

Lignin Modification and Its Application in Polymeric Materials

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Abstract Polymer materials are widely used in modern industry and life, and their performance and functional requirements are constantly increasing. Lignin, as a rich renewable resource in nature, a by-product of the pulp and paper making and bioenzymatic processes, is a natural polymer material with good stability, and mechanical and chemical properties. Therefore, the application of lignin in polymer materials can improve the strength, stiffness, heat resistance, weather resistance and chemical resistance of the materials, providing a new way of application of polymer materials. However, the structure and chemical properties of lignin isolated during industrial production have changed considerably, and its use as a polymer is associated with problems of dispersion and poor compatibility, so it is necessary to modify lignin to improve compatibility with natural or synthetic polymers and to expand the range of lignin applications. Starting from the structure and properties of lignin, this paper explores a variety of lignin material modification methods, such as chemical reactions and physical blending to compound lignin with phenolic resins, polyurethane, polyolefins and other materials. Applications of lignin composite functional materials in new functional materials, energy storage materials, environmental protection and medicine are also presented, which are of great importance in promoting high performance and sustainable development of lignin materials.

1 Introduction

The increasing depletion of fossil fuels has raised concerns about climate change and the energy crisis, and the search for renewable and clean energy sources has become a hot topic. As a natural polymer material, lignin is the most abundant source of renewable organic carbon in nature. With its simple structure, stable properties and wide range of sources, it is widely used in the enhancement, modification and functionalisation of polymer materials. In recent years, scientists have conducted a great deal of research, mainly focusing on the conversion of biomass feedstock into biofuels and value-added products. Industrial lignin is mainly derived from by-products in the paper industry. The pulp and paper industry obtains around 50 million tonnes of lignin by-products per year, of which more than 95% is discharged and discarded, or directly burnt after treatment, with very little being effectively utilized [1]. Although biorefining has been extensively researched, there is still a shortfall in economic viability when scaling up production, and the lignin separation and modification will remain the focus of future biorefineries.

In nature, lignin is an amorphous phenolic polymer with a stable steric conformation consisting of a benzene propane structure linked by a carbon-carbon bond to an ether bond. It is randomly branched and cross-linked with cellulose and hemicellulose. Lignin polymers are mainly composed of three different structural units, namely p-coumaryl alcohol, pineal alcohol and mustard alcohol (Fig.1).

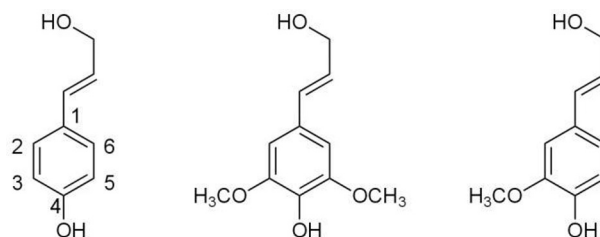


Fig.1. Three different phenylpropane monomer molecules constituting lignin (Picture credit: Original)

Grass lignin basically consists of all three of these units, with softwood (coniferous) lignin containing mainly pine alcohol and hardwood (broadleaf) lignin containing pine alcohol and mustard alcohol. Depending on the type and content of monomers, the bonds formed during polymerisation are different, with coniferous lignin containing more carbon-carbon bonds than broadleaved lignin. The diversity of structural unit content and bonding makes it extremely difficult to determine the exact chemical structure of each isolated lignin [2]. Lignin molecules contain a wide range of functional groups, have high UV absorption, antibacterial, antioxidant, biocompatible and potentially reactive properties, and are renewable, biodegradable, abundant and cost-effective, making them promising for a variety of applications.

This paper will start with the structure and properties of lignin-based polymers, discuss the modification methods of lignin in polymer materials, and introduce lignin composite functional materials, lignin carbon functional materials and their applications and exploration in new functional materials, energy storage

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materials, medicine, etc., and make certain generalization and outlook on their application prospects and development trends.

