Extraction Methodologies and Applications of Renewable Polymers

Yinuo Li*

Department of Chemistry, University College London, London, United Kingdom

* Corresponding Author Email: yinuo.li.21@ucl.ac.uk

Abstract. Since there are large scales of production in modern industries all over the world, non-biodegradable materials would cause serious environmental issues when dealing with pollution treatments. To reduce environmental impact, it is said that producing renewable polymers is an effective method to maintain production yields without harming the environment. Renewable polymers are polymeric materials derived from renewable carbon wastes, and reused or biodegraded at the end of life cycles. This article introduces four examples of common renewable polymers with different bio-based platforms by comparing their structures, extraction methodologies, and applications respectively. The opportunities for sustainable polymer development would be based on performances while applying to industrial and commercial use. Although some renewable polymers are still not widely used on a grand scale due to yields or costs, the researchers would continue to investigate methods to improve the situation. Because of the appealing advantages of the production of renewable polymers, the future of manufacturing would be significantly beneficial to both environment and the whole economy.

Keywords: Renewable polymers, extraction methodologies, bio-fuel, 3D printing.

1. Introduction

With the development of industries, the majority of large-scale production of commercial polymers would result in serious environmental pollution because the major materials for essential products in modern life have a great contribution to petro-chemicals. Since they are not degradable in nature during the process of disposal, people are responsible to keep the world environmentally friendly. According to the importance of tackling problems, scientists find that the production of renewable polymers may be one of the solutions to facilitate the economy with pollution minimization. Renewable polymers are defined as recycled polymers with high biodegradability and sustainability from carbon feedstock. The demand for renewable polymers had an upward trend in manufacturing industries due to their accessibility since the 19th century [1].

However, the challenge faced is that the efficiency and costs of renewable polymers are unable to satisfy the levels which nonrenewable polymers could reach. If using nonrenewable sources, people would undertake the due obligations from the increased greenhouse effects even though taking advantage of low costs.

Recent studies show that biomass, as an important source, would efficiently replace fossils during large-scale manufacturing in the near future [2]. To classify four renewable polymers from different biodegradable sources in nature, polyesters, polylactic acids (PLA), polycarbonates, and polyurethanes would be covered. The effectiveness and yield of bio-based polymers largely depend on the preparation process, such as extraction methodology. More importantly, the applications of renewable polymers for different fields would be described in detail.

Considerable published reports discuss the performances, drawbacks, and development of renewable and sustainable polymers, but seldom focus on the connections among different polymers with the same practical use [3]. In the following content, it is stated to analyze the potential and limitations of four renewable polymers when they are applied in real production and consumption.

2. Lignin

Lignin becomes a very powerful renewable polymer in the paper and pulp industry because of its biodegradability and high productivity. Lignin is an amorphous phenolic polymer that has randomized branches and cross-links with cellulose and hemicellulose. It is ranked number two among the most plentiful naturally occurring polymers with a high durability on Earth after cellulose [4]. Three common types of lignin are derived from guaiacyl, syringyl, and p-hydroxyphenyl monolignols, where guaiacyl lignin is most widely used [5]. The monomer types of lignin are acid and alcohol. After condensation polymerization, polyesters would act as polymer forms.

In addition, the extraction methods of technical lignin are various. The methodology can be classified by conditions, i.e., with or without the addition of the sulfur process. On the one hand, Kraft pulp and sulfite processes are traditional extracting processes from biomass when sulfur has participated in the polymerization. The success of Kraft pulping is the ability to recover chemicals and energy from the residual feedstock. Three stages are included in the pulping process. Initially, delignification takes place at <140 ℃, while both the extraction of lignin and degradation of hemicellulose is achieved [6]. Followed by higher temperatures, the acceleration of the delignification rate would remain at a high level unless the removal of the majority of lignin is finished [6]. Lastly, when the main residual is a carbohydrate, the deliginification becomes slower at the end [6]. On the other hand, organosolv and soda processes are two ways under an un-sulfonated situation [7]. The organosolv process is to dissolve lignin by using an organic solvent with 30-70% concentration, such as low-cost ethanol, and the addition of an acid catalyst at a high temperature of 170-220 ℃ [6]. Lignin extracted from the organosolv process would have higher purity compared with the pulping process because sulfur is absent in the byproducts [8]. However, the probability of alternating compositions and properties of monomers is high under changing conditions, such as acidity and temperature. To deal with this problem, researchers suggest that the generation of transgenic lines by not affecting cell wall properties would help with high-quality lignin production [9].

