

Review

# Bio-Based Polyurethane Resins Derived from Tannin: Source, Synthesis, Characterisation, and Application

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**Citation:** Aristri, M.A.; Lubis, M.A.R.; Iswanto, A.H.; Fatriasari, W.; Sari, R.K.; Antov, P.; Gajtanska, M.; Papadopoulos, A.N.; Pizzi, A. Bio-Based Polyurethane Resins Derived from Tannin: Source, Synthesis, Characterisation, and Application. *Forests* **2021**, *12*, 1516. <https://doi.org/10.3390/f12111516>

Academic Editor: Angela Lo Monaco

Received: 4 October 2021

Accepted: 29 October 2021

Published: 3 November 2021

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**Abstract:** Tannins are soluble, astringent secondary phenolic metabolites generally obtained from renewable natural resources, and can be found in many plant parts, such as fruits, stems, leaves, seeds, roots, buds, and tree barks, where they have a protective function against bacterial, fungal, and insect attacks. In general, tannins can be extracted using hot water or organic solvents from the bark, leaves, and stems of plants. Industrially, tannins are applied to produce adhesives, wood coatings, and other applications in the wood and polymer industries. In addition, tannins can also be used as a renewable and environmentally friendly material to manufacture bio-based polyurethanes (bio-PU) to reduce or eliminate the toxicity of isocyanates used in their manufacture. Tannin-based bio-PU can improve the mechanical and thermal properties of polymers used in the automotive, wood, and construction industries. The various uses of tannins need to be put into perspective with regards to possible further advances and future potential for value-added applications. Tannins are employed in a wide range of industrial applications, including the production of leather and wood adhesives, accounting for almost 90% of the global commercial tannin output. The shortage of natural resources, as well as the growing environmental concerns related to the reduction of harmful emissions of formaldehyde or isocyanates used in the production of polyurethanes, have driven the industrial and academic interest towards the development of tannin-based bio-PU as sustainable alternative materials with satisfactory characteristics. The aim of the present review is to comprehensively summarize the current state of research in the field of development, characterization, and application of tannin-derived, bio-based polyurethane resins. The successful synthesis process of the tannin-based bio-PU was characterized by Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), MALDI-TOF mass spectrometry, and gel permeation chromatography (GPC) analyses.

**Keywords:** bio-based polyurethane; extraction; synthesis; tannin; tannin source

## 1. Introduction

Tannins are naturally occurring phenolic compounds consisting of poly-hydroxy polyphenols that are found in various plant parts, including fruits, wood, leaves, and bark. After cellulose, hemicellulose, and lignin, tannins are the fourth-largest substance of vegetable vascular tissue. Thus, tannins represent an important group of secondary

plant metabolic products. At present, over 8000 different tannin types have been isolated and defined, and the highest concentration of tannin compounds was determined in tree bark [1]. Tannins can account for one-fifth of a plant's dry weight, though the amount might vary based on environmental conditions [2]. Plants that contain high tannin concentrations have been traditionally used in the leather production industry in the tanning of animal hides because they are capable of binding and settling proteins. Due to their antimicrobial, antioxidant, and anti-inflammatory properties, many polymer industries have widely used tannins in their production [3]. Tannins have more reactive properties than phenols, and tannin extraction from tree bark has been developed since the 1970s for various industrial applications, particularly wood adhesives and pharmaceuticals [4,5]. From a chemical point of view, tannin is an aggregation of complex organic compounds, rather than a simple substance [6]. Tannins are therefore considered as polyphenols with high molecular weights ranging from 300 Da to 3000 Da [7]. In the chemical structure of tannins, there are also multiple functional groups, such as hydroxyls, which enable the formation of bonds with other compounds, such as proteins or carbohydrates [8]. According to their structural characteristics, tannins can be classified into three types of hydrolysable tannins; i.e., gallotannins, ellagitannins, and complex tannins (sugars and ellagic derivatives); and condensed (nonhydrolysable) tannins. Tannins are a class of complex structural polyphenols, including tannins that are hydrolyzed, proanthocyanidins (also called condensed tannins or polyflavonoid tannins), and phlorotannins [9]. They are present in a limited number of botanical sources and plant components, depending on their chemical structure [10].

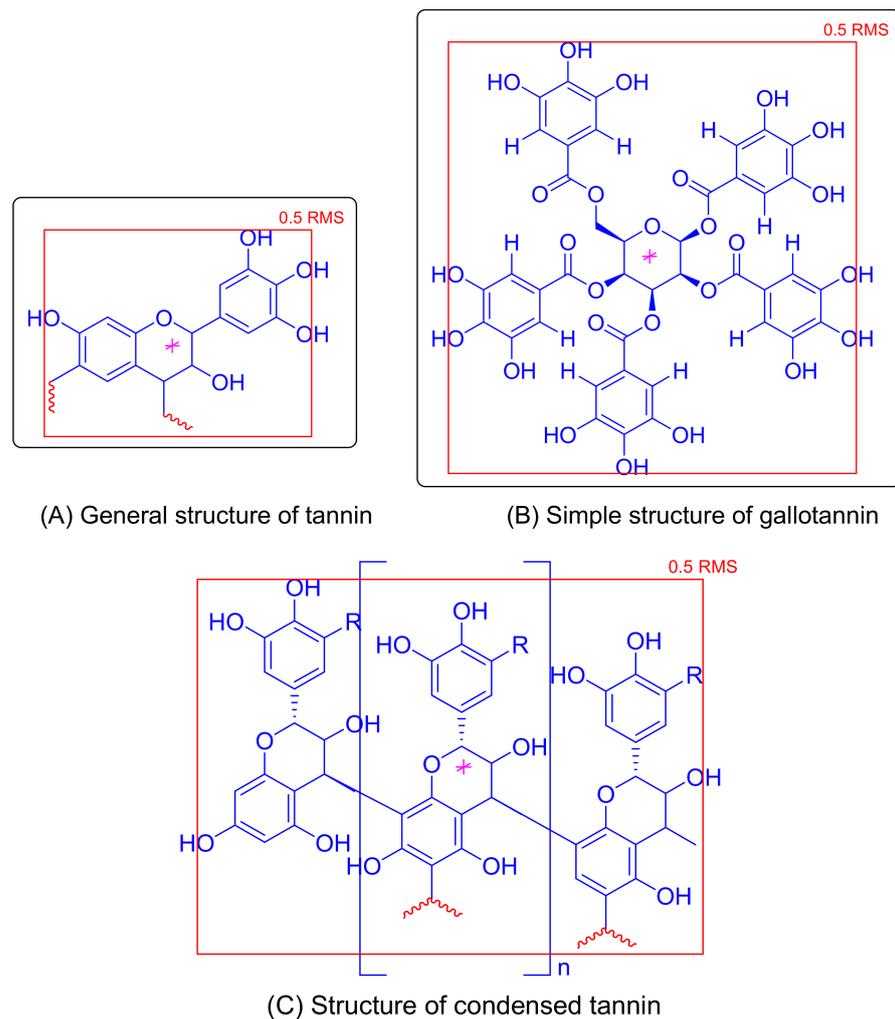
Acid, alkali, warm water, and a few enzymes easily react with hydrolysable tannins. The main chemical scaffolds in hydrolysable tannins are connected by hydrolysable ester bonds, whereas the monomers in condensed tannins are linked together by C-O-C or C-C bonds. Condensed tannins are characterised by greater resistance to microbial degradation compared to hydrolysable tannins, and exhibit stronger therapeutic properties. Complex tannins are generated when proanthocyanidins and hydrolysable tannins create C-C bond conjugations [11]. The presence of multiple esters of gallic acid and glucose is used to distinguish the types of hydrolysable tannins that are widely found in nature. Recently, more than 500 glucogalloyl derivatives were identified [12]. Tannins typically have 5–7 aromatic rings and 1000 relative molecular units per 12–16 phenolic substituents. Hydrolysable tannins are also composed of phenolic acid esters, such as those usually found in the glucose of ellagitannins, also a polyol. There are two main types of hydrolysis tannins; i.e., gallotannins and ellagitannins, which are derived from the hydrolysis of gallic acid or ellagic acid, respectively [10]. By further esterifying or crosslinking the galloyl groups via oxidation, a more complex hydrolysable tannin is generated [13]. Gallotannins, polygalloil esters of glucose found in red oak, bordering cups, staghorn sumac, oak pedunculates, and other plants, are the most basic hydrolysable tannins. Ellagitannins are formed by intramolecular coupling and result in C-C and C-O-C connections between galloyl glucogalloyl residues. Ellagitannins are common biological tannins found in fruits such as *Fructus chebulae*, *Punica granatum*, and *Phyllanthus emblica* [14].