2 Lignin-based polymers

2.1 Lignin-based polyurethane

Polyurethane materials are prepared by reacting the active hydroxyl groups of lignin with isocyanates. Depending on their properties, polyurethanes made from lignin and its derivatives can be used as engineering plastics, adhesives, foams, films, etc. The main factors affecting the properties include the type of lignin, its content and molecular weight, the type of isocyanate and the NCO/OH molar ratio. In the preparation of lignin polyurethanes, the lignin molecule acts as both a cross-linker and a hard chain segment, and the increase in lignin molecular weight increases the cross-link density. The key to the preparation of lignin polyurethanes is to increase the degree of the chemical reaction between the two and to increase the number of alcohol hydroxyl groups, which can be achieved by hydroxyalkylation and caprolactone derivatization reactions.

Luo et al. prepared polyurethane foams by reacting lignin with methyl diphenyl diisocyanate, showing that lignin can react with -NCO through active hydroxyl groups, which was simple and resource-saving, and that the mechanical properties, thermal properties and biodegradability of the foams obtained were improved 3. Li et al. used lignin as a raw material to prepare high-strength and high-tenacity polyurethane 4. The thermal stability and glass transition temperature increased with the increase in the amount of lignin, and Young's modulus, tensile strength and strain at break reached the maximum at a molecular weight of 600 and a dosage of 40%, and the lower the molecular weight of lignin, the better the dispersion in the polyurethane. Zhu et al. used enzymatic lignin to replace some petroleum-based polyether polyols to prepare bio-based polyurethane foam 5. The effect of the amount of lignin on the morphology and mechanical properties of the foam was studied, and the compressive modulus, compressive index and compressive strength were greatly improved at higher lignin content, which is an effective method to improve the mechanical properties of polyurethane foam.

2.2 Lignin-based phenolic resins

Phenol, the raw material for phenolic resins, is costly and non-renewable. Lignin, with a similar structure to phenol, is an ideal material that can replace phenol in the preparation of phenolic resins. Lignin can react with formaldehyde both as a phenol under alkaline conditions and as an aldehyde with phenol under acidic conditions. Lignin phenolic resins can be prepared in three ways 6. (1) by adjusting the acidity and alkalinity to control the reaction sequence between lignin and phenol or formaldehyde; (2) by reacting lignin with methyl phenolic resins to prepare phenolic resins, which can produce better chemical affinity through copolymerisation and cross-linking; (3) by adding lignin

during the curing reaction of phenolic resins, a graft copolymer is formed between the components. The lignin acts as a chain expander. The properties of the lignin phenolic resins prepared by these three methods decrease in sequence, but the amount of lignin can be increased gradually. In addition, lignin can be blended with phenolic resins. Although no chemical reaction occurs between the components, structural similarities and interactions between polar groups lead to partial compatibility between the components.

Zhao et al. prepared phenolic resins by condensation of enzymatic lignin with phenol and then with formaldehyde 7. Scanning electron microscopy analysis showed that compared with the pristine unmodified phenolic resin, the structure of phenolic resins modified by enzymatic lignin was more complete, with denser and more uniform voids and smoother surfaces. The introduction of lignin into the phenolic resin therefore significantly improved the insulation and modulus at high temperatures while maintaining the mechanical properties and thermal stability of the material.

However, the large size of the lignin molecule and the steric hindrance on the aromatic ring have the disadvantage of insufficient reactivity, and even prevent the normal condensation of phenol and formaldehyde. Although it can be compensated by methylation or hydroxymethylation-modified lignin, it is still difficult to completely replace phenol.

2.3 Other lignin-based polymers

Epoxy resins are thermosetting polymers consisting of monomers with at least one epoxy group. The epoxy group can be homopolymerised using anionic or cationic polymerisation or copolymerised with co-monomers such as amines, acids, anhydrides, alcohols, thiols and phenols 8. Lignin itself does not contain epoxides, but its macromonomer phenolic structure can be used to synthesise polyurethanes and polyesters, or as a cross-linking agent to synthesise epoxy resins. The reaction of epoxy resins with lignin components is usually catalyzed by small amounts of amine, or amine is added quantitatively to the reaction as an additional cross-linking agent. Liang et al. synthesised epoxy resins with ammonium polyphosphate, melamine and alkali lignin in a one-step reaction, and the addition of 20% flame retardant resulted in an increase in carbon residue, limiting oxygen index values and a significant increase in flame retardancy 8. It also has the advantage of a low heat release rate and shows excellent smoke suppression.

