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Chapter 5

Micro- and Nanolignin Particles: Development and Potential Applications

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Abstract

Lignin represents an untapped opportunity for the production of high value-added bioproducts. Lignin is the second most abundant biopolymer in the biosphere after cellulose and is the main natural source of aromatic compounds. As lignin is biodegradable, antimicrobial, antioxidant and carbon dioxide neutral, low-cost industrial lignin waste could be converted into high value-added micro- and nanoparticles that retain their inherent structure, composition and colloidal properties. Lignin micro- and nanoparticles have emerged as a promising alternative to fossil-based chemicals and products due to their excellent properties. This chapter discusses the possibilities of synthesising lignin micro- and nanoparticles from the different sources of lignin available. It also presents the available routes for the production of micro- and nanoparticles, as well as the most commonly used modification mechanisms to confer specific properties for the different applications of interest. Finally, a review of the different applications of interest is presented, with emphasis on the use of micro- and nanolignin as a reinforcement agent and as an antioxidant and UV-blocking agent.

1. Introduction

Lignin is the second most abundant component of plant biomass, after cellulose [1]. It comprises between 20% and 30% of woody plants cell walls and, by forming a matrix that surrounds cellulose and hemicellulose, provides structural rigidity and protection to the plant. Lignin is a highly cross-linked three-dimensional macromolecule, formed by three types of substituted phenols, namely, coniferyl, sinapyl and p-coumaril alcohols, which produce large numbers of functional groups (such as ortho aromatic hydroxyl and aliphatic hydroxyl) [2]. These substituted phenols are linked mainly by two types of bonds: fused bonds (e.g., 5-5 and β -1 bonds) and ether bonds (e.g., β -O-4 and σ -O-4). Ether bonds are the dominant bond type between the three types of substituted phenols [3].

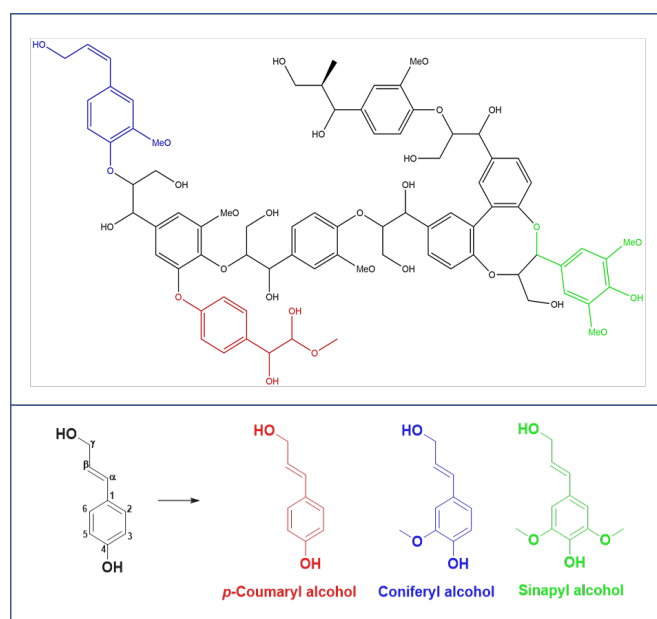


Figure 1: Chemical structures of lignin (p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) (Adapted from reference [4])

Lignin main source, easily available for use on a larger scale, comes from spent pulp liquors and chemical release of cellulose fibres from wood in pulp and paper industries. Lignin is also produced on a large scale as a by-product of biorefineries that process plant biomass for the production of fuels and chemicals, such as biorefineries for the production of second-generation bioethanol [5]. Global production of lignin-based chemicals and materials exceeds 50 million tonnes per year, with the consequent lignin residue generation [6]. Dessbesell et al. estimated technical lignins annual global production around 100 million tonnes per year, mainly from pulp and paper industry [7]. It is estimated that about 95% of the lignin obtained is burned in boilers for steam recovery and power generation. Only about 5% (mainly ligno-sulphonate) is used for the production of high value-added bio-based products such as dispersants, adhesives and surfactants [8].

As the second most abundant biopolymer after cellulose, lignin is readily available, but it is used for fairly low value applications. Rather than treating lignin as waste, it is well suited for the production of improved composites, polyblends, carbon fibres, plastics, nanomaterials,

and building blocks to replace fossil-based chemicals, that offer both economic and environmental benefits [5]. The use of natural materials such as lignin for high added value applications has the advantage of a low processing cost with low energy requirement. However, its use on a macro scale presents several challenges due to its extremely complex and heterogeneous chemical structure.

Production of lignin micro- and nanoparticles emerges as a promising alternative to extend potential applications of this biopolymer. Micro- and nanolignin have recently gained interest due to improved properties compared to the standard lignin available today [9]. Lignin preparation at micro- and nanoscale, also known as micro and nanolignin, can introduce new means of high value applications of lignin-based products, which further promotes lignin valorisation. Lignin nanoparticles have shown improved properties compared to initial lignins: higher antioxidant properties, thermal stability and antibacterial properties [10].

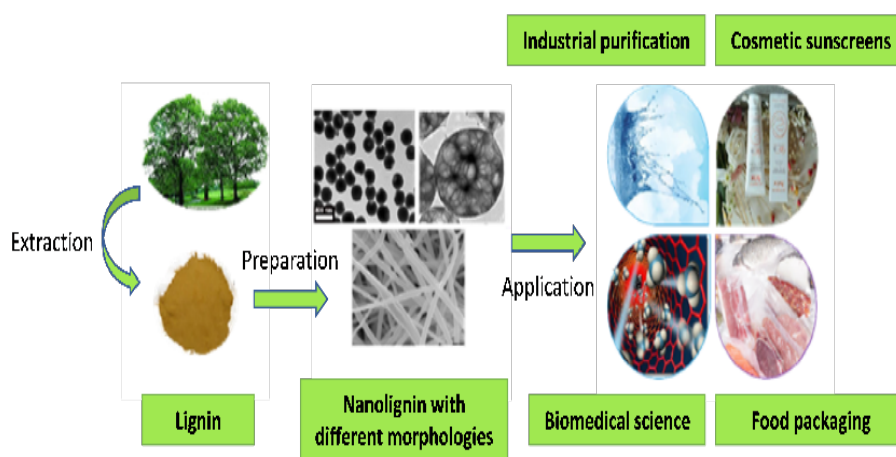


Figure 2: Nanolignins with different morphologies and their applications in different fields (Adapted from reference [11]).

This chapter will discuss micro- and nanolignin main sources, newest production, extraction and derivatization methods, as well as their main potential applications.

2. Lignin Sources

Lignin sources have been classified into three main groups according to their monomer units chemical structure: softwood lignin (pine, spruce, sawdust...), hardwood lignin (mainly eucalyptus), and grass lignin (*Salix purpurea*, wheat straw...). Softwood lignin is an aromatic polymer based on guaiacylpropane units connected by ether and carbon-carbon bonds. Hardwood lignin is made up of roughly equal amounts of guaiacyl and syringylpropane units. Grass lignin is made up of guaiacil, syringil, and p-hydroxyphenyl propane units [12].