Tahir et al. (2019) reported that gallic acid, ellagic acid, and other similar acids are hydrolysed by heating into dilute acid [6]. In addition, gallotannin (mainly glucose and gallic acid) and ellagitannin (consisting primarily of digallic and ellagic acid penta-galloyl-glucose) are divided into tannins. Gallotannins consist of a fundamental element of glucose, or shikimic acid or quinic acid less generally, that is esterified by up to five gallic acids. UDP-glucose and gallic acid esterification forms 1-galloyl- $\beta$ -d-glucose in plants, and is called glucogallin. Glucogallin then functions in biosynthesis as both an acyl donor and an acceptor. Through the use of depsidate bonds and up to 13 groups, galloyl groups may be externalized further, leading to the trideca-galloylglucose previously identified in Chinese sumac (*Rhus chinensis*) tannin extracts. 4,5-di-galloyl-quinic, 3,4,5-tri-galloyl-quinic, 5-mono-galloyl-quinic, and 1,3,4,5-tetra-galloyl-quinic in tara (*Caesalpinia spinosa*) extracts were previously identified as the primary structures in tara extracts, and can be

esterified via linkages by additional gallic acids. The shikimic galloy is rare, although the shikimic 3-O-galloyl was previously detected in a ciculatory plant of erodium [15]. The tannin classification consists of several combinations, with the n-galloyl-glucose oligomers being the most important, and its derivatives of rearrangement, such as vescalline and vescagalline. Pentagalloyl glucose and polyester produced from gallic acid and hexahydroxydiphenic acid are core repetition units of the hydrolyzed tannin structure. Tannins that can be hydrolysed are usually found in wood or stems [10]. Examples of hydrolysed tannins are chestnuts, myrobolans (the genera *Terminalia* and *Phyllanthus*), and divided tannins (*Caesalpinia coraria*) [6].

Tannins are ubiquitous and can be found in food, including grape seed, apples, berries, red wines, chocolate, cacao, and others, and are also known as proanthocyanidins. The condensed tannins in plants are more abundant than hydrolysable ones, and compared to the hydrolysable tannin, have a more complicated structure. Proanthocyanidins are polymers consisting of monomeric units of C-4 → C-8 bonds, connected by flavan-3-ol connections, and in rare cases C-4 → C-6 connections [8]. All feature asymmetric cores, including gallo catechin, (-)-epigallocatechin, (+)-catechin, and (-)-epicatechin. The ability of condensed tannins to react with proteins and metal ions is primarily due to the presence of numerous hydroxyl groups in the condensed tannin structure. Catechin and epicatechin units include proanthocyanidins, which are abundant in vegetables (procyanidins). Less frequently found tannins that have been identified in grains such as barley, wide beans, red kidney beans, red currant, pinto beans, black tea, and cinnamon are proparganidin or gallo catechin basic units, which include (epi) afzelechines or (epi) pinto beans [8,14]. The phloroglucinol oligomers generated in brown algae with tannin operations are tannin-like, such as the phlorotannins (Figure 1). At first, isolation of phlorotannin required free phenolic hydroxyl groups to be methylated or acetylated into the molecules. Moreover, phlorofucofuroeckol-B, an identified antiallergic product from *Eisenia arborea*, was employed for a long time in Japanese gynecopathic herbal medicine. It has been mentioned that the pharmacological properties of derivative phlorotannins have been masked by acetylation and methylation [16]. Both hydrolysable and condensed tannins include reactive OH groups, which constitute protein complexes such as enzymes and polymers; e.g., cellulose and hemicelluloses [17].

Several researchers have investigated the interactions of tannins and proteins while taking into account their size, stereochemistry, type of protein, and the optimal interaction medium (ionic strength and pH) [18,19]. In order to form tannin–protein complexes, tannins should have a high molecular weight and mobile structures, whilst proteins should possess flexible structures, be rich in proline, and have a large molecular size. These interactions may occur via covalent or ionic connections, the interaction between hydrophobic or bonding of hydrogen. Bound tannins and repetitive amino acid sequences influence the stability of the tannin–protein complex [13]. These are dynamic as well as long-term interactions. In addition, the binding flexibility of both tannins and proteins is a crucial addition to enhancing interaction. Protein binding effectiveness is increased, apart from the phenolic groups and aromatic rings that enable tannins to function as a multidentate ligand on a protein surface, such as polyphenols [17]. The condensed tannin (polyflavonoids) are polymers consisting of 2 to 50 flavonoid units that are not susceptible to hydrolysis. They are correlated with flavan 3-ols, flavan 3,4-diols (precursors), other flavonoids, carbohydrates, amino acids, and imino acids [1,20]. Condensed tannins (proanthocyanidins) are polymerized for water-insoluble phlobaphene. Currently, more than 90% of the global industrial extraction of tannins, amounting to more than 220,000 tons annually, is composed of polyflavonoid tannins [4,19]. They are present in the wood and bark of a variety of tree species in high concentrations, and the most often investigated species are: *Acacia mearnsii* (wattle or mimosa bark extract), *Schinopsis*, hemlock bark extract, *Rhus* (sumac extract), *Pinus radiata*, pine bark extract, and the *Carya* genus [21].



**Figure 1.** Structures of tannins [16]: (A) general structure of tannin; (B) simple structure of gallotannin; (C) structure of condensed tannin.

In the leather industry, tannins have been employed for a long time to disguise processes and leather colours [22]. However, the phenolic nature of tannins can be applied in different applications, such as insulating foams, the mineral and wine industry, veterinary medicine, petroleum, and the gas industry [23], as well as in sewage- and corrosion-resistant metals [24,25]. Tannins also are used in the wood industry in various applications, such as in biocides, fungicides, and development of tannin-based wood adhesives [26–29]. They can also quickly synthesize proteins and other polymers for application in medical sciences, such as pectin [30,31]. Due to all these application areas, tannins are significant “green” biochemicals that have attracted the interest of many researchers [30,32–34]. Pine and Norway spruce (*Picea abies*) bark tannins have been used to produce bio-based foams and glucose-based nonisocyanate polyurethane (NIPU) foams [19,35–38]. In another study, condensed tannins were extracted from radiata pine (*Pinus radiata*) barks to produce polyurethane foams. These bio-based foams exhibited improved thermal stability and strength, and demonstrated their effectiveness in the construction process [39]. In addition, tannins may be utilized as a mud viscosity modification to increase the production and quality of residential and architectural bricks. However, further steps aimed at thoroughly studying the tannin properties for their efficient utilization in high-performance applications should be implemented [40]. Condensed tannins are employed in a variety of industrial applications, including leathers and wood adhesives, accounting for almost 90% of global commercial tannin output [41]. Tannin reactivity is measured by the phenolic

hydroxyl groups [42]. The number of hydroxy groups (OH value) and tannin molecular weights vary depending on the source and method of extraction from tree barks, which affect tannin solubility and viscosity [43].

Solid and liquefied condensed tannins were utilized in polyurethane foam as a sustainable feedstock [37]. In addition, the functionality of tannins and their UV stability [44], antimicrobial activity [15], and mechanical and thermal properties [45] were improved. However, tannins' insolubility in appropriate solvents and their high viscosity are the key barriers to be addressed when used in polyurethane systems. Attempts to improve tannin solubility by liquefaction of phenolic hydroxy groups with oxiranes or acylating agents and to reduce viscosity were also reported [46,47]. The phenolic groups are functionalized into aliphatic alcohols, whereas tannins containing epoxides are chemically modified. We mentioned the production of hydroxy-alkylated *Pinus radiata* bark tannin as a path to sustainable polyurethane polyols. The previous study showed that butylene oxide was used in hydroxyl alkylation to produce polyols with appropriate viscosities to make polyurethane foams. In addition, aromatic rings in a polymer chain were created to boost thermal stability and improve the mechanical properties of polymers [48,49]. As a result, polyurethane foams with improved thermal and mechanical stability are being pursued in industrial applications, especially in the construction and building industries [50]. This aim of this review was to comprehensively summarize the current state of research in the field of development, characterization, and application of tannin-derived, bio-based polyurethane resins.

