The recent development of sustainable polymers from biomass: cellulose, lignin and vegetable oil

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Abstract. At present, biomass-based polymers can be applied in several fields, such as medicine, biology, aerospace and so on. Due to their good biodegradability, more environmentally friendly products with desirable functions can be designed and processed by people. Therefore, it can be a potential candidate to solve the serious environmental pollution caused by using petroleum-based polymeric materials in the production process. In this article, cellulose, lignin and vegetable oil are taken as examples, all of which are typical biomass-based polymer monomers, by reviewing their synthesis process and applications based on the recent studies on their production, modification and performance enhancements. The properties of final products in the industry stand out compared with many other products synthesized from petroleum-based polymeric materials as there exist different scientific modification methods to synthesize materials with desirable properties. One of the most practical applications is that all of them can be used to synthesize composite materials with enhanced properties. However, more research is required to quantify the environmental benefits and reduce the costs of biomass-based polymers so that we can make full use of biomass-based polymers and even expand their application fields. The article analyzed the application of biomass-based polymers and proposed some suggestions for its future development to help solve the present environmental problems.

Keywords: polymers; biomass; cellulose; lignin; vegetable oil.

1. Introduction

Nowadays, polymers have been increasingly used in almost all aspects of human activities including clothing, packaging, the auto industry, aeroplanes, even medicine application, electronic devices and so on [1, 2]. In many cases, polymers seem to be an ideal material that no better substitute is available, considering its performance, environmental impact, and cost. For instance, plastics contribute significantly to packaging since the existing substituents are either too poor in mechanical properties or more complicated to fabricate and leading to more serious pollution. Petroleum is the main resource to derive the commercially used polymers, but this kind of resource is finite, and many environmental problems are associated with this [1]. Biomass has shown great potential for future commercial production of polymers. Nevertheless, it is important to point out that whether the polymers are degradable is not determined by which sources are used, but by the exact polymer structure. Therefore, one of the challenges is the low-cost and efficient transformation of renewable biomass. Besides, it is important to design degradable chemical structures and investigate better end-of-life options [3]. The last challenge is to achieve better mechanical and chemical properties of renewable polymers than conventional ones.

To promote the development of biomass-based polymers, abundant research has been done and mainly focuses on two strategies: 1) degrade the biomass and convert it into monomers to further produce commonly used polymers such as PET, polypropylene [4-6]; 2) and directly use biomass to fabricate nanocomposites [7-9]. Cellulose, one of the main compositions of lignocellulose which is the most abundant natural polymer in the world, is seen as the promising feedstock to replace petroleum thanks to its desirable mechanical strength, chemical uniqueness, biodegradability [10].

The transformation of cellulose into small monomers was thoroughly studied and in recent years the value of cellulosic nanocomposites is recognized. Some reviews have comprehensively summarised the development of cellulose [1, 6, 10, 11]. In addition, 15-30% of lignocellulose is lignin which is also a promising raw material for polymer production and functionalization [12]. Another readily available and renewable bio-based feedstock is vegetable oils, and much effort has been dedicated to producing vegetable oil-based polymers, mainly including polyurethanes, epoxy resins and the tailoring of them [13-15]. To the best of our knowledge, few reviews have summarised the strategies and application of cellulose, lignin, and vegetable oils together and given the comparison.

This review focuses on the most promising and important strategies for utilizing biomass to achieve sustainable materials with ready availability, degradability, high mechanical properties, and or electrical properties, including conversion of cellulose to known monomers, cellulose-based nanocomposites, lignin degradation, a graft copolymer of lignin, vegetable oil-based epoxy resins and PU, as well as their applications. Ultimately, an outlook for the application of biomass is presented.

2. Cellulose-based polymer

2.1. Cellulose

Cellulose, as the most abundant biopolymer, can not only be found in plants such as pines, birches and so on, but also is presented in algae, bacteria, and some other sea animals [4]. Cellulose is a linear syndiotactic homopolymer composed of D-anhydroglucopyranose units, which are linked by b-(1/4)-glycosidic bonds. Due to the high number of hydroxyl groups on the glucose rings, there is great amount of hydrogen bonding between individual cellulose chains (figure 1) [10], resulting in crystallization of multiple cellulose chains into insoluble microfibrils and two structural regions.

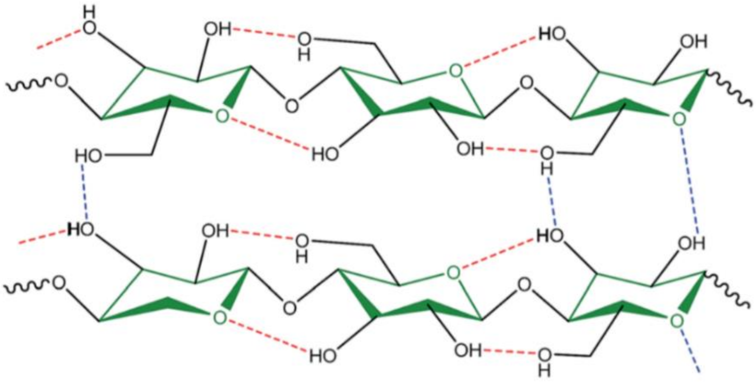

Figure 1. Intra- and inter-molecular hydrogen bonds in molecular structure of cellulose. Anhydroglucose units are linked by 1,4-β-glycosidic bonds [10].

2.2. Fabrication

2.2.1. Conversion of Cellulose.

At an earlier time, the conversion of cellulose to small monomers for further polymerization was thoroughly studied. To realise low-cost and efficient one-pot catalytic conversion from cellulose to EG, Zhang's group developed a binary catalyst by combining Raney Ni and H_2WO_4 and achieved high reusability in 2013 [5]. The insoluble tungstic acid dissolves into the water at high temperature and forms H_xWO_3 when H_2 exists to serve as active species to catalyse the selective breakage of C-C bonds in cellulose, and then the high activity of Ni promotes the hydrogenation to eventually generate EG. Amazingly, the inertness of Raney Ni for EG's degradation improved yield to 65% which is superior to other metal catalysts. Besides, the phase transfer behaviour of H_2WO_4 and easy separation of Ni by magnets and low cost of Ni lead to great ability to be commercialized. This work provides a valuable guideline for cellulose-based polymers, but it is hard to separate cellulose with low cost and ease due to the strong hydrogen bonding between other components in raw biomass.

One year later, they investigated conversion from miscanthus to EG in the same way (figure 2) [16]. Unfortunately, the yield was lower and declined to 13.6% as the miscanthus concentration grew, which was attributed to the aggregation of lignin and epidermal protectors at the surface of Ni (figure 3). To address this, ethanol-NaOH pre-treatment was used to partially remove the soluble components and lignin and a 39% yield of EG at 10% concentration was achieved.