Depending on the method of lignin extraction from the above-mentioned sources, it is found technical lignins. Technical lignins are the by-products of the pulp, paper, cellulosic ethanol and other industries. Depending on the applied processing method, these lignins are known as milled wood lignin, enzymatic lignin, Braun lignin, Kraft lignin, lignosulphonate,

soda lignin, organosolv lignin and Klason lignin [13,14]. Lignin powders obtained are brown and amorphous. Their size and colour depend on the preparation method selected and employed for the extraction process [15]. **Table 1** gives an overview of the different types of lignin depending on the extraction method used.

Table 1: Different types of lignin depending on the extraction method (Adapted from reference [14]).

Type of lignin	Extraction methodology
Milled wood lignin (MWL)	Extraction in aqueous dioxane solution from finely ground wood
Milled wood enzymatic lignin (MWEL)	Residue remaining after hydrolysis of carbohydrates in finely ground wood
Cellulase enzymatic lignin (CEL)	Soluble fraction resulting from MWEL
Braun lignin or native lignin	Ethanollic extract of residual wood (sawdust-like particle size)
Kraft lignin	Sulphate pulping, carried out at elevated temperatures and pressures
Lignosulphonate	Sulphite pulping, performed at elevated temperatures and pressures
Soda lignin	Dissolving in an alkaline medium of non-wood fibres such as straw, bagasse, bagasse, cane fibres, etc.
Organosolv lignin	Lignin from organosolv treatment of lignocellulosic biomass
Klason lignin	Insoluble condensed residues after hydrolysis of polysaccharides with sulphuric acid

Different lignin extraction or separation processes result in different physical and chemical properties, such as surface properties, solubility, molecular weight and functional groups. All these affect the preparation, performance and even the application of lignin micro- and nanoparticles [16]. **Table 2** summarises the main characteristics of commercially available lignin types.

Table 2: Characteristics of different types of commercial lignins (Adapted from reference [14]).

Parameters	Type of lignin			
	Sulphite lignin	Kraft lignin	Soda lignin	Organosolv lignin
Ashes (%)	4.0 – 8.0	0.5 – 3.0	0.7 – 2.3	1.7
Moisture (%)	5.8	3.0 – 6.0	2.5 – 5.0	7.5
Carbohydrates (%)	–	1.0 – 2.3	1.5 – 3.0	1.0 – 3.0
Acid soluble (%)	–	1.0 – 4.9	1.0 – 11	1.9
Nitrogen (%)	0,02	0.05	0.2 – 1.0	0.0 – 0.3
Sulphur (%)	3.5 – 8.0	1.0 – 3.0	0.0	0.0
Molecular mass	1000 – 50 000 (up to 150 000)	1500 – 5000 (up to 25 000)	1000 – 3000 (up to 15 000)	500 - 5000
Separation method	Ultrafiltration	Precipitation (pH change) and ultrafiltration	Precipitation (pH change) and ultrafiltration	Organic solvent extraction

Considering both the different species used as raw material and the different types of technical lignins used mentioned above, the current section summarizes main sources employed on lignin micro- and nanoparticles production.

Many works produce micro- and nanolignin from different soft and hardwoods species. For example, Pylypchuk et al. produced nanolignin from Kraft lignins from both, hardwood (*Rose Gum Eucalyptus Grandis*) and softwood (*Norway Spruce*) [17]. Also, Chen et al. produced lignin nanoparticles with spherical structure from both softwood and hardwood lignin, i.e., hotwater pretreated hardwood aspen and eucalyptus lignin, and steam pretreated softwood lodgepole pine [18]. Windsten et al. also employed both softwood (*Pinus sylvestris/Picea abies*) and hardwood (*Eucalyptus* sp.) industrial Kraft lignins, which were precipitated using carbon dioxide from the black liquor of pulp mills that produce paper-grade Kraft pulp to produce lignin nanoparticles [19]. Yearla and Padmasree fabricated dioxane lignin micro- and nanoparticles and alkali lignin micro- and nanoparticles from two different sources of lignin, i.e., hardwood dioxane lignin extracted from subabul stems and softwood alkali lignin, using nanoprecipitation method [20]. Busatto et al. produced microlignin from spruce softwood ionic lignin [21]. In addition, there are several articles that produce micro- and nanoparticles from softwood Kraft lignin. Cailotto et al. produced lignin microparticles from softwood Kraft lignin by comparing two different methodologies [22]. Setälä et al. used tall oil fatty acid ester of softwood kraft lignin to prepare lignin microparticles in water [23].

Likewise, some works in the literature have also produced nanolignin from wood waste. For example, Zikeli et al. produced lignin nanoparticles from mix sawdust of Iroko and Norway spruce by a non-solvent method [24].

The valorisation of agricultural waste for the synthesis of lignin micro- and nanoparticles has been studied in recent years. Proof of this are the different scientific works that are available in the literature. These are some of the studies that have been carried out in this field. Rahnman et al. have synthesized lignin nanoparticles from steam exploded rice straw [25]. Juikar and Vigneshwaran extracted nanolignin from coconut fibers using a controlled microbial hydrolysis process, high shear homogenization and ultrasonic irradiation processes [26]. Cui et al. produced lignin microparticles from wheat husks [27]. Beisl et al. produced micro- and nanolignin from organosolv wheat straw using different precipitation setups [28]. Recently, Rizal et al. produced lignin nanoparticles from empty fruit bunches using high-energy ball milling [29].

In addition, many works feature synthesized micro- and nanolignin from herbaceous biomass. Lou et al. have synthesized nanolignin from wheat straw by deep eutectic solvent [30]. Stewart et al. produced microlignin from the shrub species *Salix purpurea* [31]. Chen et al. produced lignin nanoparticles with spherical structure from herbaceous corn stover lignin [18].

Furthermore, there are different technical lignins used in the literature for micro- and nanolignin production. Richter et al. described the colloidal synthesis and interfacial design

of lignin micro- and nanoparticles from Kraft lignin and high purity organosolv lignin [32]. Chen et al. produced a lignin nanoparticle dispersion by ultrasonication treatment from alkali lignin [33]. Chen et al. synthesized an environmental responsive nanocapsule via a thermally induced interfacial thiol-ene crosslinking reaction in miniemulsion, from allyl modified sodium lignosulfonate [34]. Gupta et al. produced spherical lignin nanoparticles by acid precipitation with hydrochloric acid from low sulphonated light brown fine powder lignin (Lignin protobind-1000) [35].

In addition to the works which use commercial technical lignins, works using other lignins have been carried on. For example, Tian et al. synthesized lignin micro- and nanoparticles from cellulolytic enzyme lignin obtained from hydrolysis of industrial relevant, steam-pretreated, agriculture residue corn stover, hardwood poplar, and softwood lodgepole pine [36]. This work also compares three lignins isolated from the three main raw materials used for lignin production mentioned above.

