Properties, Preparation and Application of Nature Fibers/Sustainable Polymers

Yinxuan Wan*

College of Materials Science and Engineering, Donghua University, Shanghai, China

* Corresponding Author Email: 201100315@mail.dhu.edu.cn

Abstract. Plastics have become one of the most indispensable items in human life. For instance, they are the package of literally everything in our day-to-day life: food packaging, water bottles, coffee take-away cups, etc. However, the outrage of plastics' production and their non-biodegradability has become a serious issue to the environment and human health. More and more plastics are manufactured to meet the demands in several industries and the growing rate of its production is soaring annually. Furthermore, there is not yet a way to degrade plastics, like polyethylene and polyethylene terephthalate, in a both low cost and efficient way. Nature fibers and sustainable polymers have been discovered to be the substitute for plastic and has now been validated that they can be put into mass production. The specific kind of fibers and polymers possess excellent degradability, meaning they can be degraded into non-toxic substances, for example H_2O and CO_2. Meanwhile, they can be acquired from the nature, for instance, trees. This paper describes three materials that have prominent future in replacing conventional plastic to take over plastic's dominating place in our daily use---poly lactic acid (PLA), cellulose and lignin. The three materials' obtaining methodology, properties and current applications are discussed.

Keywords: Environmental problems; biodegradability; nature fibers; sustainable polymers; renewable polymers.

1. Introduction

Nowadays, a splendid number of productions is based on non-biodegradable polymers, and it has led to numerous problems. One of them is that those polymers are not capable of degradation and so, the useless or used products are piling up in corners all around the globe, disturbing not only human health, but also have detrimental impacts on animals, especially marine life that may accidentally eat the plastics for food or being trapped in the plastic bottles and bags. In addition, the ecosystem is disturbed to a great extent as the soil become toxic by the day because the plastic discards are buried under. The chemical fiber, which is one of the most applied fibers in human life, is made from fossil resource. Fossil resources are now exhausting, and it is not a renewable nature resource. Plus, it is not a degradable one, polluting the earth from the beginning to the end. In China, up to about 2 billion tons of chemical fibers are now hoarding and is estimated to see a 10-million-ton increase annually. Therefore, finding bio-based, biocompatibility and most fundamentally---degradable polymers and nature fibers to substitute conventional ones should be prioritized. This kind of sustainable polymers, also known as bio-based materials, are made from renewable nature resource, for instance from corn, wheat or trees. Then, olefins or organic acids can be obtained through chemical, physical or biological methods to be later fabricated into appliable materials. PLA is considered one of the most promising candidates to replace plastic packing. Lignin is a prominent nature fiber that not only see a bright future in wound dressing, but also play an important role in bio-fuel. Cellulose, also originate from nature, is one of the most commonly applied, environmentally-friendly fibers that has a great potential in the upcoming future. The paper is going to illustrate all the three materials' preparing and extracting methodologies in detail. Then, their properties are described for further understanding in their applications. Finally, their current uses in several industries are described. It is worth mentioning that the applications mentioned in this paper do not include all fields that they can be applied to or have been applied to now. Sustainable polymers are being highly spoken of because of their moderate mechanical properties that are adequate for daily using applications, their excellent biodegradability in that they can be fully degraded into objects that are of no toxicity, like water and carbon dioxide.

Moreover, the degradation process is accessible with low cost and no toxic chemical solution is acquired, indicating that the process is environmentally friendly. Therefore, more emphasis should be put on the research in degradable polymers and nature fibers and more applications should take sustainable polymers into considerations for manufacture's raw materials to address the serious environmental problems from the very beginning.

2. Poly Lactic Acid (PLA)

2.1 Polymerization Methodologies of PLA

Corn is the great abundant natural resource for lactic acid. After obtained from corn, lactic acid is polymerized. Three most used ways are direct polymerization, ring opening polymerization and polycondensation. With the help of catalyst and the heat, lactic acid is polymerized through condensation is called direct polymerization. Products obtained through this method has relatively high purity with low cost, less environmental impacts than solvent polymerization, but rather a lower molecule weight compared with other polymerization methodology. The difference between direct polymerization and polycondensation method is that a prepolymer is first acquired in the polycondensation right before it turns into poly lactic acid. The last methodology, ring opening polymerization, is the most used one to produce PLA worldwide. Latic acid first form its oligomer. Then the oligomer is converted into lactide. Finally, lactide opens its ring and form poly lactic acid. The PLA produced through this method has a comparatively high molecule weight and strength.

2.2 Properties of PLA

The most outstanding property of PLA is its biodegradability. It can be fully degraded into carbon dioxide and water through microorganism or light degradation, so that there should be no extra byproducts aside from CO2 and H2O theoretically. Moreover, lactic acid can be metabolized by human body. The biocompatibility makes it one of the promising materials to in medical area to be implanted into human body for medical purposes. In addition, PLA is polymerized from lactic acid which can be easily extracted from nature resources such as corn and wheat, meaning it is a bio-based product with almost no harm to the environment during the manufacturing procedure, from the beginning to the end. The melting point of PLA is high, the crystallinity is fine, and PLA has certain degree of strength so that the material can be simply manufactured and well-applied.

2.3 Applications of PLA

2.3.1. Food packaging

PLA's most applied field is food packaging. Compared to conventional food packaging, for example PE and PET, PLA can store the food stuff longer. PLA is a hydrophobic crystalline polymer, making it water-resisting and oil-resisting, so that it can extend the food shelf life [1]. In addition, research now have found that adding antioxidant and antimicrobial extracts, for example rosemary extracts and green tea extracts, into PLA can extend the food lifespan even longer without sacrificing too much of PLA's mechanical properties by delaying the lipid oxidation in food, especially those with high fat content [2]. Those extracts are nature resources, remaining PLA's biocompatibility and bio-degradability.