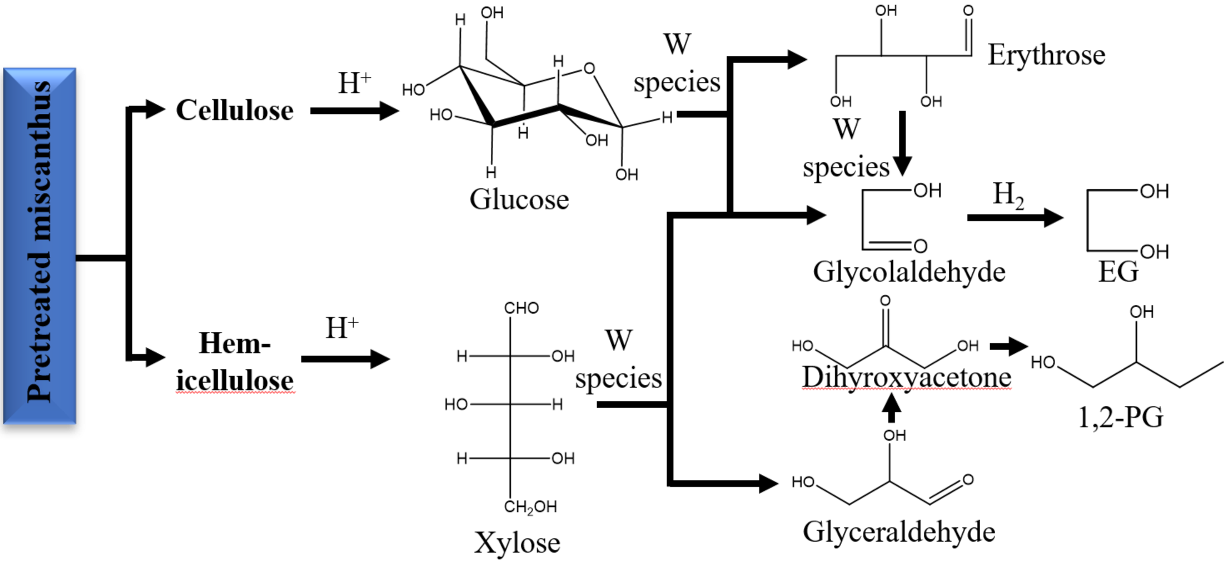

Figure 2. Pathway for catalytic conversion of miscanthus into glycols [16].

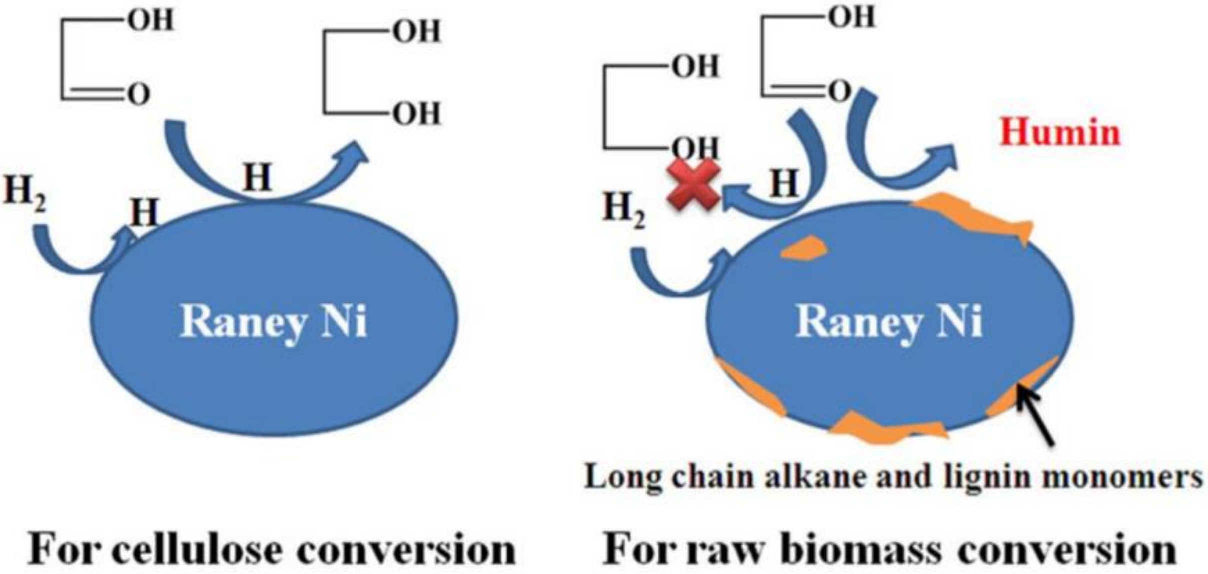

Figure 3. Scheme of catalyst deactivation with raw lignocellulosic biomass as the feedstock [16].

Apart from one-pot conversion, catalytic fast pyrolysis (CFP) with zeolites as catalyst was also thoroughly investigated to convert cellulose, but some products like polyaromatic are undesired, nevertheless. Wang *et al.* used boron impregnation to reduce the effective pore volume of ZSM-5's pores where the polyaromatic are formed [17]. As a result, more desired monoaromatics were formed, especially for *p*-xylene at 1wt%. Besides, it was found that co-feeding with low-density polyethylene has a synergetic effect on boron. In 2015, Claus and his coworkers realized one-pot hydrogenolysis of cellulose by a different catalyst system which is synthesised by impregnation and reduction of ammonium metatungstate hydrate and ruthenium nitrosyl nitrate [18]. After 3 h of reaction, 84% yield (maximum) of polyols, containing EG, PG, sorbitol and so on, was achieved. However, a small loss of catalyst each time it was recycled resulted in low reusability (6 times) in contrast with Zhang's work (17 times).

2.2.2. Cellulose-based composites.

In recent years, more and more efforts are put into the direct use of cellulose as a matrix or filler to fabricate composites, especially functional films, or membranes. In 2016, Peter Szabo's group comprehensively compared the performance of polylactide/cellulose nanofibres (PLA/CNF) and PLA/nanocrystalline cellulose (PLA/CNC) [19]. Overall synthesis consists of washing sisal fibres with NaOH, mercerization, bleaching with acetic acid and NaClO2, being acetylated by nitric acid and acetic acid, and finally, the pulp was centrifuged and hydrolysed to get CNF and CNC respectively. The nanocomposites were prepared by solvent casting. Acetylation and DMF improved the dispersion of nanofillers, which ensures great transparency. Later, Carreau and his coworkers thoroughly investigated the properties of PLA/CNC nanocomposites under different loadings [20]. Similar impacts on mechanical, thermal properties were demonstrated, and a percolation model was utilized to find the temperature-depended strength of the continuous CNC network [21].

Cellulose's superiority was also applied in the electrical field. In 2017, Yu *et al.* dissolved α-cellulose in [Bmim]Cl to form Cel/IL gel which was then soaked into distilled water to obtain hydrogel [22]. The hydrogel was sandwiched between two PTFE Millipore membranes and finally dried to complete the mCel-membrane which possesses high transparency and flexibility, highly uniformly distributed mesopores of around 24.7 nm and high porosity of 71.78%. The Solid-State mCel-membrane-based EDLC in a sandwich structure with activated carbon, Ketjen black and PTFE working as outer electrodes and KOH saturated mCel-membrane serving as inner electrolyte. In terms of mCel-Membraned-Based MSC, with the mask of PTFE, active materials were directly deposited on the membrane, followed by dipping into the water and drying to give MSC without using any complex devices (figure 4a).