3. Micro- and Nanolignin Preparation Methods

In recent years, different lignin micro- and nanoparticles from various resources were synthesized by different chemical/physical approaches. The following section provides a review of the approaches most commonly used in recent years to obtain lignin micro- and nanoparticles. **Table 3** summarises some of the production methods found in the literature with their main advantages and disadvantages.

Table 3: Chemical modifications for the synthesis of modified lignin nanoparticles.

Lignin source	Particle scale	Preparation method	Modification method	Advantages	Disadvantages	Ref.
Lignin isolated from black kraft liquor	Microparticles (310 nm)	^a P	Ball milling	-	Increased UV protection Greater thermal stability Better mechanical properties Improved O2 barrier properties Good antioxidant capacity	(37)
Black liquor from the soda pulping process of empty fruit bunches	Nanoparticles (83.6 nm)	P	Ball milling	-	Improved physical, mechanical, thermal, and water barrier properties	(29)
Lignin isolated from softwood kraft black liquor	Nanoparticles (< 100 nm)	P	High shear homogenization	-	Good particles homogenization Improved thermal stability Good dispersion	Little agglomeration (38)

Lignin source	Particle scale	Preparation method	Modification method	Advantages	Disadvantages	Ref.	
-	Microparticles	P	Grinding	Grafting with polylactic acid	Improved UV protection Improved barrier properties Improved migration activity Improved antioxidant properties	Reduction of tensile strength Reduction of elastic modulus	(39)
Lignosulfonate from black liquor of a mixture of species (poplar, berry, and fig)	Nano- and microparticles (440-25.5 nm)	P	Oil-in-water microemulsion and sonication	Acetylation with acetic anhydride	Nanoparticles were homogenized and spherical Nano-scale increased the acetylation efficiency and reduced the time and temperature of acetylation		(40)
Lignin isolated from black kraft liquor	Microparticles	P	Sonication	-	Low agglomeration Great stabilization Removing of impurities Improved antioxidant properties Improved thermal stability		(41)
Wheat straw lignin and Sarkanda grass lignin	Microparticles (100-500 nm)	P	Sonication	-	Ultrasound irradiation time and/or power can be modulated depending on the nature of lignin	Depolymerization	(42)
Softwood Kraft lignin	Nanoparticles (10-50 nm)	P	Sonication	-	Excellent colloidal stability Improved polarity that correlates with improved stability in water Excellent dispersion Improved mechanical properties Slight improvement of thermal stability		(43)
Alkali lignin	Nanoparticles	P	Spray freezing	-	Not require special equipment Scalability of the process		(44)
Alkali lignin	Microparticles (200 nm)	^b C	Acidic treatment with HCl	Acetylation with citric acid	Improved dispersion Improved aggregate size Increased ductility Colour reduction	Reduction of UV protection Reduction of antioxidant properties	[10]
Alkali lignin	Nanoparticles (60±15 nm)	C	Acidic treatment with HCl	Acetylation with citric acid, with sodium hypophosphite as catalyst	Increased thermal stability	Lower dispersibility in polar solvents	[45]

Lignin source	Particle scale	Preparation method	Modification method	Advantages	Disadvantages	Ref.
Alkali lignin	Nanoparticles (60±15 nm)	C	Acidic treatment with HCl	Esterification and etherification with citric acid	Higher thermal stability Higher antioxidant properties Excellent nucleation agent	Reduction of UV protection [46]
Sodium lignosulfonate	Micro- and nanoparticles (10-200 nm)	C	Acidic treatment with HCl	Esterification with maleic anhydride	Improved the tensile strength Improved elongation at break Improved tensile modulus Improved flexural modulus	[47]
Kraft water soluble lignin with a low sulfonate content	Nanoparticles (80 nm)	C	Acidic treatment with HCl	Phosphorylation with diethyl chlorophosphate and diethyl (2-(triethoxysilyl) ethyl) phosphonate	Lower reduction of thermal stability Increased ignition time	Small reduction of thermal stability [48]
Organosolv lignin from wheat straw, spruce and beech	Nano- and microparticles (67.8-1156.4 nm)	C	Precipitation by solvent-shifting	-	Antioxidant activity	Dark colour [49]
Organosolv lignin from spruce	Microparticles	C	Solvent extraction/evaporation	-	Regular and spherical	[50]
Organosolv lignin from <i>Salix purpurea</i>	Microparticles (100-200 nm)	C	Antisolvent precipitation with water	-	Inhibited agglomeration producing smooth, spherical and monodisperse particles	[51]
Alkali lignin from wheat straw	Nano- and microparticles (52-210 nm)	C	Antisolvent precipitation with water	-	Good stability for over two months Particle size easier to control	Depolymerization [52]
Soda lignin from a mixture of wheat straw and sarkanda grass (<i>Saccharum bengalense</i>)	Microparticles (128-560 nm)	C	Antisolvent precipitation with THF	-	Good stability	Purification step required [53]
Low-sulfonated lignin	Nanoparticles (50 nm)	C	Antisolvent precipitation with HNO ₃	-	Simple and inexpensive method Non-toxic for microalgae and yeast	Stable only at pH below 5 Agglomeration [54]
Kraft lignin and organosolv lignin	Nano- and microparticles (45-250 nm)	C	Flash precipitation with HNO ₃	-	Non-agglomeration Stable in aqueous dispersion Stable within a broad pH range Organosolv particles are strongly hydrophobic	[32]

Lignin source	Particle scale	Preparation method	Modification method	Advantages	Disadvantages	Ref.
Kraft lignin	Nanoparticles (38 nm)	C Supercritical antisolvent process with CO ₂	-	Purification step not required Uniform and nearly spherical particles Improved UV protection Dispersion stability Enhanced solubility Homogeneous thermal degradation activity	Relatively higher BET surface area	[55]
Kraft lignin, alkali lignin and organosolv lignin	Nano- and microparticles (30-2000 nm)	°O Aerosol-flow method	-	Excellent mechanical integrity Hydrophilicity Method scalable		[56]
Kraft lignin	Nanocapsules	O Self-assembly method (ethanol/water)	-	Not require any chemical modification, template, and core removal Low cost and totally green process		[57]
Bulk lignin extracted from coconut fibers	Nanoparticles (27.5 nm ± 2.7 nm)	O Microbial hydrolysis	-	Antibacterial properties UV blocking Antioxidant activity		[58]

"_a P: Physicochemical / _b C: Chemical / _c O: Others"

3.1. Lignin microparticles preparation

Microparticles refers to very small particles with sizes ranging from 0.1 to 1 µm. Various methods of lignin microparticle production have been reported in the literature, such as solvent or pH change, polymerization, ice segregation, aerosol processing, or mechanical processing, among others [9].

3.1.1. Physicochemical methods

Mechanical processing is a simple method to produce microlignin. This process has advantages over chemical routes because it is operationally simple and chemical-free. Gomide et al. produced microlignin using mechanical ultrasound treatment [41]. During the sonication process, bond breaking and chemical reactions occur in the lignin structure, strongly related to the phenomenon of cavitation, and in the case of polymers, ultrasound produces the formation of homolytic chain breakage, producing depolymerization with the formation of lignin monomers [42]. De Oliveira Begali et al., produced lignin microparticles from lignin isolated from black Kraft liquor by employing a ball mill [37].