Lignin can also be used as a reinforcing agent in rubber instead of conventional carbon black, saving resources. The hydroxyl groups in lignin will form hydrogen bonds with the electron clouds of the double bonds in the rubber to achieve reinforcement, while the smaller the particles of lignin, the better the compatibility with the rubber and the better the reinforcement effect. The dispersion of lignin in rubber is influenced by the particle size, structure and purity of the lignin. For example, the hydrogen bonding between lignin molecules makes it easy to aggregate, and the larger the particle size of lignin, the more uneven the dispersion will be. The way to improve the compatibility between

the two is to modify the lignin or make the lignin fine-grained.

3 Material modification methods and performance optimisation

The structure and chemical properties of lignin isolated during industrial production have changed considerably and have disadvantages such as poor water solubility, high viscosity and poor dispersion properties. Industrial lignin has problems such as poor dispersion and compatibility when used as a polymer. The modification of lignin improves its physicochemical properties, gives it excellent properties for specific applications, improves its compatibility with natural or synthetic polymers and also extends its application areas.

3.1 Lignin blended polyolefin

Lignin and its derivatives can modify olefin polymers such as polyethylene (PE) and polypropylene (PP), polyvinyl chloride (PVC), polymethyl methacrylate (PMMA), polyvinyl alcohol (PVA) and ethylene vinyl acetate copolymers by blending. Lignin, in addition to its reinforcing effect, also improves the thermal stability and resistance to photodegradation of the material. PE/lignin blends are enhanced by up to 30% (wt) lignin content through the use of ethylene-acrylic acid copolymer bulking agents in combination with titanate, which improves the mechanical properties of the material and increases the breakdown voltage.

In the blending of lignin with PE and PP, Kharade et al. added ethylene-acrylic acid copolymer as a bulking agent, which improved the compatibility between lignin and polyolefin and significantly improved the mechanical properties of the blended materials 10. Yue et al. prepared polyvinyl chloride (PVC)/wood flour composites 11. The study showed that the interfacial bond between the modified lignin and the composites was enhanced, the lignin was more uniformly dispersed, and the tensile and impact strengths of the composites were improved.

3.2 Chemical modification of lignin

3.2.1 Graft copolymerisation modification

Graft copolymerisation modification of lignin is a widespread and important method of giving new properties to lignin according to the requirements of the application. The graft copolymerisation reaction generally involves the polymerisation of monomers on the lignin structure in the presence of an initiator, resulting in a polymer with the copolymer as the main chain and the homopolymer as the branched chain, as shown in Figure 2.

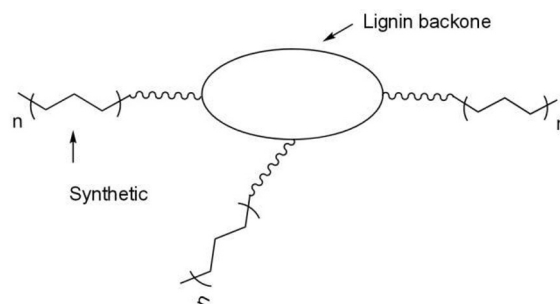


Fig. 2. Schematic diagram of the lignin graft copolymerisation reaction (Picture credit: Original)

Atom transfer radical polymerisation (ATRP) is a rapidly developing free radical polymerisation technique in recent years. Surface modification of lignin using ATRP can provide lignin with multiple functions by grafting different functional monomers onto the lignin surface, which has important application values.