In addition to α-cellulose, O-(2,3-Dihydroxypropyl) cellulose (DHPC) was also used to fabricate cellulose papers [21]. But poor mechanical properties limit its practical application. To address this, Zhang et al. introduced stiff tunicate cellulose nanocrystals as a reinforcement phase to fabricate tough DHPC nanocomposite papers (figure 4b). Due to the good compatibility between matrix and fillers, a uniform dispersion was achieved, preserving high transparency, and increasing the mechanical properties.

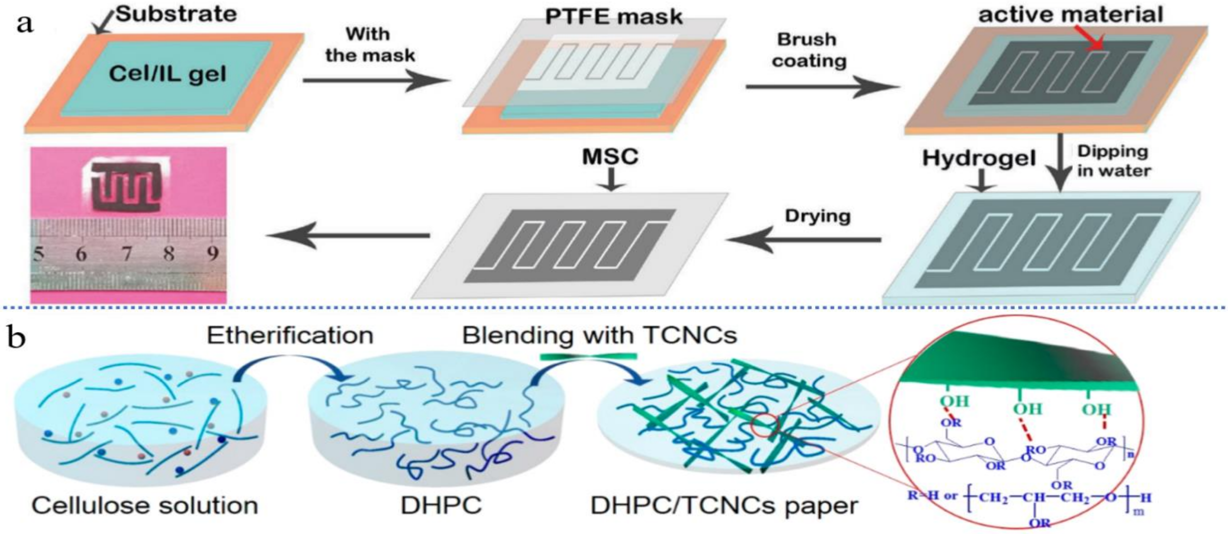

Figure 4. a) Schematic diagram of the preparation of the mCel-membrane-based MSC [22]; b) Schematic illustration of the fabrication of cellulose-based nanocomposite papers [21].

In the same year, Lu and his coworkers developed the cellulose hydrogel-coated mesh to explore greener and inexpensive materials for oil/water separation [23]. They simply dipped the wire mesh into cellulose solution and heated it to crosslink after gelation at room temperature (Figure 5). Instead of using cellulose as fillers in composites, Lu's group facilely fabricated strong and transparent regenerate cellulose film (CF) by water evaporation induced dense packing and construct Ag-CF nanocomposites by *in situ* synthesis [7].

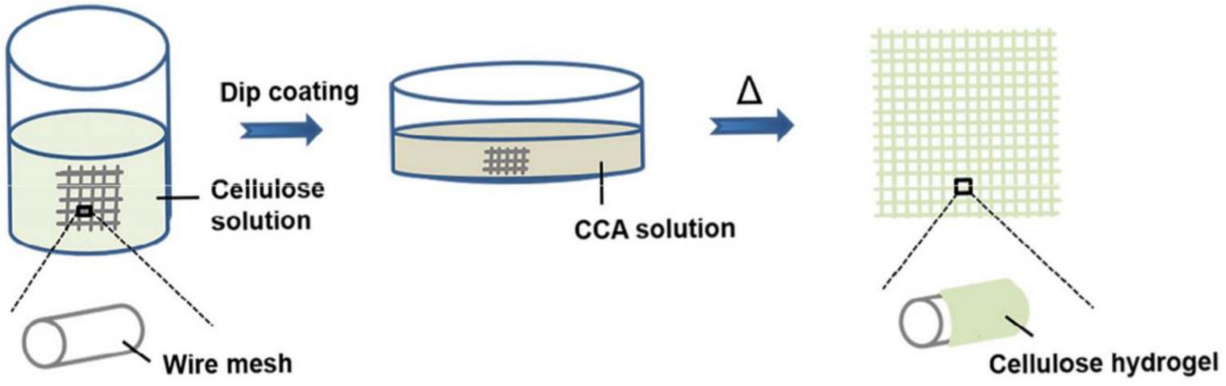

Figure 5. Schematic of the fabrication process of the superhydrophilic and underwater superoleophobic CHMs [23].

In 2019, a startling work that achieve multifunctional cellulose nanocomposites was reported. Epichlorohydrin (EPI) was added to the cellulose solution for chemical crosslinking, followed by being poured into moulds for gelation [8]. After that, the gel was stretched to get a temporary highly oriented structure. Subsequently, remove the alkali/urea between cellulose chains by sulfuric acid to freeze this structure and the anisotropic dual-cross-linked cellulose films were obtained. The highly oriented and compact structure is attributed to the high strength, record-high toughness of 41.1 MJ m-3, light management, stability, and other desired properties. Still taking the advantage of hydrogen bonding, Zhang et *al.* introduced dynamic imine polymer into cellulose paper matrix by soaking the paper in partially cured imine solution and subsequently being hot pressed [9]. Then multiple single-layer paper polyamine composite sheets were laminated. Its impressive that not only hydrogen bonding between polyimine and cellulose gives high strength, but also that the composites are fully recyclable due to dynamic imine bond exchange. Previous investigation on polymer/cellulose nanocomposites mainly realized by solvent casting which has been summarised. Recently, the production of poly (butylene succinate)/nanofibrillated cellulose (PBS/NFC) by the masterbatch process was reported by Platnieks [24]. In this work, PBS and NFC were dissolved and mixed, followed by fully drying in a vacuum furnace. Then the 50 wt% PBS/NFC was mixed with PBS granules to undergo the masterbatch process.

2.3. Application

2.3.1. Monomer production.

According to the previous summary, by using different catalyst systems cellulose can be converted into various monomers, including EG, PG, aromatic monomers and so on, and the obtained monomers are the same as petroleum-based monomers [5, 16-18]. Therefore, it opens a new avenue for industrial production for some commercial polymers. The Raney Ni/H_2WO_4 catalyst system for cellulose conversion has already reached a high yield of EG of higher than 65% [5]. The feasibility also was proved by another research [16, 18]. Besides, CFP with zeolites as catalysts achieved the control of the distribution of aromatic products. However, one drawback of the acidic tungstic compound containing a catalyst system causes corrosion of the stainless-steel reactor [18].