3.1.2. Chemical methods

Different chemical treatments can also be used to obtain lignin microparticles. Cui

et al. employed pH change method for siliceous lignin microparticles synthesis [27]. In the described method, solution's pH value for sequential precipitation of lignin and silica from the alkaline treatment of wheat husks is modulated at ambient temperature, by the addition of sodium hydroxide (NaOH) and hydrochloric acid (HCl), followed by a self-associating reaction between lignin and silica in situ at temperature of 50-100°C.

Busatto et al. produced lignin microparticles by solvent extraction/evaporation techniques and by microfluidic techniques [21]. For the production of microparticles by extraction/evaporation methods they used ionic liquids and dichloromethane. Ionic liquids have the advantage of being a "green" and recyclable option in comparison to environmentally harmful organic solvents, as they have negligible vapour pressure and are non-flammable. A co-flow microfluidic device was used to prepare the microparticles by microfluidic techniques. Taverna et al. also prepared lignin microparticles by the solvent extraction/evaporation technique, using ionic imines [50]. On the other hand, Stewart et al., explored an antisolvent precipitation technique to produce lignin microparticles, in which an aqueous ethanolic solution of lignin was added to a much larger volume of distilled water under simple stirring [51].

3.1.3. Other preparation methods

Ago et al. developed an aerosol-flow method to synthesize spherical particles (30 nm–2 µm) with different lignins (Kraft lignin, alkali lignin and organosolv lignin) from the respective water or N-N-dimethylformami solution via in situ size fractionation. Resultant dry lignin particles displayed excellent mechanical integrity [56].

3.2. Lignin nanoparticles preparation

Nanomaterial refers to ultrafine particles with the sizes in the range from 1 to 100 nm. Nanomaterials have the basic characteristics including small size effect, surface effect, quantum size effect, macroscopic quantum tunnelling effect, and dielectric confinement. All these characteristics lead to many special physical and chemical properties, such as melting point, vapour pressure, optical properties, chemical reactivity, magnetism, superconductivity and plastic deformation, which make them ideal candidates for a large number of potential applications [59].

Lignin microparticles conversion into lignin nanoparticles holds promise for achieving sustainability [60]. Lignin nanoparticles have been prepared following various approaches, including CO₂ saturation, solvent exchange of pure lignin, acetylated lignin, and dialysis, flash precipitation, sonication, water-in-oil microemulsion techniques, or pH-lowering precipitation methods with an acid, among others [25].

3.2.1. Antisolvent precipitation method

One of the methods to extract nanolignin is through the action of an antisolvent. This method consists on the dissolution and re-precipitation of lignin. In this method, tetrahydrofuran (THF) and N-N-dimethylformamide (DMF) are commonly used as organic solvents to dissolve lignin, due to their excellent performance and because they do not affect lignin structure. It has the advantages of being a relatively simple method and minimal equipment requirement [11].

One of the antisolvents used is water. In this method, water acts as a non-solvent that reduces lignin degrees of freedom, causing the segregation of hydrophobic regions in compartments within the nanoparticles in formation. Then, dissolved lignin will be subjected to a dialysis process, on which the size of the lignin nanoparticles obtained will depend. Liu et al. prepared lignin nanospheres from commercial alkaline lignin using imidazole ionic liquids by adding water antisolvent [52]. Lievonen et al. also used this method to obtain spherical lignin nanoparticles from residual lignin obtained from Kraft softwood pulp, dissolving Kraft lignin in THF and subsequently introducing water into the system through dialysis that acts as an antisolvent [61].

Acids can also be used as an antisolvent. The principle of acids used as an antisolvent is analogous to water, based on lignin's solubility difference in organic solvents and acid solutions. It offers the advantage that lignin nanoparticles are easier to precipitate due to the large amount of H^+ present in the acid solution [11]. Acid precipitation method was developed to carry out the high-performance synthesis of lignin nanoparticles in polyol medium in different media, i.e., castor oil, ethylene glycol and water [25]. Lee et al. synthesized soda lignin nanoparticles by nanoprecipitation process in three different concentrations of THF with various molecular sizes of soda lignin obtained from sequential extraction with solvents [53]. Chollet et al. investigated the effect of using lignin at nanoscale as new flame-retardant additive for polylactide [48]. For this purpose, lignin nanoparticles were prepared from Kraft water-soluble lignin microparticles through a dissolution-precipitation process, from ethylene glycol solution adding a 0.25M aqueous HCl solution. For their part, Yang et al. considered different acidic conditions (HCl, H_2SO_4 , and H_3PO_4 at different pH) to produced lignin nanoparticles from a dissolution of pristine alkali lignin into ethylene glycol, reaching high yields (87.9 % in the case of HCl) [62]. In addition, another approach of precipitation with HNO_3 from an aqueous NaOH solution were used by Frangville et al., who prepared nanoparticles stable only at pH below 5 [54]. These nanoparticles showed excellent degradability and environmental compatibility, being non-toxic to microalgae and yeast.

Acid precipitation presents the disadvantage that lignin nanoparticles produced are susceptible to agglomeration. To overcome this problem, flash precipitation method can be used as an alternative, where the acid addition step for nucleation and nanoparticle growth occurs rapidly compared to the dropwise addition in acid precipitation [63]. Following this approach, Richter et al. synthesised lignin nanoparticles through instant precipitation with

nitric acid from a lignin polymer dissolved in ethylene glycol, using high purity Kraft lignin as precursor, which allowed the formation of nanoparticles in the size range 45-250 nm [32].

An alternative to water or acids as an antisolvent is the use of compressed/supercritical fluids for the formation of polymer nanoparticles. Supercritical fluids, such as supercritical carbon dioxide (CO₂), are of particular interest as they are cheap, abundant, non-toxic, non-flammable and environmentally friendly. In addition, supercritical antisolvent process has the advantage that nanoparticles can be produced without organic solvents, so no separation or further purification is required [63]. Lu et al. employed the supercritical antisolvent method for the preparation of nanolignin (144 ± 30 nm), using acetone as solvent and supercritical CO₂ as antisolvent, in order to improve the antioxidant activity of lignin [64]. Myint et al. developed nanoparticles from commercial Kraft lignin by the CO₂ antisolvent method, using DMF as an organic solvent to prepare the lignin solution [55]. As a result, they obtained uniform and nearly spherical nanoparticles with an average particle diameter of 38 nm.

3.2.2. *Physicochemical methods*

Another method used in the literature is ultrasonication, which makes it possible to obtain stable colloidal suspensions of small-sized lignin nanoparticles (10 to 50 nm) by means of a simple physical treatment. The main advantages of this method are its simplicity and easily. However, ultrasonication presents the disadvantage of broad size distribution [16]. García González et al. synthesized nanolignin from Kraft softwood lignin by means of ultrasonic treatment to obtain lignin-water dispersions with excellent colloidal stability [43]. Gilca et al. reported that ultrasonic irradiation obtained lignin nanoparticles in aqueous lignin suspensions (0.7%) for 60 min using two types of commercial lignin (wheat straw and Sarkanda grass) [42].