## 2. Sources of Tannin

Tannins can be sourced from a wide variety of tree species and bushes. Some of the most important commercially extracted tannins include black wattle (*Acacia mearnsii*) bark extracts, oak (*Quercus* spp.) bark extracts, sweet chestnut (*Castanea sativa*) wood, and quebracho (*Schinopsis balansae*) wood extracts. Other well-known sources of commercial tannins are gambir (*Uncaria gambir*), *Acacia mangium*, sumac (*Rhus coriaria*), tara (*Caesalpinia spinosa*), *Caesalpinia coriaria*, the wood of mangroves, and a wide variety of pine and fir barks; e.g., *Pinus radiata* and *Pinus nigra* [51].

To produce tannin-based adhesives for plywood adhesives, Paridah et al. extracted tannins from mangrove and mangium barks [6]. Work remains to be done on *Eucalyptus* spp., but the first conclusions revealed that it produces far less than mimosa, mangium, oak, and mangrove [6]. Tannins can be produced at temperatures and conditions slightly different from those employed on a commercial level from tree barks and wood [52]. The material from the ground plant is poured into a range of enclosed or covered vats (autoclaves) with water at a temperature below 100 °C. Using an opposite strategy, the extraction solution is gradually expanded as it passes between vats. Lower temperatures are preferred (between 70 °C and 90 °C) because the extract yield increases, but no tannins yield as the temperature increases. Instead, other elements, particularly carbohydrates, are produced to a greater extent. Tannins are generally composed of a combination of mono- and polyflavanoids and considerable quantities of nonphenolic material such as simple sugars and polymeric carbohydrates [6].

Natural sources of tannins primarily include the following: *Cola vera*, *Camellia sinensis*, *Coffea* spp., *Paulliniacupana*, and *Theobroma cacao*. Tannins are also present in a variety of cereals, fruits, legumes, forage, vegetables, herbs, spices, and condiments [53]. Tannins are widely spread throughout the Plantae kingdom, primarily found in trees and other relatively high plants, shrubs, and legumes, while the smaller plants, including mosses, fungi, and algae, contain tannin, but only in trace quantities [54]. Tannins have been discovered in plants that have adapted to hot climates and have larger leaves, including *Sorghum bicolor*, *Lespedeza cuneata*, and others. Numerous tannins have been detected in a few sections of some plant species; e.g., in white clover (*Trifolium repens*) and seed coats of other plants (Alfalfa or *Medicago sativa*) [55]. Tannins can also be found in a variety of plant parts, including leaves, roots, stems, fruits, peels, seeds, shells, and bark (Table 1).

**Table 1.** The presence of tannins in various elements of plants and their vital functions [46,48,49].

No.	Plant Elements	Specific Position	Utility
1.	Woody parts	Secondary xylem and phloem	Stimulates and controls tissues growth.
2.	Branch	Field of active matured	Has significant impact on the growth and regulation of such issues.
3.	Heartwood	Conifers heartwood	Has antimicrobial activity and thus naturally increases wood durability.
4.	Germ	Slick between aleurone and external integument	Aids in maintaining plant dormancy. Bactericidal and allopathic properties are also available.
5.	Bud	External elements of bud	Provides freezing protection.
6.	Leaves	Epidermis	Protects against predators by reducing palatability.
7.	Rows	Hypodermis	Blocks the colonial structure of pathogens. Tannin and other polyphenols affect plants' growth and development.

Sorghum, a food source in Asia and Africa, is high in tannins. While cereals generally have fewer tannins than millets and barley, millets, barley, and legumes such as chickpea, fava bean, pinto bean, common bean, cow pea, and kidney bean are all common tannin-containing foods [56,57]. Curry leaves (*Murraya koenigii*), spica *prunellae* (*Prunella vulgaris* L.), hairy agrimony (*Agrimonia pilosa*), ma-huang (*Ephedra sinica*), Chinese rhubarb (*Rheum palmatum*), flowering plants (*Lespedeza*), sainfoin (*Onobrychis*), clover (*Trifolium*), lotus (*Nelumbo nucifera*), crown vetch (*Securigera varia*), and others contain high levels of tannins [58]. Tannins are frequently employed as flavouring ingredients in many meals, in condiments, and in spices such as coriander, tamarind, turmeric, and chilies. Tannins are found in bark, seeds, roots, leaves, and grains of numerous plant species, as well as in vegetables and fruits [59–63]. The several sources of tannins and their concentrations are described in detail in Table 2. The use of naphthalene, cresols, and other superior hydrocarbons as starting materials could be unnaturally generated in manufactured tannin sources. Plant tannins such as digallic acid, ellagic acid, metallic acid, flavellagic acid, luteic acid, and others are unnaturally generated; in the case of a wide range of industrial uses, synthetic tannins such as Neradol D, Neradol N, Ordoval G, and tannic acids (found in galls) are utilized mostly in the food and leather industries. In methyl alcohols and ethyl alcohols, digallic acid is soluble, but is only partially soluble in hot or cold water. Gallic acid is obtained by hydrolysis, and ellagic acid and luteic acid by oxidation. Ellagic acid is highly soluble in caustic potash, but is only mildly soluble in ether, water, and alcohol. Neradol D is water-soluble, and is employed along with natural tannins in the leather sector due to its low cost, so it is commercially favourable. Higher formaldehyde hydrocarbon condensation is a byproduct of Ordoval G. With 40 kg Ordoval G equal to 100 kg of vegetable tannins, it is considerably better than natural tannins [64].

**Table 2.** Different tannin sources and concentrations.

No.	Types	Name of Plant	Tannin (%)	References
1.	Fruits	<i>Quercus infectoria</i>	10.62	[57,65,66]
		<i>Acacia arabica</i>	7.27	
		<i>Emblca officianalis</i>	4.15	
		Ripened banana	0.025–0.48	
		<i>Areca catechu</i>	1.52	
		<i>Vitis vinifera</i>	0.23	
		<i>Phoenix sylvestris</i>	0.23	
		<i>Vitis vinifera</i>	0.11	
		<i>Amomum xanthiodes</i>	0.14	
		<i>Rojo Brillante</i>	9–27	
		<i>Kaki Tipo</i>	17–32	
		<i>Ikanekpo variety</i>	4.48	
<i>Prosopis cineraria</i>	0.14			

Table 2. Cont.

No.	Types	Name of Plant	Tannin (%)	References
2.	Leafy vegetables	Whole	2.71	[67–71]
		Dehulled	3.91	
		<i>Moringa oleifera</i>	0.08	
		<i>Chenopodium album</i>	0.116	
		<i>Centella asiatica</i>	0.123	
		<i>Amaranthus gangeticus</i> L.	0.171	
		<i>Amaranthus tricolor</i>	0.305	
		<i>Trigonella foenum graecum</i>	0.163	
		<i>Trianthema portulacastrum</i>	0.061	
		<i>Celosia argentea</i>	0.113	
		<i>Polygala eriopter</i>	0.098	
		<i>Boerhaavia diffusa</i>	0.094	
		<i>Coleus aromaticus</i>	0.015	
		<i>Digera arvensis</i>	0.079	
		<i>Cocculus hirsutus</i>	0.205	
		<i>Commelina benghalensis</i>	0.105	
		<i>Gynandropsis pentaphylla</i>	0.136	
		<i>Cucurbita maxima</i>	0.157	
		<i>Delonix e.</i>	1.330	
<i>Carduus leaves</i>	0.36			
3.	Cereals and millets	<i>Oryza sativa</i>	0	[56,72–75]
		<i>Triticum aestivum</i>	0.041	
		Red sorghum grain	1.54–7.44	
		White sorghum grain	0.55	
		Yellow sorghum grain	0.2–2.0	
		<i>Pennisetum typhoideum</i>	0	
		Eleusine coracana	0.36	
		Brown finger millet	0.12–3.47	
		White finger millet	0.04–0.06	
		Pearl millet	0.152	
4.	Seeds/Nutseeds	<i>Cuminum cyminum</i>	0.23	[56,76–79]
		<i>Mangifera indica</i>	0.35	
		Dry fenugreek	0.01	
		<i>Monsooned malabar</i>	0.08	
		<i>Monsooned robusta</i>	0.15	
		Castor seeds	0.6–3.68	
		Faba beans	0.7–3.8	
		Tamarind seeds	20	
		Almond	0.07–0.29	
		Brazil nut	0.01	
		Cashew nut	0.03–0.04	
		Virginia peanut	0.16–0.29	
		Walnut	0.18–0.34	
		Pistachio	0.02–0.22	
		Pecan	0.84–0.88	
		Pine nut	0.01	
Hazelnut	0.04–0.23			
Macadamia nut	0.01			
5.	Legumes	Pigeon pea	4.3–11.4	[72,80]
		Chick pea	1.9–6.1	
		<i>Phaseolus aureus</i>	0.437	
		Bengal gram	0.33	
		<i>Cajanuscajan</i>	0.607	
		<i>Glycine max merr.</i>	0.045	
		<i>Dolichos lablab</i>	1.024	
		<i>Vigna catjang</i>	0.175	

Table 2. Cont.

