epoxy resin and possesses the role of a curing accelerator for epoxy resin.¹⁶⁴ The subunits of tannin, namely, catechin, epicatechin, and 2 flavon-3-ol epimers are widely spread across the plant kingdom. In catechin, the molecular structure has two phenolic rings which differ by the hydroxylation pattern: the hydroxyl groups (two OH groups) of the I-ring are in the meta position, whereas in the II-ring they are in the ortho position, as shown in Fig. 2.

Another study reported the preparation of epoxy acrylate resin, using glycidyl ether tannin (GET) and acrylic acid.¹⁶⁸



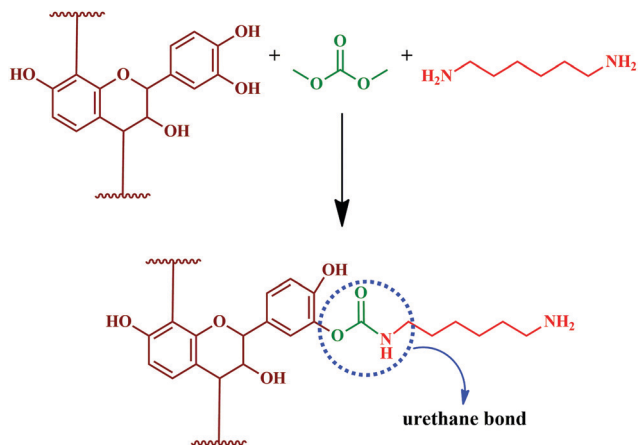


Fig. 14 Preparation of novel bio-derived tannin-based non-isocyanate polyurethane (NIPU) by the chemical reaction between free hydroxyl groups of flavonoid tannin with dimethyl carbonate followed by hexamethylene diamine.

are by π - π stacking, offering it as a potential bio-derived precursor for NIPU.

Likewise, the carbohydrate fraction of the tannin extract also seemed to be carbonated, and their reaction leads to the formation of isocyanate-free urethane linkages with aminated tannin. Thus, it can be inferred that the polyphenolic fraction of the tannin extract and other components also has a significant role in the PU synthesis. Hence, it is possible for the

preparation of bio-derived NIPU for adhesives and surface finishes, which can be obtained through the reaction of carbonated condensed flavonoid tannin. The carbohydrate fraction of the tannin extract can also be carbonated and reacted to generate isocyanate-free urethane linkages with aminated tannins. Carbohydrates in tannin extracts are either monomers or oligomers, resulting from the hydrolysis of hemicellulose during tannin extraction.^{61–64}

These findings showed that the entire tannin extract, including polyphenolic components, can be used to prepare PUs.¹⁹⁴ Hydrolysable chestnut tannin possesses a small amount of hydroxyl group; after reacting with dimethyl carbonate, it reacts with hexamethylene di-amine later. Hence, it can be noted that in PU synthesis, isocyanate is not involved as a reactant; instead, it is carried out using renewable materials, like hydrolysable chestnut tannin. Thébault and colleagues reported the preparation of NIPU using hydrolysable chestnut tannin.¹⁹⁶ Preparation of NIPU involved carbonation of hydrolysable chestnut tannin with dimethyl carbonate followed by reacting with hexamethylenediamine. In another study, Thébault and colleagues prepared NIPU from condensed flavonoid tannin and tested it for their applicability in surface coatings.¹⁹⁷ The study involved evaluation of condensed flavonoid tannin from different sources such as maritime pine, radiate pine barks and quebracho wood. Urethane linkages were engineered by the reaction of condensed flavonoid tannin with dimethyl carbonate and hexamethylene diamine (Fig. 16). Urethane linkages were evidenced from FT-IR analysis