An alternative physical method used for the preparation of lignin nanoparticles is the spray freezing. This simple method does not require special equipment for lignin nanoparticle synthesis. Mishra and Ekielski employed this methodology to produce spherical lignin nanoparticles obtaining good results [44].

In addition to ultrasound and spray freezing, another physical method for the production of nanolignin is high shear homogenization. In this method lignin chemical bonds are broken under a high shear force. Nail et al. fully homogenized Kraft lignin particles with a wide distribution from large micron particles to nanoparticles with sizes less than 100 nm after 4 h of mechanical shear [38]. Rizal et al. used high-energy ball milling to produce lignin nanoparticles [29]. Life cycle analysis carried out by Teh et al. revealed that homogenization emits lower human toxicity potential and consumes a lesser amount of water than ultrasound

method [65].

3.2.3. Chemical treatments

Chemical treatments such as organosolv or acid treatment can also be used to obtain lignin nanoparticles. Among the organosolv treatments found in the literature, Adamczyk et al. extracted lignin from wheat straw, spruce and beech using an organosolv pretreatment with ethanol at temperatures between 160–220°C [66]. Resulting extracts were standardized to the lowest lignin content and precipitated by solvent displacement to produce lignin micro- and nanoparticles with mean hydrodynamic diameters of 1156.4 up to 67.8 nm. Regarding acid treatments, Buono et al. obtained lignin nanoparticles by HCl treatment of an alkali lignin precursor [67]. Gilca et al. presented a chemical method to modify lignin by hydroxymethylation to obtain nanoparticles [68].

3.2.4. Other preparation methods

The self-assembly method, as an upstream synthesis route, is also used to synthesize nanolignin. Li et al. used Kraft lignin to form hollow sphere nanocapsules by self-assembly method in a solvent mixture of ethanol and water [57].

Another alternative method is microbial hydrolysis. Juikar and Vigneshwaran used a controlled microbial hydrolysis process to produce nanolignin from bulk lignin extracted from coconut fibers, for which they used the ligninase-secreting fungal isolate, *Aspergillus nidulans* [58].

4. Modification Methods

Reactivity and surface properties of lignin micro- and nanoparticles can be effectively improved through functional groups chemical modification. Chemical functionalisation adds functionalities to the lignin structure to facilitate its incorporation into multiple potential applications, overcoming the molecule's limitations, such as low water solubility, which hinders its industrial processing. **Table 3** summarises some of the modifications found in the literature with their main advantages and disadvantages.

The most widely studied modification in the literature is the acetylation of lignin micro- and nanoparticles with different esterifying agents such as acetic anhydride, citric acid or maleic anhydride.

Moradi et al. performed modification of micro- and nanoligninsulfonate particles by acetylation, using a mixture of acetic anhydride/pyridine. Lignin microparticles were modified under the reflux condition at 75 °C for 72 h with a yield of 10%, while the yield of acetylated nanoparticles reached 50% at the same temperature after 24 h. Results demonstrated an increase

in efficiency and a reduction in acetylation time when lignin microparticles were converted into nanoparticles [40].

Cavallo et al. used unmodified and chemically modified lignin microparticles as nanofillers for extrusion-prepared polylactic acid films [10]. Chemically modified microparticles were acetylated or treated with citric acid. Chemical modification by acetylation and by treatment of the microparticles with citric acid had a significant effect on the polarity of the nanoparticles, showing a higher compatibility with chloroform. When used at 1 wt.%, they showed improved dispersion and reduction of aggregate size in polylactic acid, together with increased ductility. The aesthetic quality of the films was also improved by reducing the dark colour characteristic of lignin. However, the UV protection and antioxidant properties of the resulting composites were partially reduced compared to unmodified lignin nanofillers.

He et al. carried out citric acid modification of lignin nanoparticles, using sodium hypophosphite as catalyst [45]. A slight increase in thermal stability and an alteration of dispersibility in polar solvents were proved. Modified lignin nanoparticles have lower methanol dispersibility than the parent nanoparticles. In another work, He et al. esterified and etherified lignin nanoparticles with citric acid, and then blended them with poly (vinyl alcohol) at various loading levels (up to 10% by weight). Modified and unmodified lignin nanoparticles were used to make the nanocomposites. Results revealed that esterification and etherification of the lignin nanoparticles with citric acid induced intermolecular hydrogen bonds between the nanofillers and the poly (vinyl alcohol) matrix. Composites showed higher transparency, higher thermal stability and higher antioxidant properties than those made with the unmodified lignin nanoparticles. Modified lignin nanoparticles acted as an excellent nucleation agent, while the unmodified nanoparticles hardly contributed to nucleation. However, the UV protection was slightly lower for the modified lignin nanoparticles [46].

Yang and Zhong prepared maleic anhydride-modified lignosulphonate nanoparticles for their incorporation into butylene-co-terephthalate adipate by melt blending, to investigate their effect on the mechanical strength and rheological features of butylene-co-terephthalate adipate [47]. Results of the mechanical analyses indicated that the simultaneous incorporation of nanoparticles improved tensile strength, elongation at break, tensile modulus and flexural modulus. In contrast, rheological analyses indicated that the viscosity and modulus decreased with the incorporation of the nanoparticles, revealing that there is relatively low compatibility between modified lignosulphonate nanoparticles and butylene-co-terephthalate adipate in the melt state.

In addition, there are works in the literature that modifies lignin micro- and nanoparticles by grafting and phosphorylation.

Yang et al. realized grafting of star-like lignin microparticles onto polylactic acid by ring

open polymerization of L-lactide, initiating from the hydroxyl groups on lignin microparticles surface. By grafting polylactic acid onto the lignin microparticles, the barrier properties against migration and UV radiation as well as the antioxidant properties were improved. This revealed the satisfactory compatibility between lignin and polylactic acid, due to interfacial reactions between the epoxy groups of microlignin and the carboxyl and hydroxyl groups of both microlignin and polylactic acid [39].

Chollet et al. modified micro- and nanoparticles of lignin by phosphorylation in order to improve its flame retardant effect on polylactic acid, using diethyl chlorophosphate and diethyl (2-(triethoxysilyl)ethyl) phosphonate [48]. The use of diethyl (2-(triethoxysilyl)ethyl) phosphonate allows a higher phosphorus content to be grafted. While a drastic reduction of the thermal stability of polylactic acid is observed in untreated lignin micro- and nanoparticles, the functionalisation of the nanoparticles allows limiting this negative effect and improving the thermal stability of the composites compared to those in which unmodified lignin nanoparticles are added, being very close to that of unfilled polylactic acid. While non-functionalised lignin nanoparticles have no flame retardant effect, modified nanoparticles allow a significant increase of the ignition time by adding them in amounts between 5 and 10 wt.%.