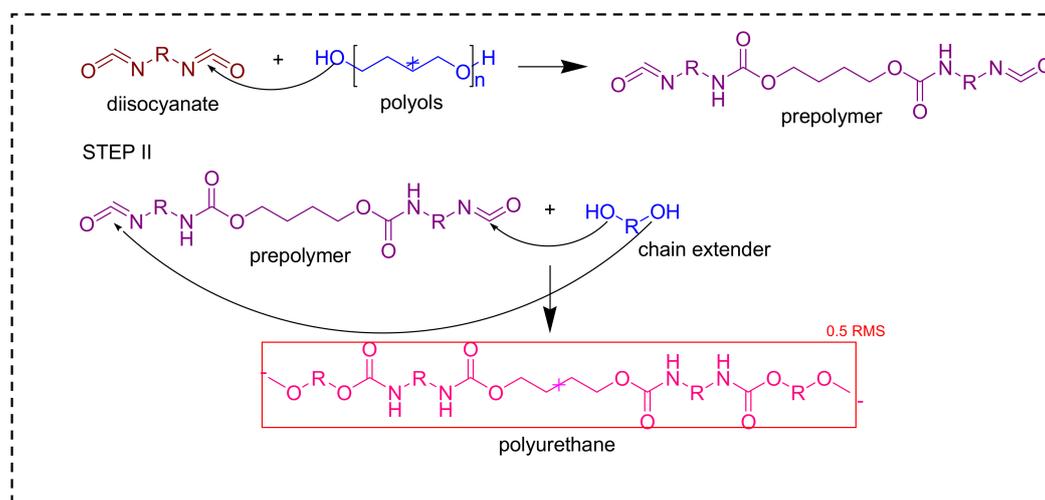
No.	Types	Name of Plant	Tannin (%)	References
6.	Beverages	<i>Tamarindus indica</i>	0.6	[57,71,72,78,81–83]
		Powdered tamarind	1.240	
		Powdered mixed condiments	0.611	
		<i>Coriandrum sativum</i>	0.311–0.82	
		<i>Curcuma domestica</i>	3.350	
		<i>Curcuma longa</i>	0.11	
		<i>Acacia catechu</i>	10.86	
		<i>Capsucum annuum</i>	0.98	
		<i>Carum copticum</i>	1.26	
		Cumin seed	0.90	
		<i>Piper nigrum</i>	0.94	
		Powdered puliogare	0.206	
		Powdered rasam	0.233	
		Powdered sambhar	0.204	
		Powdered bisibele-bhat	0.216	
		Perilla leaves	0.556	
		<i>Potentilla officinalis</i>	15–25	
		<i>Cinnamomum zeylanicum</i>	0.35	
<i>Allium sativum</i>	0.12			
<i>Zingiber officinale</i>	0.54			
7.	Condiments, spices, and herbs	Apple juice	0.005	[56,72,84]
		Red wine	0.075	
		Tea	0.195	
		Black tea	13.36	
		Green tea	2.65	
		Oolong tea	8.66	
		Cranberry juice	0.025	
		Dry red wines	0.236	
		Sweet white wine	0.036	
		Sweet red wine	0.096	
		Sparkling wine	0.035	
		Pomegranate juice	0.015–0.054	
		Dry white wine	0.039	
		White	0.025–0.031	
		Red	0.14–0.32	
		Bordeaux	0.15–0.49	
Madeira	0.08			
8.	Masticatories/Stimulants	Batelnuts ( <i>Areca catechu</i> L.)	8–15	[81]
		Betel leaf ( <i>Piper betle</i> )	1.0–1.3	
		Coffee beans	0.7	
		Roasted coffee beans	1.7	
		Guarana	12	
		Dry tea leaves	3.7	
		Kola nuts ( <i>Cola acuminata</i> , <i>Cola nitida</i> )	3.9–4.4	
		Katha (from catechu)	11.7–14.2	
		Cassava leaves	0.15–3.0	
9.	Gels	Aloe vera	0.14	[57]

### 3. Synthesis of Tannin-Based Bio-Polyurethane Resins

Bio-polyurethanes (bio-PU) are created by containing polyol with isocyanates or nonisocyanate routes [85]. Isocyanates, which involve the hazardous and toxic phosgene, are used in conventional PU resins. PU resins are manufactured by combining polyisocyanate and polyhydroxy compounds with several –NHCOO– in the active site, repeating

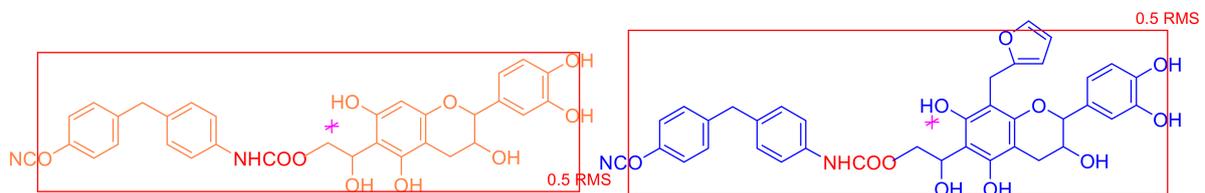
macromolecular substances. PU resins are the fifth most abundant plastic. They are more commonly used in modern industry as a polymer organic material, and are widely used in everyday life due to their superior performance. Otto Bayer successfully synthesized PU in Germany in 1937 [86]. PU resins have a nearly 80-year history. Following World War II, the US and Great Britain obtained the method for creating PU from Germany, and implemented it on an industrial scale. Nevertheless, at the beginning, the use of such PUs had a limited importance. Over time, the United States began researching PUs, and their technology evolved; after their introduction in the early 1950s, the PU, ethylene oxide, copolymer ether, and toluene diisocyanate were the first to be combined into PU foam. It was an important finding that marked the turning point in global PU development. PU resins are very polar and are insoluble in nonpolar solvents, since the molecular chain comprises a group of carbamates. The material is incredible, although when various raw materials and compounds are applied in PU synthesis, there will be a diversity of characteristics of the end product, such as elastomers, thermoplastics, and thermal resin. Many monomers for polymerization PU are available. Examples include toluene diisocyanate (TDI), diphenylmethane, and other basic polyols [87]. Polyester-based polyurethanes were produced using terminal polyester oligomers containing hydroxyl. PU resins' raw materials include isocyanate, polyester polyol, polyether polyol (PPG, POP, PTMEG), a solvent (DMF, TOL, and MEK), a chain expander (BDO), and different additional additives. Isocyanates are compounds ( $R-N=C=O-N$ ) in isocyanic acid ester. The presence of the NCO group in isocyanates can be applied to classify them (e.g., isocyanates ( $O=C=N-R-N=$ ) and polyisocyanates). For instance, the most often utilized substance in daily life is toluene diisocyanates (TDI) [86].

There are two PU synthesis methods: one-step and two-step synthesis. Both are distinct, but have a common chemical concept. The only distinction is the action of the sequence. Nevertheless, most scientists believe that the two-step approach is superior to the one-step method because the two-step method produces a higher-quality result. To complete the isocyanate and polyol processes in a single step, the various PU synthetic ingredients are mixed in a one-time reaction, including the reaction of the manufactured prepolymer with the crosslinker. The two-step procedure requires reacting the polyol with the polyisocyanate, and as a result, a prepolymer with a suitable molecular weight is formed. Polyols and polyisocyanates manufactured by the prepolymer reaction are soft materials with a very low strength; therefore, to create a polymer with relevant properties, a chain extender must be added [86]. Figure 2 depicts two processes in the manufacture of polyurethane using isocyanate. The reaction of diisocyanates and polyols yields urethane prepolymers terminated with isocyanate groups and extended with small-molecular-weight chain extenders in the first stage (e.g., diamines or diols).