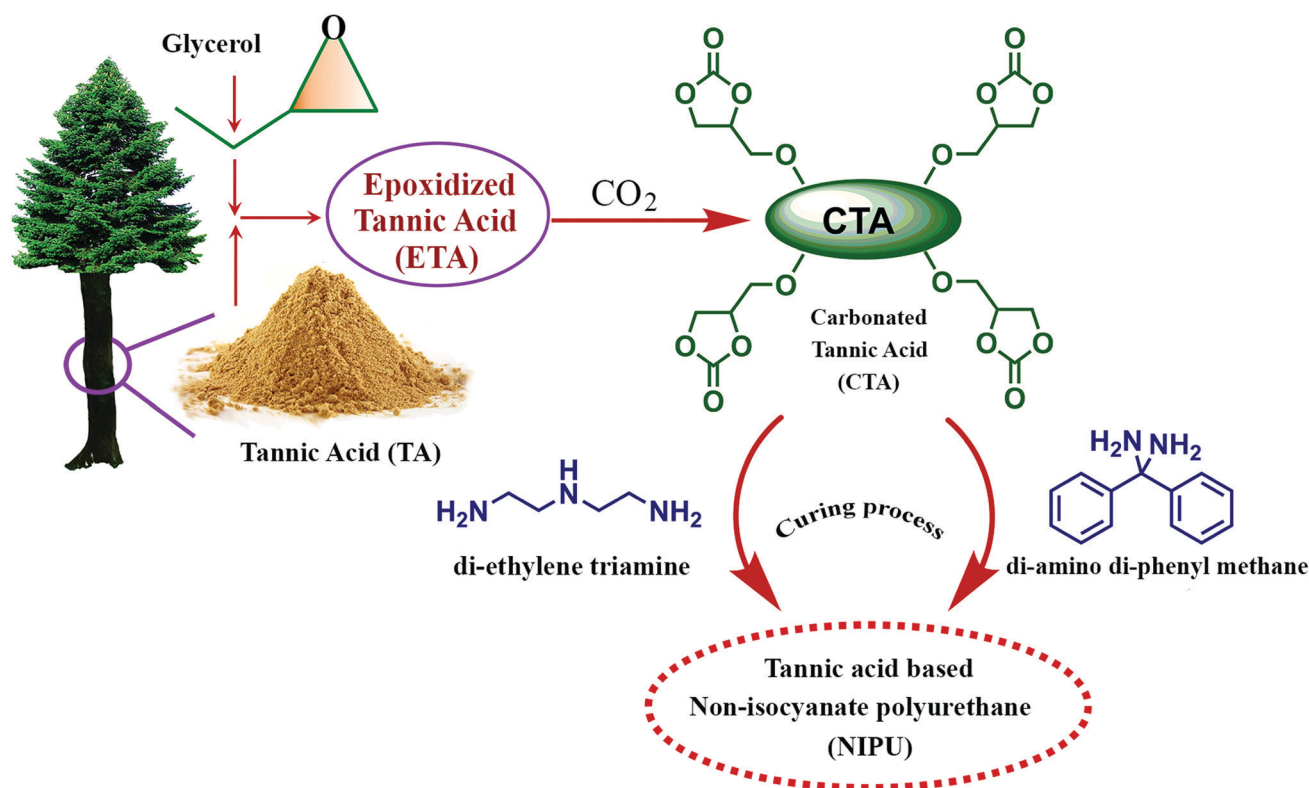


Fig. 15 Schematic illustration of the synthesis of non-isocyanate polyurethane (NIPU) by a three step preparation method from tannic acid (TA).



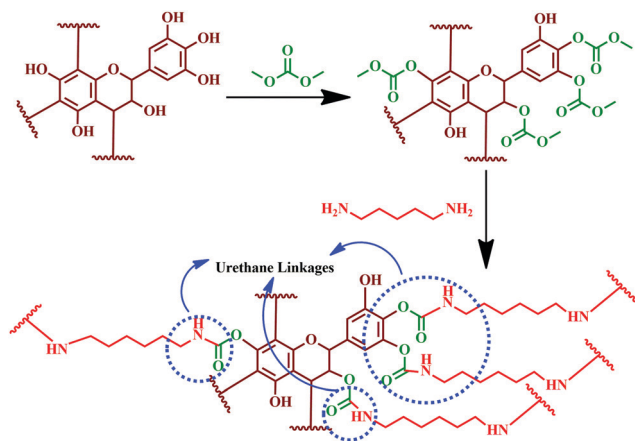


Fig. 16 Reaction mechanism showing the formation of urethane linkages by the chemical reaction between condensed flavonoid tannin, dimethyl carbonate and hexamethylene diamine.