The applications of lignin have great coverage in medication, bio-fuel, and three-dimensional (3D) printing. Wound dressing is one of the practical uses of medication. Lignin is considered a potentially powerful material when producing hydrogels, for which hydrogels are useful 3D network polymers for drug delivery [10]. Because of the antibacterial properties of lignin and the high absorption capacity of hydrogels, the removal of undesirable metabolites from the wound would be of high efficiency [11]. For bio-fuel production, as one of the main compositions in plant cell walls, lignin is a favorable resource for heating and combustion due to its high calorific value [2]. 3D printing would benefit from plastic materials with the composition of biodegradable lignin instead of petro-based materials [12]. Different compositions would result in a different extent of 3D-printability. One study shows that properties of strength, ductility, and toughness of thermoplastic elastomers would be enhanced if 30 wt% of lignin is incorporated [9]. Despite the brittleness of lignin due to the rigid aromatic structure, the potential of applying high-content lignin in 3D-printing gains much attention for bio-friendly purposes.

3. Polylactic Acid

Polylactic acid (PLA), as an example of polymer with biodegradability, plays a significant role in daily life. A large number of manufacturers tend to use bio-plastics (PLA) instead of non-biodegradable plastics. It is an essential substitute for packing because it has a greater load-bearing capacity than non-renewable materials. The bio-based platforms of PLA are natural polymers such as straw, corn, and seaweed. Due to stereochemistry, the structures of PLA contain poly (DL-lactide) (PDLLA), poly (L-lactide), and poly (D-lactide) [13].

As there is a great amount of need for polylactic acid, it is important to explore efficient ways for the production of PLA. The formation of lactic acid (2-hydroxy propionic acid), acting as a monomer, is essential before the synthesis of PLA. When using the chemical method, the intermediate lactonitrile is produced from the reaction of acetaldehyde with the addition of hydrogen cyanide and

catalyst. Following that, the hydrolysis is processed under the temperature of 100 ℃ in the presence of sulphuric and hydrochloric acid. Hence, the mixture of DL-lactic acid is formed, which means the properties are not under control [13]. To solve this problem, a biological method, fermentation, attracts researchers because of its low costs, environmentally friendly performance, and production of pure optical isomers [13].

The conversion of lactic acid (LA) into PLA can be separated into three steps, i.e., fermentation, polycondensation, and ring-opening polymerization (ROP) [14]. The production of fermentative lactic acid has great impacts, such as the formation of two enantiomers L- and D-lactic acid, economically friendly effects, and high productivity. Then, polycondensation is applied to remove water during synthesis at high temperatures and pressure. Finally, ring-opening polymerization of lactic intermediates produces PLA under controlled temperature and catalysis [14].

PLA displays a wide range of applications in industries, and food packing is the most common practical use. The properties, such as high resistance with different solubility of water, and biodegradability, are advantageous to be used in packing. In comparison to non-renewable plastics, such as polyvinyl chloride (PVC) and polyethylene terephthalate (PET), PLA is an ideal material with superior molecular weight and machinability. However, thermal stability is a big issue for commercial PLA food packaging since the deformation occurs at high temperatures. Moreover, PLA has a great influence on medical treatment. It will undergo a spontaneous breakdown via hydrolysis at the implantation site, which means no further steps are required for the removal of the equipment. The excellent biocompatible feature of PLA will reduce the probability of the activation of the immune response, which may potentially increase the recovery rate and decrease healthcare expenditure [14]. Furthermore, PLA has also been applied to the agricultural sector. The plastic industry is not dependent on pure PLA because of the limitations of mechanical and thermal characteristics. Instead of using only PLA to produce multch films, a combination of PLA and other polyesters with biodegradability is blended together. For commercial mulch films, plasticizers are frequently used since biodegradable LA derivatives or oligomers have been created [14]. However, this high-cost technology still requires to be improved in the near future.

4. Polycarbonate

The reduction of emission of carbon dioxide (CO2) becomes more and more prior because it is the main source of greenhouse gas. The transformation of CO2 into renewable polymer polycarbonate (PC) shows a positive effect on environmental issues. Polycarbonates are a category of thermoplastic polymers with carbonate groups included. Polycarbonates are known for durability and toughness in the field of engineering.

With the addition of a catalyst, the synthesis of CO2-based polycarbonate has two results, i.e., reductive and non-reductive transformation. For the reductive transformation of CO2, the reducing agent, such as H2 and hydrosilanes, and a large amount of energy are required to produce various substances HCOOH, HCHO, CH3OH, CH4, alcohols, alkanes, and so on [15]. In contrast, the non-reductive transformation would produce polymers, while polycarbonate is the highlight during the synthesis. For the production of PCs, two methods can be employed, either the phosgene method by using phosgene as a source of carbonyl, or utilizing deriving diols and organic carbonates from CO or phosgene by transesterification [15].