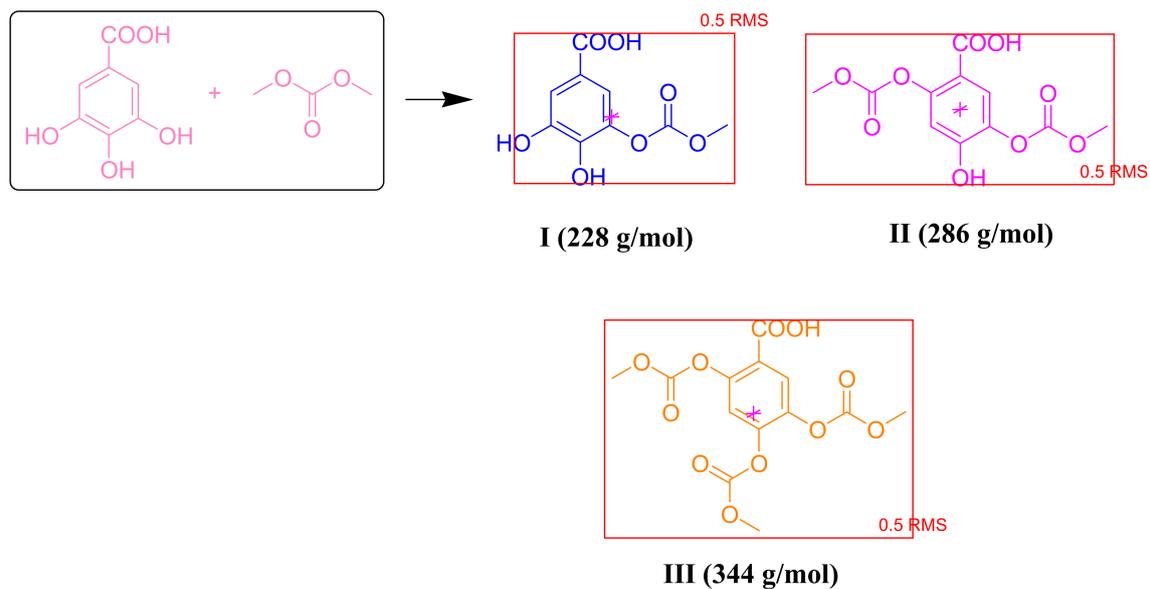
**Figure 2.** Synthesis of polyurethane in two stages utilizing diisocyanate, polyol, and a chain extender with a low molecular weight [88–90].

In addition, tannin-furfuryl alcohol is a natural material that is reacted with isocyanate polymer in the industry to develop rigid polyurethane foam phenolic blends. As a result, copolymerization of different oligomers is formed. Urethane is generated from two flavonoid tannin sites, mainly on the flavonoid hydroxyl group at C3, and also some that occur on the phenolic hydroxyl group of the flavonoid oligomer. Tannin-furfuryl alcohol is a natural substance that responds to the industrial use of isocyanate polymer to produce rigid phenolic foam mixtures of polyurethanes. Consequently, several oligomers have been copolymerized. Urethanes are produced from two tannin sites, principally in the C3 hydroxyl group of flavonoids, some of which are found in the flavonoid oligomer's phenolic hydroxy group. Glyoxal additive with the use of phenol sulfonic acid and furfural can also be used for the urethane group. The reaction with the flavonoid ring through the methylene bridge, however, considerably contributes to the reaction of the urethane group with the isocyanate group. All materials are used to react and produce urethane and methylene bridges. Thus, two types of bridges react and act along with tannins, furfuryl alcohol, isocyanates, glyoxal acids, and phenol sulphonic acids from a two-, three-, or even four-component combination [91]. Tannins and glyoxal reactions entail propylation of tannins, and yield the outcomes expected. Hence, tannins are the components utilized for polyurethane synthesis, and can be employed as polyols. The glyoxal reacts rapidly with tannins to create a hydroxyl group that, with the polyurethane terpolyoxalate one-step method, is much easier to approach by the isocyanate group. Following the industrial practice, the reactions can be done simultaneously. Figure 3 shows a polyurethane of tannin with an isocyanate group that, on the previous reaction of the glyoxal group, utilized a tannin unit of flavonoids. A reaction analogous to the reaction of the  $\text{CH}_2\text{OH}$  group, which is created by the interaction of formaldehyde with tannins, as well as the synthetic amino and phenolic resins, occurs when glyoxal reacts with tannins and then with isocyanates in urethane groups [91].



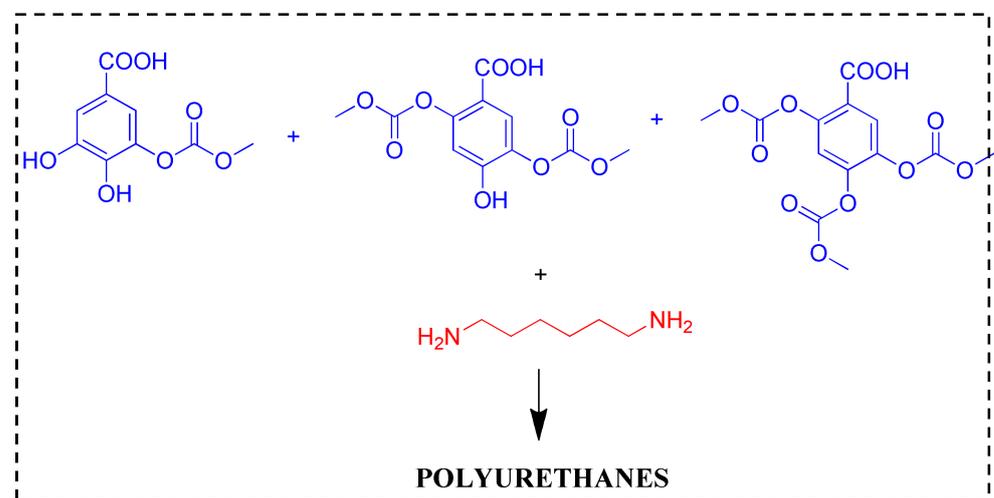
**Figure 3.** Tannin-based polyurethane with an isocyanate group reaction on a glyoxal group previously reacted using a flavonoid tannin unit [91].

PU resins are ubiquitous and adaptable to a wide variety of material applications. Great strides have been made in preparing them from bio-sourced polyols. Isocyanates are the key materials used in their preparation, but they have one major drawback; i.e., their toxicity [92,93]. Due to this, chemical synthesis routes for nonisocyanate polyurethanes (NIPUs) have been developed. Wood-based panel adhesives also make use of polymeric diphenyl-methane diisocyanate (pMDI) [94,95]. The toxicity of pMDI has redirected research towards developing isocyanate-free polyurethanes (NIPUs) [96–99]. Tannins include phenylpropane units containing aromatic and aliphatic hydroxyl groups. The aromatic hydroxyl group is attached to the unsaturated carbon ( $\text{sp}^2$ ) in the benzene ring, which is the benzene ring that can resonate to stabilize the negative charge of the phenoxide ion, while the aliphatic hydroxyl group is located in a chain on the saturated carbon ( $\text{sp}^3$ ). These differences can lead to interbehavioral actions in the process of making isocyanate-free polyurethanes [100]. The toxicity of isocyanates has recently been removed by interactions of synthetic polyols with cyclic and bicyclic carbonates, and afterward by the use of diamines, to produce nonisocyanate polyureas. In the process reaction between the carbonate dimension or a complex cyclic carbonate and tannin extract, followed by a carbonated tannin reaction with diamines, the poly-hydroxyurethane reaction occurs [101]. Thebault et al. (2014) reported the following two stages of NIPU production (Figure 4).



**Figure 4.** Major products with their respective mass molecules from the reaction between gallic acid and dimethyl carbonate [102].

Carbohydrates in tannins can also be modified by carbonation because they are a type of polyol. The dried extracts yielded by the first reaction were approximately 38.7%. Water and carbonates can evaporate at a temperature of 103 °C, and the major products (I, II, and III), have a low stability at that temperature; they can also be hydrolyzed to remove the carbonate groups they contain. The second step is a reaction of a mixture of compounds (major preconceived products) with diamines, using hexamethylenediamine (Figure 5) [102]. This second procedure yielded a dry extract at a concentration of 50.3%.



**Figure 5.** The second reaction between major preconceived products with hexamethylenediamine [102].

Fourier-transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC) were used to confirm successful urethane bond formation. However, GPC analysis could not be carried out on some samples due to their insolubility. This signified that the sample had been cured, resulting in the formation of a three-dimensional polymer cross-bond as part of this mass. A portion of all its mass having the PU oligomer is soluble, and can be used as a sample for analysis using MALDI-TOF mass spectrometry to determine the presence of the carbonation or urethane groups included. In an article by Thebault et al. (2015), TGA analysis showed that this tannin-based NIPU began to

decompose at temperatures ranging from 180 °C to 200 °C, making it suitable to be used as a wood coating. For example, the surface coating of a medium-density fibreboard (MDF) panel was implemented at 170 °C under a mild pressure to maintain the minimum filming temp, so it could produce good hydrophobicity on the surface [103].