5. Applications

Lignin micro- and nanoparticles are an environmentally friendly material, from natural and abundant sources, with antibacterial, antioxidant or ultraviolet absorption properties, as well as biocompatibility and biodegradability, which has led to a significant increase of their interest for different applications [9,11]. Their good qualities make them excellent substitutes for some compounds that are used in the manufacture of various current materials that are considered to be harmful to both the environment and humans [11]. Micro- and nanoparticles of lignin enhance the inherent properties of lignin because of their small size, which gives them a higher surface-to-volume ratio. This is often an advantage for their use, but sometimes becomes a problem, as the smaller particle size increases their surface energy, promoting their agglomeration [11]. Therefore, depending on the application, the modification of these surface properties could be necessary for the production of different materials. There are many and diverse uses of lignin micro- and nanoparticles which are currently investigated, including drug delivery [69], antioxidant agent [70], UV absorbent [71] and reinforcement material [72] among others. Lignin micro- and nanoparticles' applicability is a rising topic and proof of this is that in addition to many related scientific studies, there are also different scientific reviews dealing with the topic [11,59,60,72,73].

The use of lignin micro- and nanoparticles for the synthesis of biocomposites with improved properties is one of the most widely used applications available for lignin nanoparticles. The addition of nanolignin to materials mainly works as a reinforcement agent to

improve the mechanical properties of the final product, or as an additive to improve antioxidant, antibacterial and UV protection properties. Therefore, in the following discussion a summary of some of the latest and most relevant works related to this topic will be presented (**Table 4**). In the study conducted for this work, it has been found that the use of lignin nanoparticles is more widespread than that of microlignin. This is also evidenced here, as most of the referenced works discussed in this chapter use nanolignin. This may be due to the fact that the nanoparticles have a higher surface/area ratio, which enhances the abovementioned properties.

Table 4: Summary of some of the applications studied for micro and nanoparticles of lignin.

Raw material	Production method	Application fields	Lignin (%)	Results to be highlighted	Reference
Calcium softwood lignosulfonates	Commercial (Lignotech Ibérica)	Resol resins (phenolic foams)	1.5-3.5	<ul style="list-style-type: none"> - Improved material modulus and strength - Savings in blowing agent 	[74]
Alkaline lignin from furfural residues	Hydrochloric acidolysis	Pickering emulsion	0.05-1	<ul style="list-style-type: none"> - The styrene was surrounded by lignin microparticles - Variable styrene droplet size depending on the microlignin concentration - Microlignin recovery 	[75]
Softwood Kraft lignin	Mechanical homogenization	PLA bionanocomposites	2.5-10	<ul style="list-style-type: none"> - Increased the thermal stability of blends - Low lignin nanoparticle agglomeration 	[38]
Steam explosion lignin	Hydrochloric acidolysis	PLA bionanocomposites	0.1-3	<ul style="list-style-type: none"> - Higher nucleation effect (1% nanolignin) - Increased elongation at break for bionanocomposites with extruded nanolignin - Increased difficulty of matrix disintegration with 1 wt.% nanolignin - Delayed and slowed down disintegration 	[76]
Steam explosion lignin	Hydrochloric acidolysis	Wheat gluten nanocomposite films	0.1-3	<ul style="list-style-type: none"> - Reduction of material transparency - Excellent UV protection - Enhanced mechanical behaviour and thermal stability 	[77]
Steam explosion lignin	Hydrochloric acidolysis	Binary and ternary PLA films with chitosan	1-3	<ul style="list-style-type: none"> - Addition of LNP enhanced the tensile strength and Young's modulus of PVA - Significantly improved thermal stability of binary and ternary systems - Film with anti-microbial capabilities - Good UV protection - Very significant improvement of the antioxidant capacity in ternary systems, 	[78]

Raw material	Production method	Application fields	Lignin (%)	Results to be highlighted	Reference
Steam explosion lignin	Hydrochloric acidolysis	PLA ternary polymeric films with cellulose nanocrystals	1-3	<ul style="list-style-type: none"> - Improved transparency and UV light blocking ability - Increased crystallinity values - Superior strength and modulus compared to pure PLA and binary PLA systems - Demonstrated antibacterial activity 	[79]
Kraft lignin	Ultrasound treatment	Waterborne PU-Based (Nano)Composites	5-20	<ul style="list-style-type: none"> - Good dispersion of the nanoparticles in the matrix - Slight improvement of thermal stability - Improved mechanical properties 	[43]
Hardwood organosolv and DES ligninS	Prevalent dialysis method	PVA composite films	0.5-4	<ul style="list-style-type: none"> - Protection against UV radiation - Increased antioxidant activities of the films - Good adhesion between the nanoparticles and the matrix 	[70]
Steam exploded rice straw lignin	Hydrochloric acidolysis	Epoxy nanocomposite coatings	0.5-1.5	<ul style="list-style-type: none"> - Dissipation of the instantaneous energy during impact test due to the presence of nanoparticles - Enhanced adhesion with the metal - Increased hydrophobic behaviour Excellent anticorrosive behaviour 	[25]
Coconut kraft lignin	Microbial process with <i>Aspergillus oryzae</i>	Finishing of Cotton and Linen Fabrics	0.4	<ul style="list-style-type: none"> - High antibacterial activity - Improved UV absorption and antioxidant properties. - Fabrics preserved their properties during 10 washing cycles. 	[80]
Steam explosion lignin	Hydrochloric acidolysis	Phenol–formaldehyde resol resin	5-10	<ul style="list-style-type: none"> - Favour the thermal cure process - Reduction of curing temperature and curing heat - Addition of 5% nanolignin increased crosslink density and enhanced strength/shear strength 	[81]
Alkali lignin	Hydrochloric acidolysis	binary and tertiary films with metal oxide particles	1	<ul style="list-style-type: none"> - Improved UV protection capability - Nanolignin enhances thermal stability - Promotion of the formation of PLLA crystals - Provides antioxidant capacity to the material 	[82]

Raw material	Production method	Application fields	Lignin (%)	Results to be highlighted	Reference
Alkali lignin	Acidolysis	Polyurethane	1-7	<ul style="list-style-type: none"> - Increases tensile strength and Young's modulus. - Effectively improved UV protection - Improved both, mechanical behaviour and thermal stability of the PU - Improved hydrophobicity of the nanocomposites 	[71]
Alkali lignin	Acid hydrophobic fractionation	Composite film	0.19-1.37	<ul style="list-style-type: none"> - Enhanced biodegradability - Improved UV protection - Biodegradable and recyclable compounds 	[83]
Oil palm empty fruit bunch soda lignin	Mechanical homogenization	Emulsifier agent	2	<ul style="list-style-type: none"> - More stable emulsions - The emulsion was maintained for 20 months - Confirmation that lignin nanoparticles are non-toxic. 	[84]

5.1. Nanolignin as a reinforcement agent

Lignin has been an interesting material for use as a reinforcing filler in the preparation of polymer-based composites [85]. This is mainly due to its large number of functional groups, which are expected to generate both covalent and non-covalent interactions between the filler material and the polymer matrix. However, the compatibility between lignin and polymeric matrices has not been found to be optimal, so other alternatives have been studied, including the modification of lignin by functionalisation of its functional groups and the reduction of the particle size. The use of nanolignin as a reinforcing material instead of pristine lignin is due to the fact that nanoparticles have a higher surface-to-volume ratio, resulting in more efficient interactions with the polymeric matrix into which they are introduced [43]. This makes the dispersion in the matrix more homogeneous, resulting in more consistent biomaterials with improved properties. Several examples of the use of nanolignin as a reinforcement agent in different biomaterials will be presented below.