Chung et al. prepared a novel lignin graft copolymer using the ATRP method, with lignin as the active centre of the reaction and polystyrene and poly(*n*-butyl acrylate) grafted onto lignin in a controlled process and with a conversion of 25% 12. Li et al. used $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as a catalyst to synthesise lignin-based copolymers with styrene and methacrylate by the ATRP method 13. The surface activity and structure of the lignin changed considerably after the modification, and the molecular weight distribution of the polymer was narrower, indicating that the graft copolymerisation reaction of lignin could be catalysed by Fe^{3+} ions and the molecular weight obtained could be controlled, which is an effective and environmentally friendly method. Youe et al. grafted acrylonitrile into the lignin structure, using azobisisobutyronitrile (AIBN) as the initiator 13. The study showed that as the amount of initiator increased, the lignin grafting rate increased and the copolymer obtained had better heat resistance than the acrylonitrile homopolymer, which could be used as a copolymer for the preparation of lignin-based carbon nanofibre composites.

3.2.2 Functional group modification

Lignin is often functionalised to create new active sites and to aid in the synthesis of new macromolecular materials, making it easier to incorporate lignin more firmly into new materials. Although lignin has many functional groups (e.g. hydroxyl or phenol), the high crosslink density or spatial resistance of lignin often obscures these potential active sites 13. Functionalisation can improve the processability of lignin by reducing its brittleness and increasing its solubility in organic solvents. Functionalised lignin can be chemically modified to add reactive groups not present in natural lignin or to enhance functional groups available on natural lignin scaffolds, which are essential for the development of the corresponding polymeric materials, and can be made more reactive in polymeric materials by chemical methods such as hydroxymethylation modification, phenolisation modification and sulphonation modification.

Lignin can be hydroxymethylated in alkaline media (Fig 3), and hydroxymethylation can occur either on the aromatic ring or on the aliphatic side chain. Priscila et al. reacted lignin obtained by delignification of acetylacetone and formacell from giant cell eucalyptus wood chips with formaldehyde in alkaline media [16]. Dynamic differential scanning calorimetry (DSC) tests were performed after hydroxymethylation to determine the relative reactivity of the two lignins. And TGA results showed that the hydroxymethylated lignin was thermally stable at temperatures up to 250 °C, while the pristine lignin began to decompose after temperatures reached 200 °C. The hydroxymethylation of acetylacetone lignin in sugarcane bagasse was also investigated by Fourier transform infrared spectroscopy (FTIR) at temperatures ranging from 40 °C and times ranging from 0.25 to 8 h. Principal component analysis (PCA) of the spectra determined that the addition of formaldehyde to the lignin fragments was completed within 4 h. After the addition, only the condensation of fragments occurred, forming a methyl-order cross-linked resin.

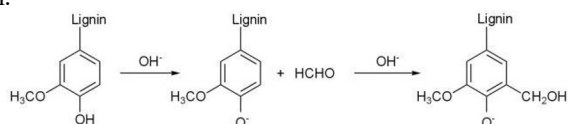


Fig. 3. Hydroxymethylation of lignin (Picture credit: Original)

In the lignin structural unit, the alpha-C atom, located on the side chain opposite the phenolic hydroxyl group, is subject to the phenolic hydroxyl group induction effect and is more reactive, and is more likely to react chemically with phenol or its derivatives. The phenolic modification of alkali lignin refers to the chemical reaction between alkali lignin and phenol under certain conditions (Fig.4), after which a phenol group is introduced into the lignin molecule, increasing the number of reactive sites.

The phenomenon of change from lignin to lignin sulphonate that occurs in the pulp and paper process is called lignin sulphonation (Fig.5). Sulphonation modification refers to the introduction of sulphonate groups on the side chains of lignin and is generally carried out by high temperature sulphonation, whereby lignin is reacted with Na_2SO_3 or Na_2SO_3 and HCHO at 140 °C to 200 °C to obtain sulphonated alkali lignin. Yasuda et al. used acid insoluble lignin as a raw material and continued sulphonation after phenolisation, thereby introducing sulphonate groups on both aromatic rings, significantly improving the efficiency of sulphonation, resulting in a water-soluble lignin product [16].