for all the tannin reaction products. The oligomeric distribution of the prepared sample was analysed by the MALDI-ToF technique. GPC analysis identified high molecular species, and showed that varying the condition alters the molecular weight of PU formed. Most of the samples showed difficulty in dissolution for the GPC analysis, which indicated the formation of a crosslinked 3D network structure. Furthermore, the GPC analysis showed a molecular weight of > 3500 Da, when the reaction was at a temperature of $103\text{ }^{\circ}\text{C}$. TGA analysis showed that the prepared PU degrades between a temperature of 180 and $200\text{ }^{\circ}\text{C}$. The sample showed suitability for wood coating applications as it displayed hydrophobic properties and a minimum filming temperature of $170\text{ }^{\circ}\text{C}$.

Characteristic peaks at 1690 , 1265 , and 1537 cm^{-1} in the FT-IR spectra confirmed the reaction and the formation of urethane linkages. Contact angle measurement showed that the coated surface has superior hydrophobic nature compared to the substrate. Thermal degradation of PU was observed between 180 and $200\text{ }^{\circ}\text{C}$ (from the TGA analysis), which unveiled the suitability as a thermally stable wood coating. This study was the first approach to exhibit that tannin can be a better substitute for polyols after reacting with dimethyl carbonate and a diamine.¹⁹⁷

Tannin-based polyethylenimine adhesives

Coupled with the health hazards of petrochemicals and formaldehyde emission, chemically modified bio-derived materials have gained significant interest.^{187–189} Marine adhesive protein (MAP), is one such bio-derived material that is formaldehyde free, and a potential material for adhesives. The main components of the attachment plaques consist of a decapeptide (Ala-Lys-Pro-Ser-(Tyr/DOPA)-Hyp-HypThr-DOPA-Lys).^{190–192,198} Recent studies have reported that DOPA, present on MAPs, has a major role in adhesion properties.^{193,194,196} Soy proteins and poly(*N*-acryloyl dopamine), which contain phenolic substituents, are widely reported as water-resistant wood adhesives.^{197,199} It is

noteworthy to highlight that these compounds also contain phenolic groups, hence it can be implied that adjacent phenolic groups play an important role in adhesion. As tannin is a polyphenolic compound, researchers have explored the possibility of using chemically modified tannin to produce a high performance adhesive. Engineering the tannin through physico-chemical modification is a greener protocol for the development of eco-friendly adhesives.⁵¹

Condensed tannins, also known as polymeric proanthocyanidins, are used extensively in the wood adhesive industry due to their abundance, low cost, and structural advantages. As their structure varies on the basis of the sources, it can be further sub-classified based on the hydroxylation pattern of the repeating flavonoid monomer units.¹⁷⁷ The most abundant form is a procyanidin polymer isolated from Douglas-fir inner bark and purified over Sephadex LH-20.^{200,201} The adhesive prepared from a procyanidin-type tannin, isolated from the inner barks of Douglas-fir inner bark, and polyethylenimine (PEI) showed good adhesion properties with its advantage as a formaldehyde-free system.²⁰² The samples exhibited high shear strengths and possessed excellent water-resistance. As tannin and PEI, represented in Fig. 17, are water-soluble, an aqueous solution of both was mixed to obtain the tannin PEI adhesive.¹⁹²

Preparation of the tannin-PEI adhesive (possible reaction is shown in Fig. 18) involved water as a solvent, making the process free from organic solvents. The work showed a detailed study on the effect of parameters like effect of mixing time, total solid content, tannin to PEI weight ratio, temperature and cure time of the adhesive.²⁰² At a total solid content of 12 – 24% , the adhesive showed good spreadability on wood veneer. From the experiments, the optimum weight ratio of tannin:PEI was found to be $2:1$, for adhesives with high shear strength and water-resistance. At a hot press temperature of $100\text{ }^{\circ}\text{C}$, and for 2 minutes of thermal application, fully cured two-plywood composites were produced. Also, long term storage of the adhesive decreased the bonding ability, with a decline in shear strength of bonded wood specimens.