#### 4. Characterization of Tannin-Based Bio-Polyurethane Resins

Following the research by Peng et al. (2013), characterization of a bio-PU was carried out based on hydrolyzed tannins containing several active sites. An active site is a group of catechols in hydrolyzed tannins used as a substitute for dopamine. In this research, the bio-PU was used for the coating process, resulting in a tannin-based bio-PU coating that showed a better adhesion performance and a faster curing process. These results indicated a similar process that occurs in dopamine-based polyurethane coatings. The tannin-based bio-polyurethane characterization was carried out using several analyses, such as Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), MALDI-TOF mass spectrometry, and  $^{13}\text{C}$ -NMR.

##### 4.1. Fourier-Transform Infrared Spectroscopy (FTIR)

Using FTIR spectroscopy, the tannin-based bio-PU showed the presence of a  $\text{N}=\text{C}=\text{O}$  asymmetric stretching vibration at a wavenumber of  $2270\text{ cm}^{-1}$ . The intensity of the absorption peak decreased due to the extended reaction time, and finally, the absorption peak disappeared [104]. The peak at  $2270\text{ cm}^{-1}$  revealed that there was no residual free of the  $\text{N}=\text{C}=\text{O}$  group in the tannin-based bio-PU. There were peaks at wavenumbers of  $3330\text{ cm}^{-1}$  and  $1540\text{ cm}^{-1}$ , including N-H stretching vibrations and deformation vibrations, respectively. Furthermore, there also was an absorption peak at a wavenumber of  $1720\text{ cm}^{-1}$  related to a functional group of the C=O's stretching vibration [105].

Chen et al. (2020) conducted a study of the preparation of rigid foams with a tannin-based NIPU by blowing. The ambient temperature FTIR analysis confirmed the NIPU. The infrared absorption spectrum of the tannin-NIPU foams produced between  $3500$  and  $3100\text{ cm}^{-1}$  showed there was a substantial absorption band associated with a stretching vibration of -OH [106,107]. The absorption spectrum at  $3337\text{ cm}^{-1}$  was described as that of the NIPU-stretching -N-H group associated with urethane as a result of tannins reacting between hexamethylene diamine and dimethyl carbonate [103]. Additionally, two absorption bands at  $2934$  and  $2860\text{ cm}^{-1}$  were connected with the C-H stretching vibrations of  $-\text{CH}_2$  and  $-\text{CH}_3$ , respectively. Additionally, there was an absorption band at  $1693\text{ cm}^{-1}$  for the C=O groups and at  $1533\text{ cm}^{-1}$  for the urethane [108].

Tannins from four tree species (mimosa, quebracho, *Pinus radiata*, and *Pinus pinaster*) were studied by Thebault et al. (2014). The reactions were carried out at room temperature and heated to  $103\text{ }^\circ\text{C}$  utilizing dimethyl carbonate as a solvent (to create fluid material containing tannin extract at a concentration of 45%–50% *w/w* of powder) and a reactant. According to the FTIR spectra of four tannin-derived products at ambient temperature, the  $1690\text{ cm}^{-1}$  stretching vibration band of the C=O double bond of amides covered all four tannin reaction products, and the  $3340\text{ cm}^{-1}$  stretching vibration band of secondary amides indicated the formation of polyurethane prepolymers (Table 3). The two pine tannins' reaction products exhibited a more pronounced urethane band at  $1537\text{ cm}^{-1}$  than those of quebracho. In addition, the typical bands of aromatic nuclei at  $1600\text{ cm}^{-1}$ ,  $1500\text{ cm}^{-1}$ , and  $1460\text{ cm}^{-1}$  were more prominent in the mimosa tannin, showing that urethane linkages are not as essential as the polyphenolic structures of flavonoids. Quebracho's tannins appeared to be a cross between pine and mimosa tannins, having more balanced absorbances at  $1690\text{ cm}^{-1}$ ,  $1600\text{ cm}^{-1}$ ,  $1537\text{ cm}^{-1}$ ,  $1500\text{ cm}^{-1}$ , and  $1460\text{ cm}^{-1}$  in its spectra. All four tannins' reaction products exhibited the same pattern when heated to  $103\text{ }^\circ\text{C}$ ; the presence of significant bands at  $3340\text{ cm}^{-1}$ ,  $1690\text{ cm}^{-1}$ , and  $1537\text{ cm}^{-1}$  confirmed the presence of urethane linkages. At  $1265\text{ cm}^{-1}$ , the major band represented an amine C-N elongation [103].

**Table 3.** FTIR spectroscopy analysis of bio-PU resins from different sources of tannin.

Source of Tannin	Band Assignment (cm <sup>-1</sup> )	Functional Groups	References
Fruit (cashew nut husk)	1690	C=O (amide I band)	[109]
	1500–1200	C-N (amide II band)	
	3000	N-H stretching	
	1330	OCONH asymmetric	
Radiata pine bark	1645	CO-N	[103]
	576–642	Plane bending O=CN	
	2300	NCO bands	
	3230	NH vibration	
	1090	Aliphatic C-O-C	
	1750	C=O Aliphatic ester	
Mimosa tannin bark	3500–3100	–OH stretching vibration	[35]
	3337	–NH stretching	
	1533	Urethane linkage	
	1261	Amines C-N elongation	
Maritime pine	1690	C=O of amides	[103]
	3340	Secondary amides	
	1537	Urethane band	
	1265	Amines C-N elongation	
Mimosa	1690	C=O of amides	[103]
	3340	Secondary amides	
	1537	Urethane band	
	1265	Amines C-N elongation	
	1600–1460	Urethane bonds	
Quebracho wood	1690	C=O of amides	[103]
	3340	Secondary amides	
	1537	Urethane band	
	1265	Amines C-N elongation	
	1600–1460	Urethane bonds	
Gambier tannin	2870–2970	Stretching –CH, CH <sub>2</sub> , CH <sub>3</sub> aliphatic groups	[41]
	980–1200	–CO stretching of ether	
	1371	–CH <sub>3</sub> groups	
Vegetable tannin	2230	Isocyanate groups	[44]
	1600–1720	Urethane linkages	
	1530	C-N and N-H	
	1200	C-O stretching of EtCO	

#### 4.2. Differential Scanning Calorimetry (DSC)

Based on the research of Peng et al. (2013), according to the DSC results analysed, the changing temperature of the bio-PU tannin samples had only one glass-switching temperature, without melting points and crystallization transitions. The temperature of transition glass ( $T_g$ ) in residential bio-PU samples of tannin content increased with a decrease in  $T_g$  from 32.91 °C to 11.91 °C. This could occur due to higher backbone stiffness and higher chain interactions in the tannin content.  $T_g$  values of bio-PU were affected by the molar ratio of NCO:OH, the degrees of substitution, and the type of diisocyanate [47]. The results of the DSC analysis are given in Table 4.

**Table 4.** Thermal behavior of bio-PU resins from different sources of tannin.

Source of Tannin	Peak Temperature (°C)	Thermal Event	References
Fruit (cashew nut husk)	260	Transition glass ( <i>T<sub>g</sub></i> )	[109]
	290	Endothermic reaction	[109]
	380	Exothermic reaction	[109]
<i>Pinus pinaster</i> bark	254	Transition glass ( <i>T<sub>g</sub></i> )	[47]
<i>Pinus radiata</i> bark	150	Transition glass ( <i>T<sub>g</sub></i> )	[110]

#### 4.3. Thermogravimetric Analysis (TGA)

In general, the thermal stability of PU resins is primarily dependent on the molecular weight distribution of aromatic molecules, as they can be resistant to urethane. Thermogravimetric analysis of PU resins, therefore, provides information on its degradability and its end use [111]. TGA analysis showed a tannin curve that underwent two stages of the degradation process at 210 °C, namely degradation of the phenyl group and the excess stage of degradation of the carbonyl group. However, the PU samples showed three stages of the degradation process. The first occurred at a temperature of 220 °C, which was due to the degradation of the urethane bonds. However, the low concentration of 3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate used for forming the PU in the study resulted in an undetectable weight loss. Then, for the second degradation step to occur at the same temperature range (from 230 °C to 290 °C), it was placed with the degradation of the tannin sample used. The weight loss observed over this temperature range can calculate the tannin content in the PU sample's increased body weight from 6% to 7.1%, in line with the concentration. Furthermore, the third stage of the degradation process occurred at a temperature range of 290 °C to 300 °C, which degraded ester groups and carbonyl groups from tannins [105].