2.3.2. Cellulose-based composite.

The multifunctionality of cellulose-based nanocomposites gives them various applications in the electronics area, packaging application, plastic replacement, and oil/water separation. In terms of packaging, PLA/CNF and PLA/CNC nanocomposites presented better barrier properties than pure PLA, which is partially ascribed to the improved crystallization rate resulting from the nucleating effect of nanofillers would be an important improvement [19]. The oxygen transmission rate was even lower than the commercially used clay/PLA composites. The PBS/NFC also has an increase in biodegradability and stiffness in comparison with neat PBS, showing feasibility in industrial sustainable composites for packaging and other application [24].

In electronics application, the EDLC and MSC reported by Yu achieved a high capacitance of 110 F g^{-1} at 1.0 A g^{-1} and high volumetric capacitance of 191.66 F cm^{-3} at 10 mV s^{-1} [22]. These findings provide a guideline not only for cellulose-based capacitors but also for portable energy storage devices. One of the hot energy storage devices is a flexible solar cell. Due to its biodegradability, high transparency, flexibility and good mechanical properties, it can work as the substrate for flexible solar cells (figure 6a) [21]. What's more, the cellulose-based composites can also be used as an optical sensing platform in environmental monitoring and food safety [7]. The small Ag nanoparticles in the Ag-CF composites can easily detect trace concentrations of iodide by colour change. As shown in figure 6b, the ACFs with highly oriented structures could depolarize the incident beam so that it goes through the analyser and be detected [8]. Birefringence behaviour and polarization features observed between two polarized filters show great potential for next-generation photocontrollable devices.

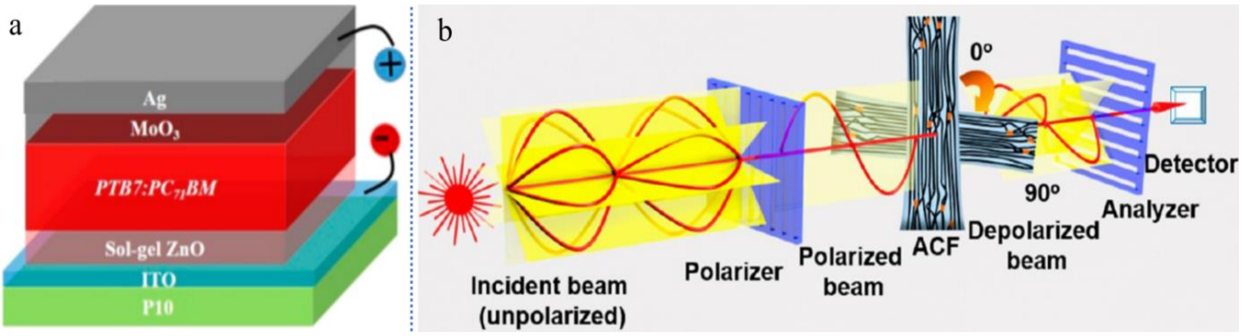

Figure 6. a) Structure of an inverted polymer solar cell [21]; b) Schematic illustration of the angle variation of the anisotropic films between the crossed polarizers [8].

For oil/water separation, the hydrogel-coated mesh reported by Lu was able to separate various oil/water mixtures with a high separation efficiency of 98.9% and a permeate flux up to 12,885 L m-2 h-1 simply driven by gravity [23]. Besides, excellent reusability was observed because the separation efficiency was still higher than 98.2% after 60 cycles. The excellent salt tolerance also showed its value for practical usage.

3. Lignin-based polymer

3.1. Lignin

Lignin is a highly branched and amorphous biological macromolecule with a molecular weight of about 1000 to 20000g·mol^{-1} and is mainly composed of three basic phenylpropanol monomers, also known as monolignols: p-coumarol, coniferol and erucinol. Lignin accounts for about 30% of the organic carbon in the biosphere and is the second most abundant lignocellulosic biopolymer after cellulose [25]. When the monomer is incorporated into a polymer formed from lignin, the units derived from mono-lignol are called p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively (figure 7) [12]. Monomers that make up the components of lignin also differ in ortho-methoxide substitution. Due to the different plant species, the composition of lignin will also make the structure of lignin different [26]. Lignin has many similar properties to other biorenewable polymers, including antioxidant, antifungal and antibacterial activity, high application in industrial waste by-products, biodegradability and CO_2 neutrality. Lignin has many potentially beneficial physical and chemical properties, including its good rheological properties, viscoelasticity, film-forming ability and compatibility with industrial chemicals [12], making it a compound with great prospects for the development of the renewable energy industry and the production of many related products.

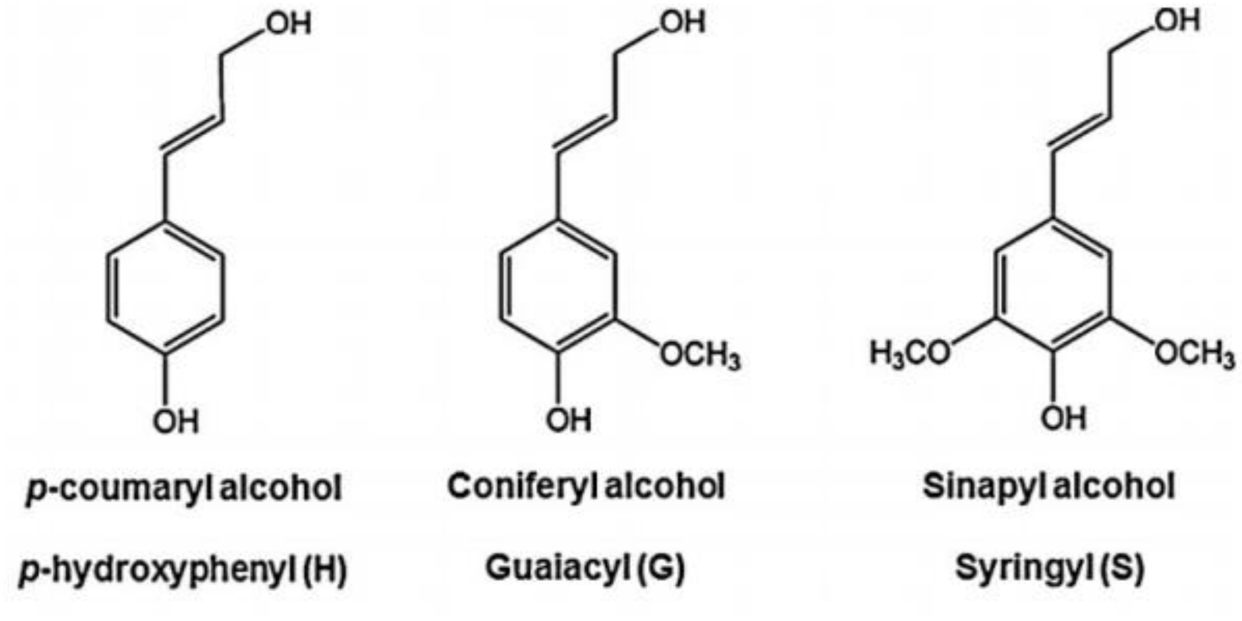

Figure 7. Monolignol monomers species present in lignin [25].