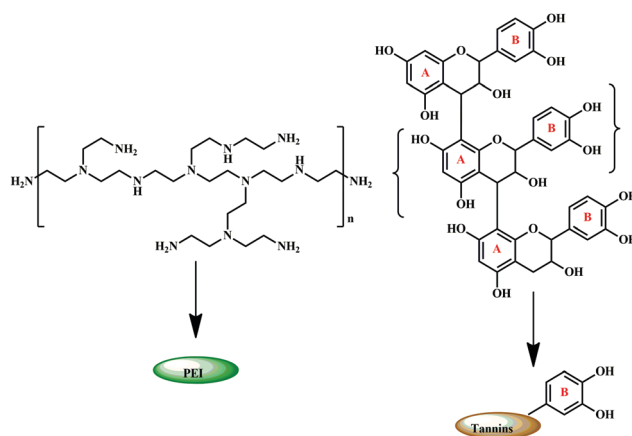


Fig. 17 Structure of polyethylenimine (PEI) and condensed tannin with their respective schematic representation.



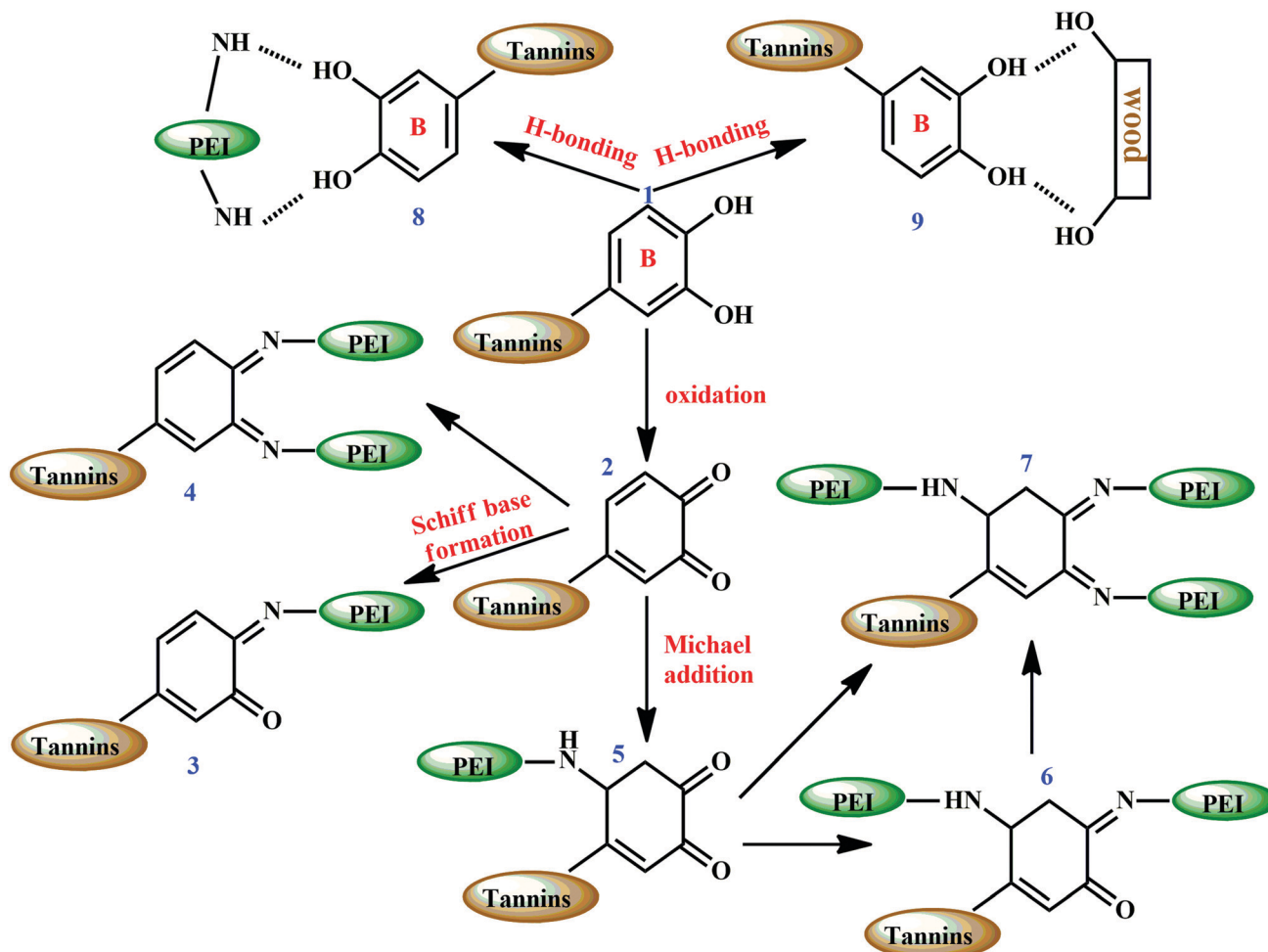


Fig. 18 Schematic illustration of the possible chemical reactions between condensed tannin and polyethylenimine (PEI). Interaction of hydrogen bonds between amine groups of PEI and free hydroxyls of tannin (represented as 8) and hydrogen bonding between the wood specimen and tannin (represented as 9).

Catechol groups (represented as 1 in Fig. 18) present in the B-ring of tannin undergo oxidation at high temperatures (hot press temperatures) and form *ortho*-quinone (represented as 2 in Fig. 18) which further reacts with amino groups in PEI. This produces Schiff bases (represented as 3 and 4 in Fig. 18). *ortho*-Quinone also reacts following a Michael addition mechanism, and forms Schiff bases (represented as 6 and 7 in Fig. 18), with 3D network structures. Moreover, there can be hydrogen bonds between amine groups of PEI and tannin (represented as 8 in Fig. 18), with the free hydroxyl groups of wood specimens and tannin (represented as 9 in Fig. 18). The hydrogen bonding between the wood specimen and adhesive sample contributed to enhancing the adhesive bonds.

Faris and colleagues reported water-resistant adhesives from a mixture of PEI, tannin and lignin.¹¹⁹ The prepared adhesive when bonded to the plywood sample showed enhanced thermal stability of 360 °C and a tensile strength value of 63.04 MPa. The solid content of the adhesive increases upon incorporation of PEI and at 56.92%, the sample showed enhancement in the tensile strength on the plywood specimen. Crosslinks created by the reaction between the amino groups of PEI and catechol

groups present tannin and lignin resulting in an enhancement in the properties.

Tannin-based furfuryl alcohol adhesives

Another potential and green adhesive system prepared using tannin as a main component is the furfuryl alcohol adhesives. Tannin furfuryl resins react with tannin rather than undergoing self-condensation reactions in the presence of an alkaline medium, as shown in Fig. 19. The reaction can be possible in three ways, namely chain condensation reaction, reaction between hydroxyl groups and rearrangement of a furanic cycle.^{203,204} The rearrangements result in crosslinking reaction, opening new avenues to develop wood adhesives, which are free from formaldehyde.

The gel time of furfuryl alcohols with either mimosa tannin extract or pine tannin extract at 100 °C at different proportions and pH was determined and studied extensively. At a particular gel time and thermo-mechanical analysis, the reaction led to