Thebault et al. (2014) described that the curve decomposition of thermogravimetric analysis and the first derivations of a tannin-based bio-PU generated at room temperature from mimosa; quebracho, radiata pine, and maritime pine exhibited a three-step thermal degradation process of oligomers formed by tannins. Between 155 °C and 190 °C, a first decomposition stage with 10% loss occurred. This could be equivalent to urethane linkage degradation. The degradation process was then extended up to 430 °C, and PU oligomers certainly could be more likely to form at an ambient temperature in the reaction products. MALDI-TOF could demonstrate their different shapes. Due to heat at higher temperatures, they were likely to polymerize. As a result, the reaction could progress from 180 °C to 450 °C due to polymerization and degradation. At 450 °C, the inflection was followed by a distinct decay step at nearly 450 °C. Thus, the thermo-oxidative degradation temperature of organic material was most likely. The residual weight was between 22% and 35% at 700 °C, and was part of the flavonoid tannin aromatic structure. For a bio-PU from tannins prepared at 103 °C, a similar three-stage thermogram could be observed in the curves of thermogravimetric decomposition and the first derived product of the tannin-based bio-PU from mimosa, quebracho, radiata pine, and maritime pine heated to 103 °C. At higher temperatures, however, the first tipping point came between 209 °C and 212 °C. The FTIR spectra revealed a greater abundance of urethane linkages in reaction products heated to 103 °C than in those obtained at an ambient temperature. Thus, urethane connections may differ from ambient reaction products for most reaction product weights at 103 °C. This is likely to lead to the marked degradation of the urethane bonds at approximately 210 °C in curves of thermogravimetric decomposition and the first derivative of a tannin-based PU heated to 103 °C of mimosa, quebracho, radiata pine, and maritime pine (Table 5). As the temperature increased when these primary bending points occurred, these connections appeared to have a higher thermal stability than if prepared at room temperature [103].

**Table 5.** Thermal stability of bio-PU resins from different sources of tannin.

Source of Tannin	Peak Temp (°C)	Weight Loss (%)	Weight Residue (%)	References
Fruit (cashew nut husk)	380	11.9	88.1	[109]
Mimosa tannin bark	790	81.3	18.7	[35]
Maritime pine	211.18	70	30	[103]
Mimosa	209.93	71	29	[103]
Quebracho wood	212.43	64	36	[103]
Gambier tannin	270	60	40	[41]
<i>Pinus radiata</i> bark	150	20	80	[110]

#### 4.4. MALDI-TOF

Analyses using MALDI-TOF have been carried out to determine the distribution and derivatives of the condensed tannin oligomer. The forming of condensed tannin-derived oligomers comprises four types of flavonoid units: fisetinidine, robinetinidein, catechin, and delphinidin. The derivative product was produced by combining these units with the reagents employed. The results demonstrated that a tannin-derived NIPU was formed during the manufacture of the tannin-based NIPU resin [102,112], and the peaks of NIPU that related with oligomers were 433.2 Da, 439.2 Da, 451.8 Da, and 556.3 Da. The tannin-derived oligomer type may be identified based on FTIR and <sup>13</sup>C NMR studies, which have indicated the presence of urethanes (–NH–CO–O–). The adhesive in tannin-based wood foam usually is hexamethylenetetramine (hexamine), as stated in the investigations [113,114]. The bonding and curing of fluid foam can also be favourable. Furthermore, tannins and hexamines have a complex chemical mechanism for polymerization. Two kinds of linkages that are still distinguishable (two different types methylene-based fragments) that are formed of hexamine can be used as interconnectors; e.g., –CH<sub>2</sub>, –(CH<sub>2</sub>)<sub>3</sub>, –CH<sub>2</sub>, –NH, and –N. Peaks at 578.3 Da, 582.4 Da, 591.2 Da, 604.3 Da, 611.3 Da, 615.4 Da, 619.5 Da, 623.2 Da, 631.3 Da, 638.4 Da, 768.7 Da, 796.5, 878.6 Da, 906.6 Da, 954.5 Da, and 963.4 Da from MALDI-TOF spectra indicated the reaction between tannins and hexamines [113,114].

Tannin-based bio-PU products produced at room temperatures were reported by Thebault et al. (2014) that, in comparison to a reference mix of dimethyl carbonate and hexamethylenediamine, the majority of main reaction product peaks within the lower range of the molecular weight, from 260 to 650 Da, differed from the reaction products of the reference combination (i.e., carbonates and hexamethylenediamine) [98]. The peak of 23 Da of Na<sup>+</sup> frequently does not appear in the MALDI-TOF flavonoid spectrum at lower molecular weights. The peaks at 290 Da and 307 Da had all four spectra present, and were considered to be catechin or robinetinidine (288.3 + 2 hydrogens: 290.3 Da), and delphinidin (304.3 + two hydrogens: 306.3 Da). A peak at 274 Da might represent fisetinidine (272.3 + 2 hydrogens: 274.3 Da); however, it could be a reaction product without tannins in the reference mix. Several series with a repeated 58 Da increase, which was most likely tannin hydroxyl carbonation, was observed from these bases. As the tannins had between four and six hydroxyl groups per flavonoid unit, several carbonations and the following amination configurations were obvious. Some smaller peaks that exceeded 800 Da were like those of the reference compound, while other peaks were not: in the mimosa and quebracho spectra, 272 Da and 288 Da were separated, which were equivalent to fisetinidin, catechin, and robinetinidin structures. The other 98 Da intervals that could be seen most often result in urethane oligomers due to a tannin carbonated hydroxyl group amination with hexamethylenediamine. Tannin-based bio-PU products were expected to be more polymerized, since they were heated to 103 °C. As a result, a molecular peak above 500 Da was more present in the 400–2500 Da range than at the ambient temperature, as the peak occurred at the range of 400–1700 Da. Nevertheless, they usually were dissimilar due to the main peaks at 612 Da and 776 Da appearing at four tannin-based compounds' spectra, but did not appear in the spectra of the dimethyl carbonate and hexamethylenediamine compound. Adding a hexamethylenediamine structure to a hydroxyl group at the same time by using a urethane connection and a sodium cation can explain the gap that occurred among those for about a

164 Da gap. In quebracho and mimosa tannin-based spectrums, in particular, a sequence with repetitive intervals between 156 Da and 168 Da peaks were detected. The periods for 156 Da could occur from the addition of hexamethylenediamine through a urethane link and then subsequent carbonation of the terminal  $-NH_2$  by leftover dimethyl carbonate. This reaction may occur at the intervals of 156 Da in the maritime pine urethane spectrum for each tannin carbonated hydroxyl group. Tannin-based bio-PU that were prepared at the ambient temperature were compared to a reference mixture of dimethyl carbonate and hexamethylene diamine product. The majority of main reaction product peaks within the lower range of the molecular weight, from 260 to 650 Da, were different from the reaction product of the reference mixture (i.e., carbonates and hexamethylenediamine) [103].

A double amination of an individual possessing at least two hydroxyl carbonated groups could create the 168 Da interval. This could lead to the complex copolymerization of dimethyl carbonate and hexamethylenediamine from carbonated moieties, and as a result, show the occurrence of the repeating sequences, with 168 Da–156 Da intervals between peaks. MALDI-TOF is thus a great method to determine the distribution of oligomers of polymer materials; for example, carbonated and urethane oligomers with molecular weights up to 3000 Da. On the other hand, materials having higher molecular weights than these were barely detectable in the spectra. Their existence is often detected by a significant increase in viscosity or gels, or even formation of solids. In MALDI spectra, peaks of high molecular materials were often found, but it was very complicated to differentiate them from background noise because they were quite small. The low strength of these peaks suggested a lack of solubility in the appropriate solvent for these fractions [103].