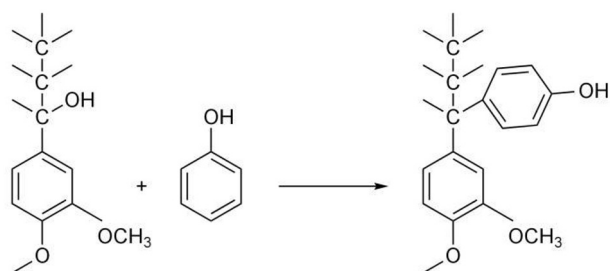


Fig. 4. Lignin phenolisation reactions (Picture credit: Original)

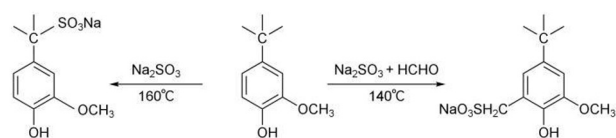


Fig. 5. Sulfonation modification of lignin (Picture credit: Original)

3.3 High performance of lignin modified materials

Lignin molecules tend to agglomerate due to the tendency of the phenolic hydroxyl groups to form intramolecular hydrogen bonds, leading to difficulties in material modification by chemically modifying the nucleus-dobby structure to prepare an astral structure or by transforming the spherical structure of lignin into a linear structure. Modification of lignin, such as improving its water solubility, surface activity, dispersibility and other properties, can give lignin materials a wider range of properties and applications. Controlled chemical modifications of the lignin structure, by increasing its chemical reactivity or controlling its aggregate state structure and the strength of the interaction forces, can lead to an optimised design of the material properties at the molecular level. At the same time, lignin-modified materials are fully characterised by high performance.

Biodegradability of lignin. Although the rate of lignin degradation is extremely slow under normal conditions, this process can be accelerated by the addition of certain small molecules or by the use of specific strains of bacteria (such as white rot bacteria), so that its degradation cycle can be controlled to some extent. High lignin content fillings have also been proposed as it has been shown that the biodegradability of lignin-based polymers generally increases with increasing lignin content.

Excellent filler reinforcement. Compared to the commonly used carbon black or other inorganic reinforcements, lignin has significant advantages as an excellent filler reinforcement for rubber and polyolefin. Because lignin has a large number of different types of reactive functional groups, it can be chemically modified to achieve different physical properties. It has been found that the construction of special network structures, the formation of star-shaped copolymers and the modulation of the strength of intermolecular interactions can lead to significant improvements in material properties. In addition, the use of lignin as a filler material can be investigated to reduce the economic cost of the application.

Flame and heat resistance. The methoxy-to-hydroxyl group on the lilac base benzene ring of the lignin molecule forms a spatially site-resistant structure, and this hindered phenolic structure can trap the free radicals generated during thermal-oxidative ageing and terminate the chain reaction, thus improving the thermal-oxidative stability of the material.

Shielding against ultraviolet radiation. Lignin has the ability to shield UV radiation due to its numerous aromatic rings. After using nitrocellulose and polyurethane graft interpenetrating network coatings to

coat a regenerated cellulose film, the transmission of UV light through the film material was found to drop to zero, which means UV light was completely shielded. Qian et al. developed lignin as a natural polymer sunscreen for use in high-end sunscreen skincare and found that the addition of a small amount of lignin significantly improved the sunscreen performance, and the sunscreen performance increased rather than decreased after sunlight irradiation 18.

4 Application of lignin in polymer materials

4.1 Application of lignin for energy storage at electrodes

The increasing depletion of fossil energy sources and their non-renewability are no longer sufficient to meet the development needs of the battery industry, and the use of environmentally friendly, cheap and safe biomass materials for battery manufacturing has become an urgent development direction. Lignin is a polymer containing a benzene ring, which has excellent electroactive redox properties and an abundance of active functional groups. Industrial lignin can be converted into high-performance carbon-based materials for the assembly of lithium-ion batteries because of its inherent quinone structure, which can provide sufficient charge density to meet the requirements of unstable electrical energy storage 19. Hydrolysed lignin (HL) can be physically activated in one step to produce graphitized carbon. Nikolenko et al. found that HL pyrolysed into layered carbon products at different temperatures could be used as a cathode material for primary current sources 19. Constant current discharges in lithium batteries at 0.5-3.0 V and a current density of 100 μ A/cm showed that the specific capacity of the thermally activated derivatives was 845 mA·h/g, whereas untreated lignin produced only 190 mA·h/g.