3.2. Fabrication

3.2.1. Lignin degradation.

Many valuable lignin raw materials can be obtained through degradation or depolymerization of lignin and eventually generate application products. Therefore, increasing efforts to pay attention to how to efficiently and quickly degrade lignin have become the focus of today. At present, there are a load of research on lignin degradation. Due to the shortcomings of the chemical and physical degradation of lignin, enzymatic hydrolysis is a better choice in both economic and environmental aspects. Laccase (LAC) is a lignin enzyme with high REDOX potential. In the presence of a medium, LAC can catalyze the oxidation of non-phenolic substances and produce an intermediate with high oxidation potential, oxidizing lignin and degrading it [27]. In addition to REDOX potential, photocatalysis is also a highly efficient way to degrade lignin. According to Jian et al., by fine-tuning the porous organic framework (POF), the obtained carbazole copolymer (CzCP) exhibits excellent REDOX potential, which can be used for the gradual photocatalytic degradation of the lignin β-O-4 model [28]. Since lignin molecules are converted into small molecules that can be further applied in many directions, the thermochemical reaction of lignin depolymerization has also been studied and discovered. For example, through pyrolysis, lignin is converted into solid carbon, liquid oil or gas for heat treatment; Oxidation yields aldehydes, and corresponding acids; Hydrolytic and hydrolytic pyrolysis of lignin prevents cross-linking reactions [12].

3.2.2 Graft copolymer of lignin.

Lignin can be used to generate lignin graft copolymers, in which the monomer reacts with hydroxyl groups present in the lignin, and the polymer chain is connected to the lignin nucleus. Detailed ring-opening polymerization of different monomers and radical polymerization of vinyl monomers are shown in (figure 8) [12]. Graft copolymers can be easily adjusted by using the lignin content and weight of different synthetic polymers, such as polyethylene glycol (PEG) copolymerization with lignin to improve thermal stability, Young's modulus and breaking strength. This kind of polymerization could be applied to lithium-ion batteries, where only attaching to thermally unstable PEG would limit their mass production. Grafting onto lignin, which has strong mechanical strength, would solve these problems. PEG-SH was synthesized by modifying PEG- OH with 3-mercaptopropionic acid by modifying lignin to lignin-olefin. Finally, the mercaptoene reaction was performed by mixing the two [12, 29].

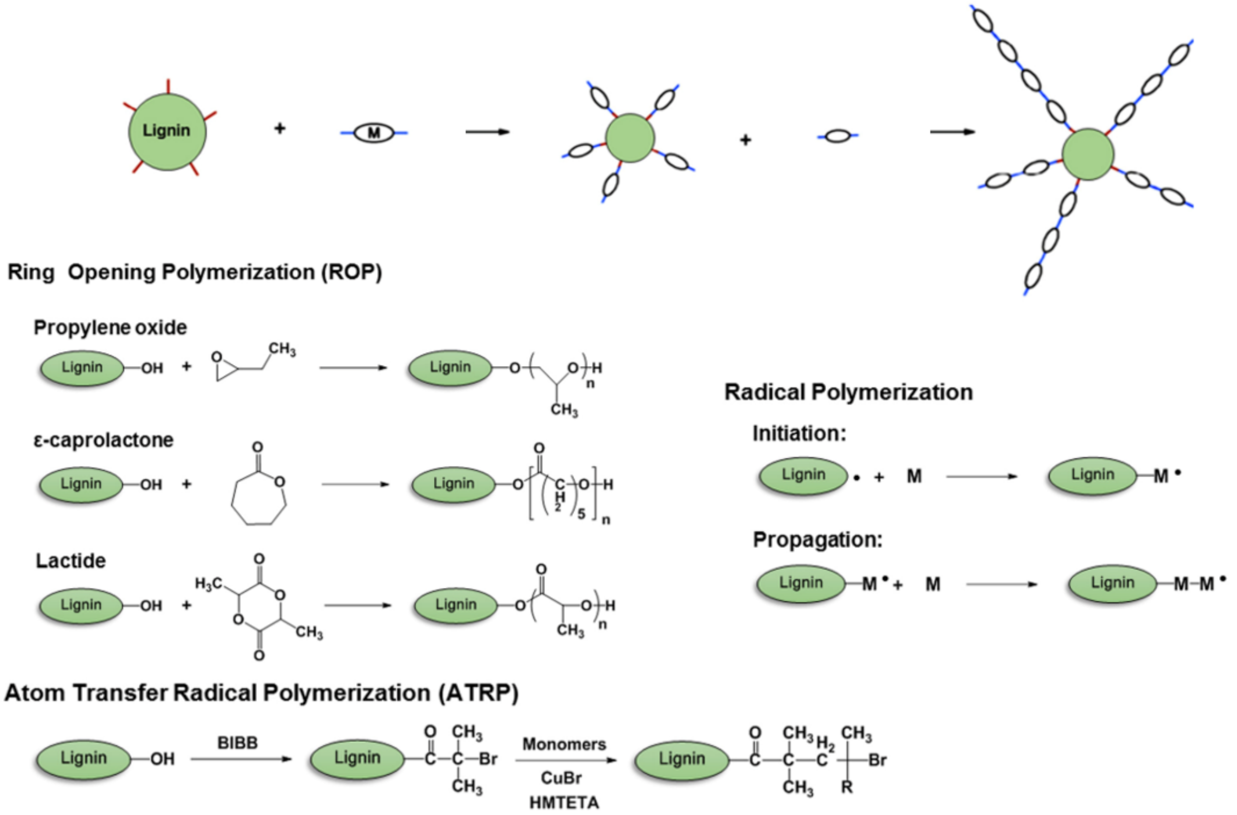

Figure 8. Schematic representation of the lignin-graft copolymers synthesis by the "grafting from" method (ring opening polymerization and radical polymerization, such as ATRP) [12].

3.3. Application

3.3.1. Lignin is found in nanomaterials.

More recently, lignin has been used to produce different nanocomposites, such as nanoparticles, nanofibers and hydrogels. The results showed that lignin was separated from bagasse and chemically modified with the quaternary amine group to form cationic surfactants. The purpose of this work is to add nano-clays into polystyrene-butyl acrylate latex, which can enhance the resistance to ultraviolet radiation [26, 30]. In the research of nano-composite materials, the production of lignin nanoparticles (LNP) is of great importance because it has key advantages and can make the polymer have stronger antioxidant activity. In addition, LNPs with special functional groups can be chemically modified to increase the application potential of polymers (figure 9). Different production methods of LNPs are described. Yearla and Padmasree produced dioxane LNP with an average size of about 104 nm and dissolved a solution of lignin in acetone and water (9:1 V/V) [31]. LNP generated in this way can be further used in food, pharmaceutical and cosmetic industries, with great development prospects. LNPs are also used as reinforcers in polymer matrices and nanocomposites for better biocompatibility, mechanical properties, and thermal properties. In the characterization of these LNPs, the weight and tensile strength of the nanocomposites were measured and found to be suitable for a variety of applications [12].