#### 4.5. $^{13}C$ -NMR Analysis

$^{13}C$ -NMR is a method used to determine the synthesized composition of a bio-PU in the synthesis process. The  $^{13}C$ -NMR tannin-based NIPU spectrum showed relatively small peaks of tannins differentiated between the shoulders at 157 ppm of tannins at C5 and C7, and broad peaks at 153–155 ppm included in the C9 flavonoid unit and C=O, which is the relationship of urethane. The small peak at 150 ppm represented the aromatic ring associated with urethane. Therefore, this proved that the urethane linkage on the aromatic tannin ring had been formed. In addition, the large and wide peaks at 24 ppm belonged to the  $-CH_2$  group of hexamethylenediamine (HDMA), and the peak at 59 ppm was the carbohydrate group present in the commercially used tannin extracts. Based on the results of these data, it can be ascertained that the NIPUs based on condensed tannins were successfully produced by mixing them with DMC and HDMA during the tannin-based bio-PU resin manufacturing stage [91].

#### 4.6. GPC Analysis

Thebault et al. (2014) reported that GPC was further used for the identification of larger fractions of molecular weight. Only the quebracho PU made at both room temperature and 103 °C, and the mimosa and maritime pine heated to 103 °C, were evaluated, because only a small percentage of the samples dissolved in the solvents, although they were heated using the ultrasound approach. The majority of polyurethane materials derived from tannins are most likely cured into three-dimensional cross-linked complicated polymers. A chromatogram of quebracho's gel permeation at room temperature showed that the molecular weight, exceeding 2000 Da for a total polydispersity of 2.45, was approximately one-half of the polyurethane species generated at room temperature. It is worth emphasizing the presence of a significant shoulder in the lower molecular weight range, between 250 and 1000 Da, which could reflect the soluble sample of the material identified in the MALDI-TOF spectrometry. In comparison, GPC profiles of tannin-based PU heated to 103 °C for mimosa, quebracho, and maritime pine were indicative of the important role to play in improving the final polyurethane's molecular weight under preparation circumstances. the polyurethane was prepared at 103 °C, resulting in the extinction of half of the species that had molecular weights of more than 3500 Da. In this case, polydispersion

declined to 1.94 in quebracho, which meant polymerization was more efficient at higher temperatures (1.75 for mimosa and 1.79 for maritime pine) [103].

### 5. Utilization of Tannin-Based Bio-Polyurethane Resins

Along with many “green” construction projects and the product demand from the automotive industry, the bio-PU market is growing. Furthermore, tannin-based bio-PU can improve the appearance and durability of products in the automotive, textile, and other industries. These bio-PU tannin resins are used in various applications, as shown in Table 6, including rigid and flexible foams, sealants, elastomers, membranes, adhesives, coatings, and fibres in the automotive, building, and construction industries; and in electrical, electronic, consumer, and industrial goods. Tannins can be used as an alternative to manufacturing bio-based polyurethane, meeting the growing demand for “green” materials, as they have good insulation properties and are more energy efficient. This foam is commonly used as a spray to seal cracks, joints, holes, and other building materials to reduce the amount of heat required in the process. Tannin-based flexible polyurethane foam is lightweight, durable, supportive, and comfortable. It is used for various purposes, including automotive, furniture, mattresses, footwear, textiles, handbags, luggage, household appliances, and packaging. It is widely used as a cushion in various consumer and commercial products such as bedding, furniture, automotive interiors, carpet backing, and packaging [115,116]. Tannin-based rigid PU foam, on the other hand, is used in a variety of end-use industries, including automotive, building and construction, insulation, and industrial equipment. Rigid foam is an excellent insulator that can be used for roof and wall insulation, window and door insulation, and as an air barrier sealant.

Tannin-based bio-PU coatings offer a smooth, long-lasting finish that is resistant to UV exposure and chemicals. These coatings improve the appearance and durability of materials in the construction, wood, textile, automotive, and other end-use industries. The tannin-based bio-PU has good characteristics as an adhesive; aside from its bonding properties, this resin has high delamination resistance, adhesion, and cohesion strength. Its tensile strength and deformation properties are comparable to those of traditional isocyanate-based PUs. In terms of physical properties, comparable water resistance, and dimensional stability to isocyanate PUs, it has a high hard-to-soft ratio, resulting in good mechanical properties. Furthermore, regarding chemical and thermal properties, the tannin-based bio-PU has better chemical resistance by 30%–50% compared to other adhesives, and a thermal stability enhancement due to the presence of aromatic tannin. In terms of economic efficiency, the tannin-based bio-PU is less expensive than isocyanate PUs, but is still more expensive than formaldehyde-based resins [85,117].

**Table 6.** Utilization of tannin-based bio-PU resins.

No.	Types	Bio-Based Additives	Utilization	References
1.	Bio-PU (tannic acid)	Epichlorohydrin; Tetrabutylammonium (TBAB); CO <sub>2</sub>	Tissue engineering scaffolds	[3]
2.	Bio-PU (mimosa tannin extract)	Dimethyl carbonate polyol	Fire retardant	[112]
3.	Bio-PU foam (tannin-furfuryl alcohol)	Polymeric isocyanate	The field of hydroponics	[101]
4.	Bio-PU (propylene oxide derivatized condensed tannin)	Polymethyldiisocyanide	Functional modifier of PLA composites	[118]
5.	Bio-PU (chestnut tannin)	Dimethyl carbonate; Hexamethylene-diamine	Wood coatings	[102]
6.	Bio-PU (condensed tannin)	Dimethyl carbonate; Diamine	Surface coatings	[103]

Table 6. Cont.

No.	Types	Bio-Based Additives	Utilization	References
7.	Bio-PU film	3-Isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate (IPDI); N,N-dimethylformamide (DMF); Ferric chloride (FeCl <sub>3</sub> )	Coatings	[105]
8.	Bio-PU rigid foams (mimosa tannin)	Dimethyl carbonate; Hexamethylenediamine; Hexamethylenetetramine; Citric acid	Coatings; wood adhesives	[35]
9.	Bio-PU foams	Isocyanate; Catalyst CRC 605; Glyoxal	Industrial continuous line applications	[91]
10.	Bio-PU foams (condensed tannin/glucose)	Dimethyl carbonate	Fire retardant	[19]
11.	Bio-PU foams (vegetable tannin)	Ethoxylated cocoalkyl amine; Methylene diphenylisocyanate	Automotive industry	[44]
12.	Bio-PU foams (hot water tannin)	Butylene oxide; Triethylamine	Building and construction industry	[39]
13.	Bio-PU (benzoylated tannin)	Hexamethylene-diisocyanate; Catalyst 1,4-diazobicyclo-(2,2,2)-octane; 1,4-Butanediol	Flame retardant	[109]

## 6. Conclusions

Tannins can be extracted from leaves, stems, or barks of plants using either hot water or organic solvents. Tannins have broad applications that can be put in perspective regarding their existing advantages and drawbacks, as well as the future potential for their wider industrial utilisation in sustainable and value-added products. As this review demonstrated, tannins are a prospective source of natural materials for producing tannin-based bio-PU resins with good thermal stability and satisfactory strength properties. In addition, they are renewable and environmentally friendly materials, which eliminates the harmful emissions and toxicity associated with the use of conventional PU resins. The synthesis processes of the tannin-based bio-PU resins can be further studied and characterised by performing FTIR, DSC, TGA, MALDI-TOF, and GPC analyses to verify their low toxicity and confirm the expected performance results.

**Author Contributions:** Methodology, M.A.A. and M.A.R.L.; validation, M.A.R.L., A.H.I., R.K.S. and W.F.; investigation, M.A.A., M.A.R.L., W.F., A.H.I., R.K.S. and P.A.; writing—original draft preparation, M.A.A., M.A.R.L., W.F., A.H.I., P.A. and M.G.; writing—review and editing, M.A.R.L., A.N.P., M.G. and A.P.; visualization, M.A.R.L. and P.A.; supervision, M.A.R.L., A.H.I., A.N.P. and A.P. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Acknowledgments:** The authors are grateful to the Ministry of Research and Technology of Indonesia for the research grant (No. 172/E1/PRN/2020) and the Integrated Laboratory of Bioproducts (iLaB), National Research and Innovation Agency of Indonesia, for the facility support. This work was also supported by the Deputy of Strengthening Research and Development, Ministry of Research and Technology of Indonesia, 2021 fiscal year (95/UN5.2.3.1/PPM/KP-DRPM/2021); the Slovak Research and Development Agency under Contract No. APVV-18-0378 and APVV-19-0269; and Project No. НИС-Б-1145/04.2021, “Development, Properties and Application of Eco-Friendly Wood-Based Composites”, carried out at the University of Forestry, Sofia, Bulgaria.

**Conflicts of Interest:** The authors declare no conflict of interest.

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