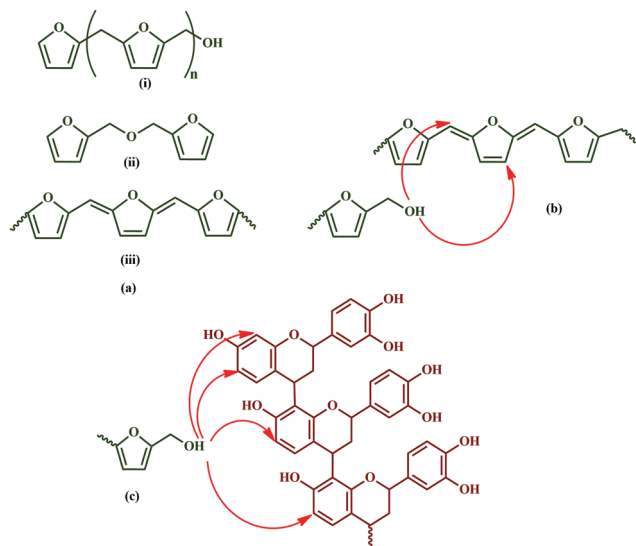


Fig. 19 (a) Self-condensation of furfuryl alcohol: (i) chain condensation reaction, (ii) reaction between hydroxyl groups and (iii) rearrangement of furanic cycle; (b) crosslinking sites for furfuryl alcohol; (c) possible reaction sites between flavonoid units and polyfurfuryl alcohol's hydroxyl group.

the co-condensation of tannin extract with furfuryl alcohol, thus leading to a bonded joint.²⁰³ The acidic conditions are avoided since the furfuryl alcohols undergo self-condensation reactions.^{203,204} Therefore, since crosslinking occurs between tannin and furfuryl alcohol, gelling and hardening occurs under alkaline conditions. Studies showed that the best results were demonstrated with 50% furfuryl alcohol and mimosa-tannin extract at pH 10. The gelation time was reduced gradually with decrease in pH and an increase in furfuryl alcohol percentage. Gelling ceases when the pH is in the range of 3–8.

Pine tannin extract shows better gel times, and from thermo-mechanical analysis (TMA) the hardened adhesive showed enhanced strength. Moreover, the eco-friendly and non-toxic tannin adhesive showed satisfactory values for bonding wood particleboards based on European standards.²⁰³

Investigation by Shirmohammadli and colleagues reported that the moisture resistance of tannin adhesives can be improved by incorporating PEI and furfuryl alcohol.²⁰⁵ Condensation reactions between amine groups in PEI and hydroxyl groups of furfuryl alcohol were evident from the FT-IR analysis. The thermal stability of the adhesives increased on addition of PEI and furfuryl alcohol. Moreover, a decrease in heat absorption peak was recorded on introducing PEI and furfuryl alcohol into the adhesive formulation. The adhesive met the moisture requirements as per the British standard 1204-2 (BS 1204-2), when the formulation had a mixing proportion of tannin:furfuryl alcohol of 1:0.75, containing 20% PEI.

Tannin-based glyoxal adhesives

Glyoxal, a non-volatile reactive aldehyde, was considered a befitting candidate to be used as an exterior grade tannin-based adhesive. Investigations have been performed on tannin-

glyoxal adhesives, and the properties evaluated based on the proportion of each constituent.^{204,206} It was observed that the gel time of the samples has direct relation with the pH. At a pH from 8 to 9.5, the tannin-glyoxal showed a similar gel time to a tannin-formaldehyde system at a range of pH 6 to 7. The study demonstrated that, analogous to the tannin-formaldehyde system, a bio-derived formulation of tannin with glyoxal at optimum concentration can serve the purpose.^{204,206}

Conclusion

As a circular economy and green protocols have been fuelled by developing sustainable materials for various applications, the requirement of potential raw materials has also been given focus. This holds true in the case of adhesives, where the focus is on unveiling sustainable material-based adhesives. Moreover, identification of formaldehyde as a carcinogen has further reduced the demand for formaldehyde-based adhesives, which catalysed a rapid increase in the growth and research of bio-derived wood adhesives. Among various renewable materials, tannin has been a material of interest in the wood adhesive sector; renewability, sustainability, and lower cost are the advantages that tannin provide compared to petrochemical-based materials. It can be underlined from the various works that tannin, due to its multi-phenolic structure, has the possibility to function as an alternative for commercial petrochemical-based resins for wood bonding. As tannin adhesives developed by the reaction of tannin and formaldehyde show brittleness, various strategies have been postulated. Enhancement in adhesion can be achieved by adding phenol and resorcinol molecules. Such additives generate bond formation between tannin molecules through methylene linkages, and reduce the inherent high viscosity of tannin. Thus, the multi-phenolic structure of tannin with certain additives can be used to improve the physical as well as mechanical properties.