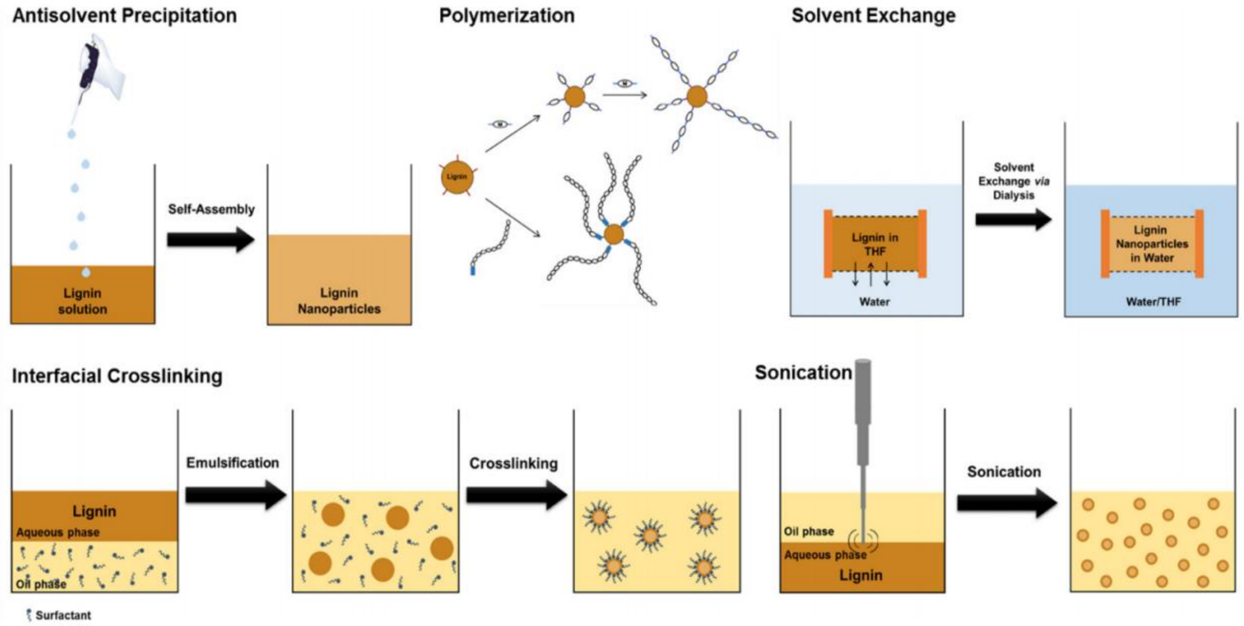

Figure 9. Schematic representation of the different methodologies to produce LNPs [12].

3.3.2. Lignin based solid polymer electrolyte.

According to the synthesis method in 3.2.2, this is an environmentally friendly photooxidation-reduction mercaptanene reaction. This synthesis method leads to the synthesis of new biomass-based copolymer lignin grafted with PEG, which is also used as a new polymer electrolyte in lithium batteries. The newly synthesized polymer is compared with PEG, a homopolymer without lignin fragments [29]. Experimental studies show that the addition of lignin improves the ambient temperature conductivity and mechanical strength, enabling long-term cycling and high compatibility after battery application. It is a promising new material.

3.3.3. Industrial application of lignin.

Lignin-based materials in industrial applications are mainly in fuels, chemical reagents, such as fertilizers and other polymers. In biofuels, lignin can be converted into fuel cells, gas turbines or even gas that can be synthesized into natural gas through gasification and pyrolysis [12]. Therefore, we can have cleaner energy carriers and improve the stability of products. At present, epoxy resins based on lignin have a good thermosetting structure and low failure strain, which is the result of the more uneven structure of lignin epoxides and the final thermosetting network [32]. These epoxies can improve the ageing resistance of pavement asphalt and the good stability of circuit boards [12].

4. Vegetable oil-based polymer

4.1. Vegetable oil

Nowadays, although the polymer processed from non-renewable resources such as fossils takes a leading position in the commercial field, it does cause serious pollution to the environment. Additionally, the difficulty in dealing with waste products is another urgent issue that has attracted people’s attention [33]. Replacing the present raw materials with renewable resources is a trend to solve this problem. Vegetable oils can be an ideal answer to it. They are widely distributed in nature and can be extracted from many plants such as Linseed, soybean, sunflower, palm and so on. Its abundance also reduces the cost in the industry. Biodegradability and low toxicity are other outstanding advantages of vegetable oils. The main component in vegetable oil is a triglyceride (figure 10a) [34], which is the ester formed from the esterification of glycerol with three fatty acids. Fatty acid takes the dominant position in the total weight of triglycerides, accounting for almost 95%. Their components vary in different plants. Both growing conditions and extraction methods can affect the quality of vegetable oils. Figure 10b presents some types of fatty acids that are applied in the research experiment to find out their potential application [34]. The chemical and physical properties of vegetable oils are mainly determined by both chain length and the type of reactive sites of the fatty acids. The unsaturated groups such as double bonds in the reactive sites of fatty acids can be functionalized so that they can be applied in polymer synthesis. However, the mechanical properties of the vegetable oil-based polymer are weakened based on research [35]. One possible method to enhance its property is to make a polymer blend.

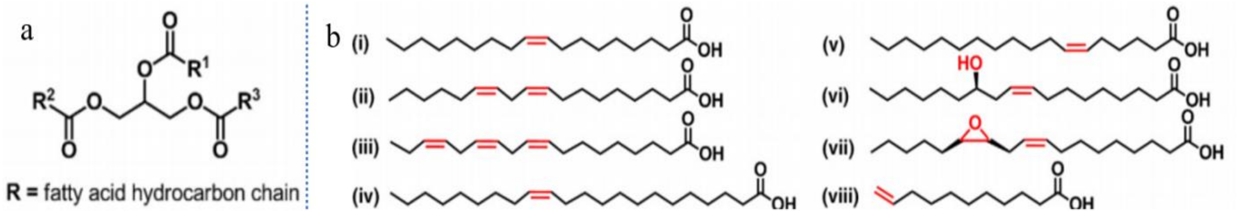

Figure 10. a) Structure of triglyceride; b) Common fatty acids [34].

4.2. Fabrication

4.2.1. Vegetable oil-based epoxy resins.

Epoxy resin is an important kind of thermoset in different fields due to the reason that they have perfect chemical resistance and desirable mechanical properties. The unsaturated reactive sites on the vegetable oils can be modified into epoxy functional groups [36]. After applying the curing agent to the resin precursors via chemical synthesis, we can obtain our favorable products. Anda *et al.* reported that they applied a stereolithographic (SLA) 3D printer set up and UV-LED lamp to produce vegetable oil epoxidized acrylates [13]. FT-IR showed that crosslinking degree is higher in AEM-LED than in AEM-3D because the laser intensity of LED is higher than SLA printer. When it comes to the thermal degradation analysis, Friedman's method indicated that the sample prepared from SLA 3D printing is approximate 24-29% more stable than that photocured by a UV-LED lamp. While undergoing thermal destruction, AEM-LED released a smaller number of hazardous gases and more CO_2 than AE-LED.