In addition to the above, the most effective synthesis is the direct polymerization from CO2 and diols with CeO2 catalyst and dehydrating agent nitrile, although the equilibrium limitation is challenging during the processes [15]. One study in 2016 initially covered that the catalytic direct polymerization of CO2 and α,ω-diols, uses a catalytic system where CeO2 and 2-cyanopyridine are involved [16]. In the study, the researchers found that the catalyst of CeO2 and nitrile, typically 2-cyanopyridine, can reach the highest yield of around 99% on direct polymerization and successfully eliminate produced water [16]. Therefore, the issue of equilibrium limitation would be addressed. However, the catalyst system with CeO2 and 2-cyanopyridine imposes a constraint on the degree of

polymerization. The reason for that may be the termination of the end OH groups of resulting polymers by picolinamide derived from 2-cyanopyridine [15].

Compared with lignin and PLA, the applications of polycarbonate are relatively limited. Firstly, because of its high resistance and ultraviolet (UV) protection properties, polycarbonate can be a widely used material for the production of safety glasses [17]. During the initial stages of the development of PC safety glasses, both impacting and burning tests give favorable outcomes. For current research, the majority of PC product manufacturers indicate that PC provides attenuation higher than 99.9% in the UV spectrum. However, it is not typically appropriate for PC safety goggles to be applied in energy-intensive lasers if there is a possibility of intra-beam viewing [17]. Moreover, polycarbonate can be used as a polymer electrolyte due to its amorphous structure. Polypropylene carbonate (PPC), a copolymer of propylene oxide (PO) and CO2, is the core material used for electrolytes because of its high performance on interfacial connection with electrodes [18]. CO2, PO, and unsaturated cyclic anhydride are crosslinked terpolymers, which are utilized as a polymer electrolytic membrane that is activated by a high-quality liquid electrolytic solution. The resulting membrane has excellent mechanical properties, thermal properties, and a high level of ionic conductivity. Therefore, it is not only useful in gel electrolytes but also in all-solid-state electrolytes [18]. Despite its high cost during production, more investigations will be conducted to solve this problem because of the biodegradability of material polycarbonate.

5. Polyurethane

Polyurethane (PU), one of the most popular polymers in the world, is a group of polymers that are made up of organic units linked together with urethane bonds [19]. With the addition of chain extenders, crosslinkers, catalysts, and other additives, PU is primarily produced through a reaction between isocyanates and polyols [20]. As a block polymer, the main chain of PU is compromising soft and hard segments [20]. Since there is a wide range of starting materials that can be utilized for PU synthesis, it is feasible to produce products with various structures and an extensive range of properties. Also, some investigations mentioned that it is possible for PU to undergo chemical recycling [19]. In other words, the polymer would be converted back into its monomers or segments. At the same time, new polymers would be made up as well.

The production of polyurethane generally involves two methods, either the single-step or two-way method. In the one-way method of synthesizing PU, the reaction between isocyanate and polyol takes place straightforwardly while the chain extender, crosslinker, and other additives are present. Whereas in the two-step method, the initial step includes the creation of a pre-polymer, in which both end groups of the molecule contain isocyanate structures. This reaction would undergo if there is an excess amount of isocyanate when the reaction of polyol processes [20]. Following that, the reaction of pre-polymers and active hydrides, such as amines and carboxylic acids, would take place resulting in the formation of substituted ureas that involves NHCONH groups. Subsequently, a curing reaction happens wherein the interaction between excess NCO groups and active hydrogen in reactions containing NHCOO and NHCONH groups with the addition of either chain extenders or crosslinkers [20].

Further explanation of the two-step synthesis will be discussed in detail. The reaction was carried out at 80 ℃ for 2 hours with the gradual addition of the diisocyanate, resulting in the production of pre-polymer. In the end, the reaction between the reaction medium and the gradually added chain extender would last for 8-10 minutes. This reaction would not stop until there is a noticeable rise in viscosity, which allowed PU chains to increase size.

The application of polyurethane in pavement engineering is becoming more and more widespread due to its outstanding properties, such as resistance to high temperature, durability, and resistance to aging and oil [20]. These advanced roadway engineering theories and technologies play an essential role in supporting the expansion of high standards of road engineering, though more studies are required to further explore the potential practical uses for polyurethane.

6. Conclusion

The increasing concern about climate change caused by the pollution of non-biodegradable waste gains more and more attention from people. Researchers attempt to find alternative renewable materials as the main sources for large-scale production in industries. In this paper, four common renewable polymers were introduced in manufacturing including lignin, polylactic acid, polycarbonate, and polyurethane. Since these econ-friendly polymers have various properties, a large number of applications make them useful in many fields. Lignin can act as a main material in the production of bio-fuel, wound dressing in medication, and 3D printing. The practical uses of polylactic acid also cover a wide range, such as food packaging and PLA-based mulch films in agriculture. Compared with lignin and polylactic acid, polycarbonate and polyurethane have relatively fewer applications. Polycarbonate is used as a material for safety glasses and polymer electrolytes. Furthermore, researchers would make use of the properties of polyurethane in pavement engineering, although it still needs further exploration. Since different renewable polymers have varying functions in every field, it is hard to identify the best biodegradable polymer among these four examples. In conclusion, renewable polymers have great potential to become an important material in every field in the future.

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