The first example of this is presented by Garcia et al., who carried out a comparison of the use of lignin and lignin nanoparticles as reinforcing agents in thermoplastic polyurethanes [43]. For this purpose, lignin nanoparticles were initially prepared by ultrasound treatment of softwood Kraft lignin. The application of ultrasound (20 kHz, 130 W, and 95% oscillation amplitude) for 6 h resulted in a water dispersion of lignin particles with a size range of 10 to 50 nm, resulting in a lignin-water dispersion with excellent colloidal stability. Subsequently, the bio-based materials were synthesised by incorporating both lignin and nanolignin into a water-based thermoplastic polyurethane matrix. The study of the results indicated that the use of ultrasound for the formation of lignin nanoparticles could induce a partial oxidation of lignin, leading to a higher concentration of -OH elements in the macromolecule, resulting in a

lower attraction between particles when they are dispersed in polar media. Characterisation of the nanolignin-based nanocomposites showed a homogeneous distribution and a high degree of dispersion in the polyurethane matrix. It was also demonstrated that the use of nanolignin slightly improved the thermal stability of the thermoplastics compared to systems synthesised with pristine lignin, especially at temperatures above 400 °C. Furthermore, tensile tests showed that increasing the nanolignin loading significantly improved the elastic modulus, tensile strength and elongation at break of the material compared to that synthesised with pristine lignin. This was correlated with the high surface/volume ratio of the lignin nanoparticles, which allows for more effective non-covalent interactions with the polymer matrix.

In their research, Del Saz-Orozco et al., evaluated the use of lignin nanoparticles as reinforcement in phenolic foams [74]. To produce the reinforced foams, the nanoparticles were mixed with the resin before synthesising the foams. The parameters evaluated in this study were the weight fraction of lignin nanoparticles (1.5-8.5 wt.%) and the amount of blowing agent (1.5-3.5 wt.%). From this study it was concluded that the use of nanoparticles improved the properties of phenolic foams, reporting values of up to 128% and 174% for compressive modulus and compressive strength, respectively. In addition, the use of nanolignin resulted in a saving of blowing agent up to 31% compared to the amount needed to produce a phenolic foam without the reinforcement. The phenolic foam that reported the highest mechanical performance ($\rho = 120\text{-}160 \text{ kg/m}^3$) was the one with 8.5% of nanoparticles incorporated. Finally, the results of this work also demonstrated that the foams reinforced with nanolignin showed mechanical properties similar or superior to those shown by other phenolic foams with different synthetic fibres (aramid or glass fibres) as reinforcing agent. It can therefore be said that lignin nanoparticles have great potential as reinforcing agents in phenolic foams, since in addition to being competitive in terms of mechanical performance, they also contribute to the reduction of the amount of foaming agent, which allows the manufacture of a more environmentally friendly material.

Wang et al. evaluated the use of lignin nanoparticles, both commercial alkaline lignin and lignin nanoparticles derived from acid hydrophobic fractionation (AHF) of poplar wood, for the production of a PVA film with improved properties [83]. For this purpose, nanocomposites of PVA and nanolignin were fabricated by direct mixing with the assistance of p-Toluenesulphonic acid (p-TsOH). The study of the film's properties led to the proposal of a reaction mechanism, where it was observed that, in the synthesis of the films, first a hydrophobic interaction between the lignin nanoparticles and the non-polar fraction of the p-TsOH molecule occurs, and then the p-TsOH/nanolignin aggregates were generated through the $\pi\text{-}\pi$ stacking of the toluene fraction. This new structure makes the hydrophobic lignin nanoparticles soluble in aqueous system, resulting in a colloidal suspension that when mixed directly with PVA forms films with improved properties. The resulting material was a highly

porous film with improved toughness. However, from the study of the thermal stability of the composite it was deduced that the use of p-TsOH decreased the stability, while increasing the amount of lignin nanoparticles significantly improved it. The new nanocomposites also had improved UV protection properties and a better biodegradability.

Nanolignin has also been used by Qi et al. in the preparation of dielectric and UV resistant polyurethanes [71]. In this research, they performed the evaluation of the use of nanolignin in a composite with good reprocessability and improved mechanical properties. The first step was to obtain the nanoparticles by an acidolysis process derived from the lignin produced by corn fractionation. From the analysis of the properties of the nanoparticles obtained, it was concluded that these particles were more reactive than pristine lignin, which is a promising result for their use as a reinforcing agent. To verify this, polyurethane nanocomposites were prepared using polyethylene glycol and diisocyanates in the presence of different contents of lignin nanoparticles (1, 3, 5 and 7 wt.%). The characterisation of the obtained materials confirmed different effects of the use of nanolignin on the properties of this material. The results of the tensile tests showed that the elongation at break exceeded 1000%, in addition to a general improvement of the mechanical performance of the polyurethanes, as well as a higher crosslinking density with the gradual increase of the nanoparticle content. Apart from the improvements in mechanical properties, it was also shown that the use of lignin nanoparticles as a reinforcement agent improved the resistance of the polyurethanes to UV radiation. These polyurethanes also revealed good thermal reprocessability due to the transcarbamylation reaction in the presence of the catalyst.

The improvement of properties due to the addition of nanolignin has also been studied in adhesives. Yang et al. conducted a study on the use of lignin in phenol-formaldehyde resin as an adhesive and evaluated the differences in the final properties provided by the use of micro- or nanoparticles of lignin [81]. Preliminary results showed that the use of a small amount of lignin is enough to improve the curing phase of the product, however, there are significant differences in the final properties. This is largely due to the higher specific surface area and reactivity of the lignin nanoparticles that promote the reaction between its phenolic units with the formaldehyde leading to a better dispersion of the lignin. Thus, the results showed that the addition of 5% by weight of lignin nanoparticles improved the shear strength from 8.7 to 10.9 MPa, and also resulted in better adhesion performance. This opens up the possibility of using nanolignin to replace traditional adhesives.

5.2. Nanolignin as an antioxidant and UV-blocking agent

In addition to the advantages derived from the use of lignin nanoparticles on the mechanical behaviour and thermal stability of bio-composites [59], the use of these particles can also provide other very interesting benefits for different biomaterials. Nanolignin particles

have been verified to have antibacterial and antioxidant properties [86], being these activities higher than those reported for lignin of normal size. This is mainly due to the enhanced surface chemistry in nanoparticles due to their higher phenolic content and lower molecular weight [87]. In addition, nanolignin has a higher surface/volume ratio, which favours the appearance of a higher number of functional groups (hydroxyl, carboxyl or carbonyl) on the particle surface, making them more active nanoparticles [63], which enhance the properties of lignin. This benefit has been observed not only in terms of higher antioxidant capacity of lignin, but has also been demonstrated for its increased antibacterial capacity and UV protection ability [78]. These properties are of special interest for a variety of applications, especially in materials for use in the food and pharmaceutical industries. For these reasons, some of the latest work showing the benefits of combining the advantages of composites and nanolignin is presented below.