4.2.2. Vegetable oil-based polyurethanes.

Vegetable oils can be modified into polyols so that they can react with diisocyanates to synthesise polyurethanes. Different kinds of vegetable oils can be transformed into polyols via different synthesis routes. Take epoxidized plant oils as an example, it follows the ring-opening method (figure 11) [37]. Properties of final polyurethanes products are weakly affected by the reactive sites in the triglycerides, but strongly influenced by the network degree of polyurethanes. The higher the cross-linking degree, the higher the mechanical properties of the polyurethanes.

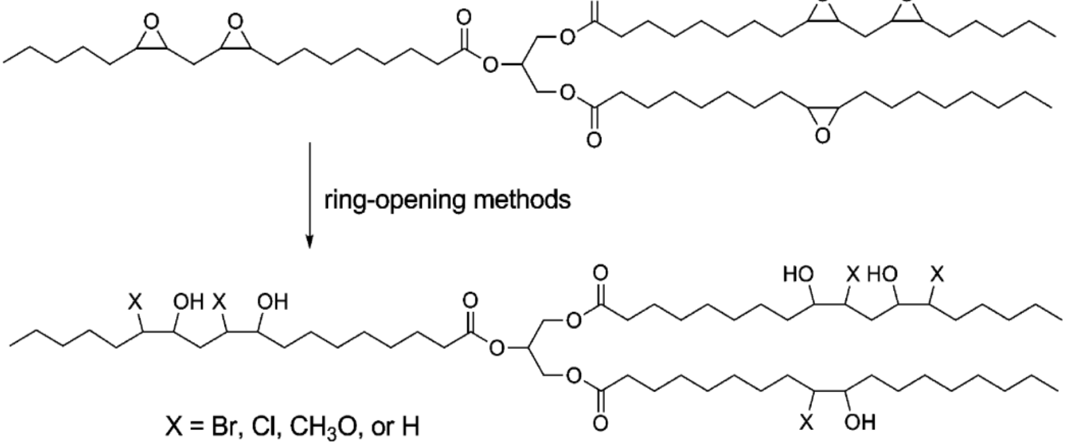

Figure 11. Scheme diagram of ring opening method [37].

4.3. Application

4.3.1. Industrial application.

Alice Mija et al. synthesized epoxidized linseed oil (ELO)-based thermosets [14]. They presented a new series of vegetable-oil based thermosetting resins by copolymerizing 12 newly synthesized EVOs with 2,2'-dithiodibenzoic acid (DTBA). As there exists little literature proposing the connection between epoxidized vegetable oils and DTBA, their work offered a possible method to take advantage of S-S leaks to form covalent adaptable networks (CANs), which can improve the efficiency in the recycling and reprocessing. As dissociation energy of the S-S bond is lower than the C-C bond, making it easier to break. Dynamic mechanical analysis indicates that Tg is higher in ELO-based resins compared with epoxidized soybean oil (ESO) curved with citric acid, resulting from the higher epoxy content in ELO. Additionally, their mechanical property test showed that the EVO thermosets are better compared with other polymers curved by carboxylic acids, which provide a better idea in industrial production. However, data related to recycling efficiency remains unclear, requiring more investigations to fully understand new EVO thermosets.

4.3.2. Electrochemical application.

Vegetable-oil based polyurethanes possess low glass transition temperature and good chemical stability, both of which make them possible to be applied as polymer electrolytes or specifically solid polymer electrolytes (SPE). It reduces the leakage compared with the liquid electrolytes. Siti Rosnah Mustapa *et al.* reported that they successfully used jatropha oil to synthesize polyurethane and prepared a solid polymer electrolyte [15]. The PU/MDI_3 was chosen to be the host for the polymer electrolyte film for the reason that it contains less toxicity and helps protect the environment. The polymer electrolyte was doped with an appropriate weight fraction of $LiClO_4$. Their characterization results showed that at room temperature it can display the highest conductivity, which offers a potential application in an electrochemical device.

5. Conclusion

Biomass-based polymers are developed to be the alternative to conventional polymers made from petrochemicals so that the severe environmental pollution caused by petrochemicals in the process can be solved to a certain degree. This article discusses the application of bio-based polymers in various fields, especially in nanomaterials, and composite materials. Several synthetic methods are introduced to transform the raw materials into biomass-based polymers. In the industrial process, multi-functions of nanocomposites obtained from biomass-based polymers are proved to be remarkable. Their mechanical properties are strongly enhanced through proper chemical modification methods. However, biomass-based polymers have not been totally commercially viable for the reason that the cost of fossil is low. Lacking enough research on the properties of biomass-based polymers is another obstacle to applying biomass-based polymers in different fields. Therefore, researchers should focus on improving the above deficiencies to achieve lower production costs and better performance of biomass-based polymers. Although the application in the electrochemical field is still a challenge at present, it is undeniable that biomass-based polymers are becoming increasingly outstanding and the potential for future development should not be underestimated. The outlook for biomass-based polymers is still promising to consider the urgent need for taking the place of petroleum-based polymers.

References

[1] Zhu, Y., Romain, C., Williams, C.K., (2016) Sustainable polymers from renewable resources. Nature, 540: 354-362.

[2] Yanikkaya, H., Turan, T., (2018) Curse or Blessing? An Empirical Re-examination of Natural Resource-Growth Nexus. J. Int. Dev., 30: 1455-1473.

[3] Lee, S.H., Cyriac, A., Jeon, J.Y., Lee, B.Y., (2012) Preparation of thermoplastic polyurethanes using in situ generated poly (propylene carbonate)-diols. Polym. Chem., 3: 1215-1220.

[4] Taylor, N.G., (2008) Cellulose biosynthesis and deposition in higher plants. New Phytol, 178: 239-252.

[5] Tai, Z., Zhang, J., Wang, A., Pang, J., Zheng, M., Zhang, T., (2013) Catalytic conversion of cellulose to ethylene glycol over a low-cost binary catalyst of Raney Ni and tungstic acid. ChemSusChem, 6: 652-8.

[6] Sternberg, J., Sequerth, O., Pilla, S., (2021) Green chemistry design in polymers derived from lignin: review and perspective. Progress in Polymer Science, 113.

[7] Wang, Y., Yuan, L., Tian, H.F., Zhang, L.N., Lu, A., (2019) Strong, transparent cellulose film as gas barrier constructed via water evaporation induced dense packing. J. Membr. Sci., 585: 99-108.

[8] Ye, D., Lei, X., Li, T., Cheng, Q., Chang, C., Hu, L., Zhang, L., (2019) Ultrahigh Tough, Super Clear, and Highly Anisotropic Nanofiber-Structured Regenerated Cellulose Films. ACS Nano, 13: 4843-4853.

[9] Su, Z.P., Huang, S.F., Wang, Y.Y., Ling, H., Yang, X.Y., Jin, Y.H., Wang, X.H., Zhang, W., (2020) Robust, high-barrier, and fully recyclable cellulose-based plastic replacement enabled by a dynamic imine polymer. J. Mater. Chem. A, 8: 14082-14090.

[10] Shaghaleh, H., Xu, X., Wang, S., (2018) Current progress in production of biopolymeric materials based on cellulose, cellulose nanofibers, and cellulose derivatives. RSC Advances, 8: 825-842.