Despite the excellent adhesion properties that formaldehyde offers, the corresponding volatile organic compounds show some malignant issues. An adequate investigation has been carried out on some of the recent adhesives, initiating from propionaldehyde, acetaldehyde, furfural, or *n*-butyraldehyde. Combining these aldehydes with mimosa tannin to produce an adhesive for wood panel applications showed retarded adhesion. In contrast, partial substitution of formaldehyde by *n*-butyraldehyde or furfural gave satisfactory adhesion results; also, the non-polarity of the carbon-chain of *n*-butyraldehyde brings hydrophobic nature resulting in superior water-resistance. In addition to the above formulation with urea, compounds such as mono-methylol or di-methylol play a significant role, to enhance the adhesion properties. Thus, the multi-phenolic structure of tannin with the opportunity for further modification and solubility in water are the key reasons for the growing interest in tannins for the wood adhesive sector.

This review paper highlighted the developments done on tannin-based adhesives for wood bonding. Different sources of



tannin and its structures have been well studied. This structural analysis helps to better understand potential sites for modification. Chemical modifications have played a vital role in expanding the applications of tannin. Chemical modifications such as acylation, where chemical bonds are formed between tannin molecules using adipoyl dichloride inter-chains, bring better flexibility. Apart from this, blending with other polymers, preparing copolymers with tannin, crosslinking, and using tannin as a precursor for other polymers are the most reported modifications.

Similarly, the usage of tannin as a precursor for epoxy resin and PU has attracted interest among researchers for further innovation and development. Condensed tannin has tremendous potential to produce a harmless industrial substitute for rigid epoxy resin obtained from woods. To name a few, its reaction with di-epoxy or pine tannin with di- or polyglycidyl ether under alkaline conditions results in epoxy resin. Hydrolysable tannin works as a crosslinking agent for epoxy resin. The high crosslinking density of tannin-based epoxy resin offers excellent mechanical and thermal properties. Other similar resins also have superb resistance properties despite being quickly broken-down for recycling.

The synthesis of bio-derived PU is fascinating and promising, due to the utilization of hydrolysable tannin, which mitigates the usage of iso-cyanates. The preparation of more than 70% bio-derived NIPU for adhesives and surface finishes obtained by the reaction of carbonated condensed flavonoid tannin extracts by reaction with aminated tannin extracts of the same nature seems to be possible. The formation of urethane linkages is evidenced from various analytical methods, and has proved their industrial viability to replace the conventional isocyanate-based systems. Moreover, recent developments in tannin-PEI, tannin-blended polymers, tannin-based furfuryl alcohol adhesives, tannin-glyoxal systems *etc.*, have emerged as a potential substituent for conventional adhesives (formaldehyde, isocyanate *etc.*). Researchers are exploring the structural and chemical modifications on the polyphenolic structure of tannin, which can update the tannin as a precursor for various bio-derived materials.

In a nutshell, the recent developments highlight tannin's immense potential for developing novel and high-performance materials in accordance with the new concept of sustainable development. In order to establish bio-derived wood adhesives, tannin, a green aromatic building block, revealed a new path and a new area for research. Hence, calculating the developments in tannin, it can be unambiguously stated that with such transformations, tannin can be a promising and exciting sustainable resource for a greener world.

Future perspectives

As tannin shows promising properties compared to petrochemicals, there are comprehensive reviews on the application of tannin in the wood adhesive sector.^{163,199} However, the present work includes a complete database with highlights from an industrial viewpoint. Although there are many limitations associated with tannin usage, promising developments have

been reported in the last few decades. Efficient and green extraction methods need to be emphasized to meet industrial mass production of tannin-based materials. Development of *in situ* techniques for the structural analysis of tannin should be a main focus, as the chemical composition of tannin varies based on its sources. Accelerated performance tests and developing possible approaches for the effective utilization of tannin and non-tannin constituents should be given equal importance. Unveiling the limitations of tannin can probably shed light on gaining interest for tannin as a precursor for replacing petrochemical-based resins.

To start with, the quantity of tannin naturally available, compared with the capacity of synthetic adhesives used in the wood industry, has resulted in a great deal of research on expanding tannin. Several companies have started building new extraction plants, as they realized the capability of the substance for tannin extraction, where this material can be extracted in millions of tons each globally. However, this movement is still at its infancy, comparatively small and underway.