Lahiri et al. demonstrated a biodegradable hybrid zinc ion battery with a polymer/lignin composite electrode as the cathode, zinc metal as the anode and bio-ionic liquid as the electrolyte 21. The lignin undergoes electrocatalytic oxidation during the charging process of the battery, generating additional energy and ultimately achieving a higher discharge capacity than the charging capacity.

Supercapacitors are electrochemical energy storage devices with high power density, fast charging and discharging rates and good cycling stability, which are in the range of energy and power density between batteries and general capacitors. Zhang et al. activated lignin by carbonisation to produce layered porous carbon 22. The unique hierarchical structure of lignin provides good ion transport pathways and high ion-accessible surface area, thus enhancing the electrochemical performance of supercapacitor electrode materials.

4.2 Lignin in carbon fibre applications

Carbon fibre based polymer composites offer unique reinforcement capabilities, combining a high strength to

weight ratio with excellent fatigue resistance. However, carbon fibre precursor materials are too expensive and lignin is the best alternative to carbon fibre precursor materials.

Lignin composite with carbon fibres has great promise for research into adsorbent materials. Multiscale carbon superparticles (SPs) are obtained by combining soft-template lignin nano- and microbeads with cellulose nanofibres (CNFs). After oxidative thermal stabilisation of the lignin/CNF structure, Zhao et al. investigated the interparticle connections and nanoscale network in SP and found that it has high mechanical strength and large surface area, so carbon SP provides graded channels that are well suited for adsorption of CO trapping sites for the graded channels of adsorption, and the advantage of relatively low-pressure drop 23. In addition, carbon SP does not require doping with heteroatoms (e.g. N) to effectively absorb CO and is suitable for regeneration after multiple adsorption/desorption cycles.

Modifying the structure of lignin-based carbon fibres can significantly improve their thermal stability to suit their application in the field of ablative materials. Xu et al. synthesised lignin-based carbon fibres (CFs) decorated with carbon nanotubes (CNTs) to produce carbon fibre precursors by electrostatic spinning of lignin/acrylonitrile solutions 23. The precursors were then pyrolysed to obtain CF, followed by the growth of CNTs on CF and the final synthesis of CF-CNT hybrid structures. The CF-CNT heterostructures produced using a palladium catalyst showed the highest thermal stability at 850 °C.

4.3 Application of lignin in drug-loaded microcapsules

The unstable nature of the drug results in a short retention time, thus requiring higher concentrations and repeated applications to achieve the desired control effect. Avermectin (AVM) is a commonly used low-toxicity, broad-spectrum and highly effective biocide, but it has poor light stability and is susceptible to microbial degradation. A variety of lignin-based drug-loaded microcapsules have been successfully prepared, and Li et al. used lignin sulfonate and cetyltrimethylammonium bromide to self-assemble to form colloidal spheres to encapsulate AVMs, which also significantly improved the photolytic properties of AVMs due to the large amount of UV-absorbing lignin in the wall material 25.

Oral drugs are widely used in clinical practice due to the advantages of easy administration, low cost and long-term administration. However, most orally administered drugs suffer from poor water solubility, low bioavailability and no target tissue selectivity, which seriously affect the therapeutic effects of the drugs. Li et al. selected the hydrophobic drug ibuprofen as a model drug and lignin complex as a wall material and prepared lignin-based drug-loaded colloidal spheres by self-assembly in an ethanol/water solvent mixture (Fig.6) 26. The drug-loaded colloidal spheres were effective in blocking the release of ibuprofen in simulated gastric fluid, and the retention rate of ibuprofen was >75% within 24 h. In the simulated intestinal fluid, ibuprofen was released rapidly and continuously, with 90% release

within 12h, meeting the requirements for the release performance of an oral drug carrier. By using green, non-toxic and pH-responsive lignin as raw material for the preparation of human oral drug microcapsules, the drug can be released at a fixed point in the human intestine,

bringing a very high added value to the application of lignin colloidal spheres.