[11] Zhao, D., Zhu, Y., Cheng, W., Chen, W., Wu, Y., Yu, H., (2021) Cellulose-Based Flexible Functional Materials for Emerging Intelligent Electronics. Adv Mater, 33: e2000619.

[12] Figueiredo, P., Lintinen, K., Hirvonen, J.T., Kostiainen, M.A., Santos, H.A., (2018) Properties and chemical modifications of lignin: Towards lignin-based nanomaterials for biomedical applications. Prog. Mater. Sci., 93: 233-269.

[13] Barkane, A., Platnieks, O., Jurinovs, M., Gaidukovs, S., (2020) Thermal stability of UV-cured vegetable oil epoxidized acrylate-based polymer system for 3D printing application. Polym. Degrad. Stabil., 181: 10.

[14] Di Mauro, C., Malburet, S., Genua, A., Graillot, A., Mija, A., (2020) Sustainable Series of New Epoxidized Vegetable Oil-Based Thermosets with Chemical Recycling Properties. Biomacromolecules, 21: 3923-3935.

[15] Mustapa, S.R., Aung, M.M., Rayung, M., (2021) Physico-Chemical, Thermal, and Electrochemical Analysis of Solid Polymer Electrolyte from Vegetable Oil-Based Polyurethane. Polymers, 13: 20.

[16] Pang, J., Zheng, M., Wang, A., Sun, R., Wang, H., Jiang, Y., Zhang, T., (2014) Catalytic conversion of concentrated miscanthus in water for ethylene glycol production. AIChE Journal, 60: 2254-2262.

[17] Zhou, G., Li, J., Yu, Y., Li, X., Wang, Y., Wang, W., Komarneni, S., (2014) Optimizing the distribution of aromatic products from catalytic fast pyrolysis of cellulose by ZSM-5 modification with boron and co-feeding of low-density polyethylene. Applied Catalysis A: General, 487: 45-53.

[18] Fabičovicová, K., Lucas, M., Claus, P., (2015) From microcrystalline cellulose to hard- and softwood-based feedstocks: their hydrogenolysis to polyols over a highly efficient ruthenium–tungsten catalyst. Green Chemistry, 17: 3075-3083.

[19] Trifol, J., Plackett, D., Sillard, C., Hassager, O., Daugaard, A.E., Bras, J., Szabo, P., (2016) A comparison of partially acetylated nanocellulose, nanocrystalline cellulose, and nanoclay as fillers for high-performance polylactide nanocomposites. Journal of Applied Polymer Science, 133: n/a-n/a.

[20] Bagheriasl, D., Carreau, P.J., Riedl, B., Dubois, C., (2018) Enhanced properties of polylactide by incorporating cellulose nanocrystals. Polymer Composites, 39: 2685-2694.

[21] Cheng, Q., Ye, D., Yang, W., Zhang, S., Chen, H., Chang, C., Zhang, L., (2018) Construction of Transparent Cellulose-Based Nanocomposite Papers and Potential Application in Flexible Solar Cells. ACS Sustainable Chemistry & Engineering, 6: 8040-8047.

[22] Zhao, D., Chen, C., Zhang, Q., Chen, W., Liu, S., Wang, Q., Liu, Y., Li, J., Yu, H., (2017) High Performance, Flexible, Solid-State Supercapacitors Based on a Renewable and Biodegradable Mesoporous Cellulose Membrane. Advanced Energy Materials, 7.

[23] Ao, C., Hu, R., Zhao, J., Zhang, X., Li, Q., Xia, T., Zhang, W., Lu, C., (2018) Reusable, salt-tolerant and superhydrophilic cellulose hydrogel-coated mesh for efficient gravity-driven oil/water separation. Chemical Engineering Journal, 338: 271-277.

[24] Platnieks, O., Sereda, A., Gaidukovs, S., Thakur, V.K., Barkane, A., Gaidukova, G., Filipova, I., Ogurcovs, A., Fridrihsone, V., (2021) Adding value to poly (butylene succinate) and nanofibrillated cellulose-based sustainable nanocomposites by applying masterbatch process. Ind. Crop. Prod., 169: 12.

[25] Boerjan, W., Ralph, J., Baucher, M., (2003) Lignin biosynthesis. Annu. Rev. Plant Biol., 54: 519-546.

[26] Grossman, A., Vermerris, W., (2019) Lignin-based polymers and nanomaterials. Curr. Opin. Biotechnol., 56: 112-120.

[27] Zheng, Y., Guo, M., Zhou, Q., Liu, H., (2019) Effect of lignin degradation product sinapyl alcohol on laccase catalysis during lignin degradation. Ind. Crop. Prod., 139.

[28] Luo, J., Zhang, X., Lu, J., Zhang, J., (2017) Fine Tuning the Redox Potentials of Carbazolic Porous Organic Frameworks for Visible-Light Photoredox Catalytic Degradation of Lignin β-O-4 Models. ACS Catalysis, 7: 5062-5070.

[29] Liu, H.L., Mulderrig, L., Hallinan, D., Chung, H.Y., (2021) Lignin-Based Solid Polymer Electrolytes: Lignin-Graft-Poly (ethylene glycol). Macromol. Rapid Commun., 42: 6.

[30] Jairam, S., Tong, Z.H., Wang, L.T., Welt, B., (2013) Encapsulation of a Biobased Lignin-Saponite Nanohybrid into Polystyrene Co-Butyl Acrylate (PSBA) Latex via Miniemulsion Polymerization. Acs Sustainable Chemistry & Engineering, 1: 1630-1637.

[31] Yearla, S.R., Padmasree, K., (2016) Preparation and characterisation of lignin nanoparticles: evaluation of their potential as antioxidants and UV protectants. J. Exp. Nanosci., 11: 289-302.

[32] Gioia, C., Colonna, M., Tagami, A., Medina, L., Sevastyanova, O., Berglund, L.A., Lawoko, M., (2020) Lignin-Based Epoxy Resins: Unravelling the Relationship between Structure and Material Properties. Biomacromolecules, 21: 1920-1928.

[33] Diez-Pascual, A.M., (2019) Antibacterial Nanocomposites Based on Thermosetting Polymers Derived from Vegetable Oils and Metal Oxide Nanoparticles. Polymers, 11: 26.

[34] Lligadas, G., Ronda, J.C., Galia, M., Cadiz, V., (2013) Renewable polymeric materials from vegetable oils: a perspective. Mater. Today, 16: 337-343.

[35] Petrovic, Z.S., Guo, A., Zhang, W., (2000) Structure and properties of polyurethanes based on halogenated and nonhalogenated soy-polyols. J. Polym. Sci. Pol. Chem., 38: 4062-4069.

[36] Zhang, C.Q., Garrison, T.F., Madbouly, S.A., Kessler, M.R., (2017) Recent advances in vegetable oil-based polymers and their composites. Progress in Polymer Science, 71: 91-143.

[37] Xia, Y., Larock, R.C., (2010) Vegetable oil-based polymeric materials: synthesis, properties, and applications. Green Chemistry, 12: 1893-1909.