Tian et al. evaluated the improvement in the properties of transparent polyvinyl acetate (PVA) polymer with the addition of lignin nanoparticles from different sources, both synthesised by the self-assembly method [70]. The inherent properties of nanolignin particles (UV protection, antioxidant capacity and biocompatibility), as well as their high content of phenolic hydroxyl groups on the surface, suggest that their use will contribute to the improvement of the properties of PVA films. This was confirmed in this work, obtaining transparent and flexible PVA/nanolignin films with improved UV protection, biocompatibility and antioxidant capacity. From the study of the properties of the elaborated films, it was deduced that they are conditioned to the lignin source, although in both cases UV protection and antioxidant capacity of approximately 80% at 400 nm and 160 $\mu\text{mol Trolox/g}$ were achieved using only 4% of nanolignin. Finally, improved mechanical and thermal properties of the PVA/nanolignin films were also demonstrated due to the good adhesion between the hydroxyl groups of the nanoparticles and the PVA matrix.

Following with the advantages of the use of nanolignin in biocomposites, it is interesting to consider the study carried out by Lizundia et al. [82]. In this study an evaluation of the use of lignin nanoparticles to improve the antioxidant and antibacterial properties of a poly(l-lactide) (PLLA) biocomposite was conducted. For this evaluation, binary and tertiary PLLA nanocomposites with nanolignin (1%) and/or different metal oxides (0.5%) were synthesised by solvent casting. In general, it was observed that the use of lignin nanoparticles resulted in films with smoother and more hydrophobic surfaces. In addition, it was also shown that the use of nanolignin improved both the antioxidant and antibacterial properties of PLLA polymers with and without metal oxides. Ternary compounds showed enhanced antioxidant capacity due to the synergistic effect between lignin nanoparticles and metal oxides. In terms of ultraviolet protection, the incorporation of nanolignin provided UV protection, which allowed the ternary mixtures to improve the results reported for other inorganic nanoparticles. These results support

the great potential of lignin nanoparticles for use as a renewable additive in materials which require antibacterial and antioxidant properties.

Apart from biocomposites, the following work performed by Juikar et al. illustrates the benefits of the use of nanolignin in the preparation of natural fabrics. In this work they studied the use of microbial nanolignin (size less than 50 nm) to improve the surface properties of linen and cotton fabrics using the dry curing method for fabric preparation [80]. For this purpose, the fabrics, after bleaching, were treated with a 0.4% solution of nanolignin, with 4% of an acrylic binder, and then dried (100 °C, 5 min) and cured (150 °C, 3 min). This treatment improved the multifunctional properties of the fabrics up to the tenth washing cycle. The two studied fabrics, after lignin nanoparticle treatment, showed antioxidant properties, increased UV protection and an antibacterial activity of 100% against the two tested bacteria. This work provides the basis for the possible use of nanolignin as a coating for the production of fabrics with improved properties.

5.3. Others

Apart from the advantages of using nanolignin either as a reinforcing material or as an additive to improve the above-mentioned properties, these nanoparticles have also proven to be very promising for use in the stabilisation of emulsions and in the pharmaceutical industry as drug carriers.

Nanoparticles derived from lignocellulosic biomass, due to their biocompatibility, biodegradability and non-toxicity, are potential materials for use as drug delivery agents. The interest in the use of nanolignin as a drug delivery agent has been rising in recent years, mainly due to the fact that these nanoparticles are amphiphilic, which allows them to interact with both hydrophilic and hydrophobic drugs. Wiyaja et al. have recently published a comprehensive literature review on this topic, which brings together the latest and most relevant studies in the field [69]. The interest in the use of lignin micro- and nanoparticles in biomedicine is not limited to their use as drug delivery, there are other promising biomedical applications such as hydrogels, electrospun fibres and 3D printing for the elaboration of organ models and/or customised scaffolds [73].

Pickering emulsions are currently being explored for the application of lignin nanoparticles. This type of emulsion has been widely explored in pharmaceutical and cosmetic applications, as well as in the food industry. The amphiphilic property exhibited by nanolignin particles makes this material a candidate for application as an emulsifying agent, especially in Pickering emulsions, which is based on the use of solid particles as stabilisers. One interesting example is the study conducted by Wei et al. which investigated the use of lignin microparticles in a styrene/water Pickering emulsion [75]. In that study, it was observed that the particle size of the styrene droplets could be adjusted by varying the concentration of lignin

microparticles, obtaining droplet sizes between 20-58.9 μm . Moreover, it was demonstrated that the microlignin could be recovered and reused again as a stabiliser, which is an advantage. A good example of this application is the one studied by Yaqood et al. In this work, they prepared nanolignin particles from a soda treatment using mechanical homogenisation for their use as an emulsifying agent [84]. The preparation of this emulsifying agent was carried out by dissolving 2 g of the prepared nanolignins in 10 mL of NaOH (1 M) and then adding water. This agent was tested in oil/water emulsions by adding 2% of the emulsifying agent to the mixture. Among the different particles tested, those that had been produced at a speed of 12,400 rpm of the homogeniser (LNP12) were the ones that gave the best results, obtaining a value of $|-32.0|$ mV in the zeta potential measurement. The images obtained from the CPM test also confirmed the good performance of these particles, as the formation of smaller and more uniform droplets were detected. Finally, from the kinetic analysis of the samples, it was concluded that LNP12 was more stable than the rest, allowing the emulsion to be maintained for up to 20 months. These results, together with the absence of toxicity of the nanoparticles measured in this work, confirm their potential to be used as an industrial emulsifying agent.

6. Conclusions

This chapter compiled the main sources of lignin used for the production of micro- and nanoparticles, the main methods for their synthesis, the chemical modification methods for their functionalisation, as well as their most interesting potential applications.

Lignin is an abundant and low-cost source, mainly produced as a by-product in pulp and paper industry. As mentioned above, there are many examples of different methods used for the production of micro- and nanolignin, which allow uniform and stable particles to be obtained. The choice of micro- or nanoscale will depend on the suitability for the specific application for which it is to be used. It is important to explore methods for lignin micro- and nanoparticles production that are simple, environmentally friendly, low-cost and can be implemented on a large scale, in order to expand high-value use. It is also important to study new functionalisation strategies for the micro- and nanoparticles obtained in order to broaden their applicability in different potential applications.

Micro- and nanolignin materials can be used in promising applications with high added value, such as their use as a reinforcing agent or as an antioxidant and UV-protective agent. Due to their numerous advantages compared to synthetic polymers, micro- and nanoparticles of lignin could play an important role in the global market. Therefore, more synthesis routes need to be explored, more interesting properties need to be found and more potential applications need to be developed. It is expected that lignin micro- and nanoparticles will show great progress to enable their application in several fields in the near future.

7. References

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