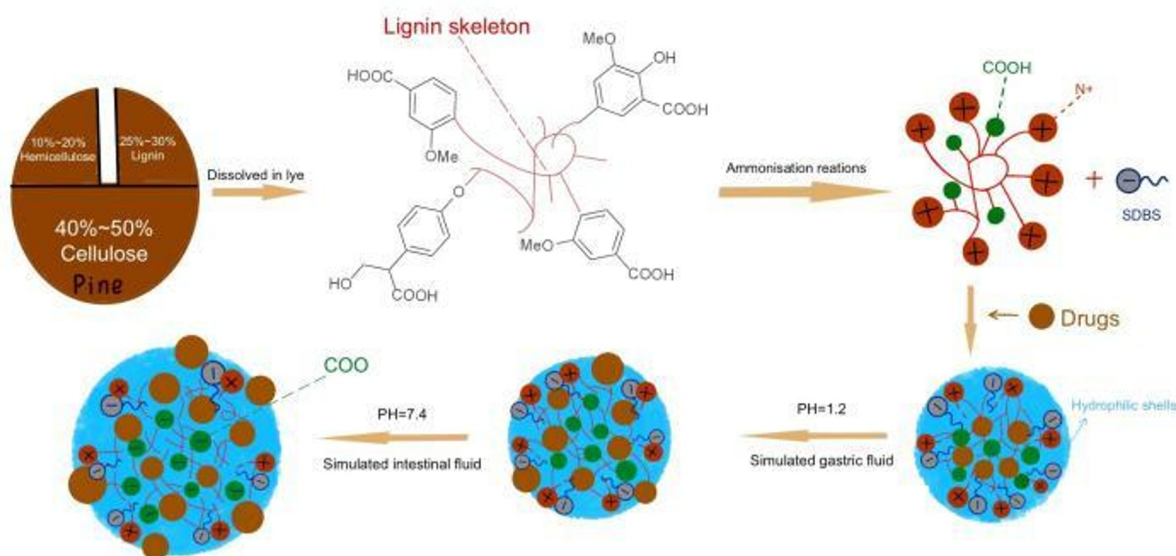


Fig. 6. Application of lignin colloidal spheres for microencapsulation of oral drug microcapsules (Picture credit: Original)

5 Conclusion

This paper discusses various modification methods based on the structure and properties of lignin, and introduces the application and research progress of lignin in polymer materials. By collating and analysing the existing studies, the following conclusions can be drawn.

Firstly, the three-dimensional mesh structure, the large number of benzene ring structures and the conjugated double bonds of lignin make it a great potential for development and application in the preparation of functional materials. By modifying it, their properties can be further enhanced and their application areas become more extensive.

Secondly, in the field of lignin polymer materials, lignin can be compounded with phenolic resins, polyurethanes and polyolefins through chemical reactions and physical blending to improve the performance of the materials and reduce costs. The potential for applications in the fields of drug carriers, energy conversion materials, energy storage materials and environmental protection are increasingly being researched and explored.

Finally, due to the complexity of the lignin structure, the effect in the modification process is difficult to control. So the application is mainly to add modified lignin as an additive to the original material to improve some properties of them, while lignin products have not been developed. Future research should focus on how to further broaden the scope of application and to use the effective structure of lignin to prepare more lignin products with excellent properties. There is also a need to explore the potential of lignin polymer materials for sustainable development and green economy. In conclusion, lignin-modified materials are a promising and far-reaching research direction for a wide range of

applications. Through continuous exploration and research, lignin-modified materials will play an increasingly important role in the future of science and technology.

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