Moreover, other approaches such as copolymerizing with sustainable and renewable materials including tannin and lignin, soy flour or soy protein and tannin, synthesis of furfuryl alcohol and tannin adhesive formulation, *etc.*, can be environmentally benign processes.^{207,208} Free hydroxyl groups of wattle tannin can be modified chemically by blending with PVA and crosslinking with boric acid.¹²⁰ Selection of similar crosslinkers and blending with a compatible commercial binder (PVA) can partially reduce the dependency of petrochemical derived binders. Recent inclusion of a circular economy and green protocol limits the usage of toxic substances,¹⁵¹ which has made researchers and industries working on wood adhesives promote bio-derived adhesives. As formaldehyde emission has an adverse impact on human health and the environment, approaches to mitigate emission have been given primary priority. Based on this search, several attempts have been proposed, of which major works on tannin are as follows:

1. Eliminating the toxic formaldehyde and replacing it with other aldehydes, which are relatively non-toxic and non-volatile,^{119,206} such as vanillin, glutaraldehyde or glyoxal. In addition, aldehydes prepared by reacting sodium periodate with carbohydrates/sucrose/glucose.

2. Utilizing hardeners which are non-aldehyde including tris-hydroxymethyl nitromethane,²⁰³ tris-hydroxymethyl amino-methane or any compounds which can act as a copolymer and hardener, such as furfuryl alcohol-based copolymer.^{107,118} Moreover, exploring the uniqueness of the polyphenolic structure of tannin and tailoring it through chemical modifications such as acylation, esterification, methylation and etherification, could further engineer tannin for its suitability as a precursor for bio-derived materials.

3. Using hexamine as a hardener leads to the formation of $-\text{CH}_2-\text{NH}-\text{CH}_2-$ a bridge between tannin units. However, the secondary amine is apt to mop-up any release of formaldehyde at the time of release itself or any other release of formaldehyde in order to develop a true no-formaldehyde emission panel.^{123,208-211}



4. Tannin can be cured by the process of auto-condensation (without the addition of hardener).^{127,131,210–212} This approach utilizes the wood substrate itself acting as a responsible candidate for proceeding auto-condensation. In the case of faster-reacting tannin, like procyanidin tannins, or pine bark tannin, as well as slower-reacting tannin, auto-condensation is carried out by adding silicate or silica or other promoters,^{127,131,210–213} allowing the formulation of wood particleboard of indoor quality.

5. Approaches to prepare tannin blended adhesive systems, with PEI, furfuryl alcohol, glyoxal as an alternative to formaldehyde, GDE as crosslinker shows comparable properties, meeting standards including BS 1204-2, Chinese National Standard (GB/T 17657–2013) *etc.* Hence further investigation of potential green crosslinkers, polymers which can be blended with tannin can open up chemically modified value-added products from tannin. Although tannin–PEI adhesives have been reported, the applicability of PEI as a crosslinker for tannin has not been explored. Studies using PEI as a crosslinker for natural polyphenolic compounds have been reported,²¹⁴ which can be established for tannin as well. Hence, investigators can explore similar works for tannin-based systems as well.

Although tannin has been commercialized for leather manufacturing industries, in the recent past, tannin has emerged as a promising natural phenolic polymer and has significant applications in various sectors, including adhesives, coatings, bio-foams, automotive and building sectors *etc.*^{215,216} Tannin as a raw material, however, for adhesive applications still poses certain issues, like short pot life, high viscosity, reactivity, and poor weather resistance. Comprehensive investigation and introduction of newer concepts like copolymerization, chemical modifications *etc.*, can catalyse the development of tannin as a sustainable raw material for adhesive applications. Furthermore, investigation on tannin resin adhesives should be taken further to other advanced wooden composites instead of limiting it to only wood panels. Besides, the industrial development of tannin-based adhesives in the domain of wood fabrication is obligatory.

Author contributions

Pritam V. Dhawale and S. K. Vineeth contributed equally.

Conflicts of interest

There are no conflicts of interest to declare from any of the contributors or institutes.

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