2.3.2. 3D printing scaffolds

PLA itself is considered a good choice for bone regeneration process because the addition of it to medical composites can enhance the species' bone remolding capability, since PLA can facilitate cell attachment and new bone formation ability. Also, PLA possess significant biocompatibility and processibility. However, PLA alone has inadequate mechanical properties. Fortunately, researchers have discovered that with the help of slight amount of graphite, the strength is greatly improved of the PLA/Gr composite without disturbing the degradability and biocompatibility of the material. In addition to that, the addition of magnesium particles enhanced the composites' ultimate tensile

strength from 46.7 MPa to 50.4 MPa and the ultimate compressive strength from 44.6 to 49.7 MPa. Mg particles increased the composites' degradation rate for about 77% because it changed the hydrophobic surface to a hydrophilic one, meaning that the composite can better dissolve in suitable solvents. Moreover, the hydrolysis of PLA owing to its ester bond will produce acidic. The magnesium particle will react with water and produce alkaline. The acidic and the alkaline will consume each other through neutralization and further encourage the increase of the degradation rate [3].

2.3.3. Wound dressing

PLA's biodegradability, biocompatibility and low manufacturing cost has made it a widely applied choice for wound dressing. Owing to PLA's hydrophobic surface and its certain extent of self-peeling characters, it can efficiently avoid making secondary injuries when removing the wound dressings. The trickiest hurdle to conquer for serious wounds to heal is that the bacterial infection could be detrimental. Therefore, finding antimicrobial material is fundamental. Silver nanowires has now been acknowledged in several research that the silver ions released perform great antibacterial properties. With the combination of the material mentioned, the PLA/silver nanowires composite is now expected to be the next most applied material in wound dressing. Tests showed that the thermal stability of the composite is fine since no massive weight loss is observed before 380℃. It is noticeable that with the more silver nanowires added, the less the weight loss there will be after 380℃. While the strength is decreased with the addition of silver nanowires, the strain in break is enhanced from 40% to 65%. The composite exhibit great inhibitory properties, especially when the content of silver nanowires reaches 10%, it could thoroughly eliminate of E. coli [4].

3. Cellulose

3.1 Extraction Methodologies of Cellulose

Similar to PLA, cellulose originate from the great nature. In addition, cellulose has the largest number of resources among all the biopolymers. Notably, cellulose can also originate from argo waste, like banana peel, coffee husk and etc. In general, the first step to extract cellulose is to add a certain amount of ethanol (often 1:1) to the original resource to make a mixture. In some situations, the mixture should be left for nights before proceeding to the next steps. Then, the delignification is carried out. Alkali, typically like NaOH, is added to the mixture to eliminate the existence of lignin and hemicellulose to purify the product. High temperature and high-pressure conditions can be applied to obtain the product with better quality. Na_2S and NaOCl are sometimes added in the delignification progress. After that, the mixture is bleached, usually with H_2O_2 or sodium chlorite or ozone. Following that, the obtained cellulose is washed first by ethanol, then by water and finally ethanol again to clean of the solution that is still attached to the product. At last, the separated cellulose is dried in an oven with specific parameters before its preservation for further applications [5].

3.2 Properties of Cellulose

Cellulose is the most abundant and the most common polysaccharide on earth, exceeding 50% of the carbon in nature. It does not dissolve in water or other organic solutions. The fiber is stable in ambient conditions attributed to the hydrogen bond in its structure. Cellulose can hydrolysis under specific conditions and break its oxo bridge. Also, cellulose can engage in redox reactions and alter its surface and structure to broaden its application and enhance its properties. The thermal stability of the fiber is fine, no obvious weight loss is observed until 150 ℃. The flexibility is low due to the strong bond between molecules and the polar effect [5].

3.3 Applications of Cellulose

3.3.1. Food packaging

The addition of cellulose exhibits the hydrophobicity because the cellulose does not dissolve in solutions in ambient conditions. Also, the thermal stability is enhanced. Mechanical properties are better as well. After the process of collecting, delignification and bleaching, the cellulose is derived from bamboo. Then, it is modified through two distinct methods before the cellulose is added to the starch-based film for fabrication. The film acquired with modified cellulose presents a more hydrophilic surface. The tensile strength, young's modulus, elongation break, and strain energy are all enhanced with the addition of bamboo cellulose, and the Starch–BamHNO3-PO4 films showed better properties than the Starch–BamChl-PO_4 films. Thermal stability is improved at the same time with the bamboo cellulose from about 300 ℃ to about 340 ℃, and this enhancement is critical for the film's application in food packaging. Another astonishing property of the composite is that it could be used as a UV protecting material. For Starch–BamHNO3-PO4 films, merely 24.8%T for UV A, 9.2%T for UV B and 2.7%T for UV C were allowed to transmit, indicating its UV absorbing property. It is also fundamental for food packing because it can serve as the UV shield for the foodstuff on the inside, extending the food shelf life and better preserve the quality of the foodstuff [6].

3.3.2. Water purification

Polymer matrix nanofibers composites is polymer matrix combined with nanofiber fillers. The matrix and the enhancement fibers interact with each other on the molecule level, leading to a higher thermal stability and improved mechanical properties of the composite. Cellulose with silver nanowires has now been considered the potential antibacterial composite to eliminate the water born germ positive and germ negative bacteria. Nano cellulose has gained massive attention for its biocompatibility, free of toxicity, fine mechanical properties. Nano cellulose can absorb the toxic matters in water through the interaction between the toxicity and the surface of Nano cellulose surfaces. The interaction could be ion exchange or interactions between molecules or more complicated chemical reactions. Moreover, Nano cellulose is expected to absorb the heavy metal to purify water. Ions like Cr^{2+}, Hg^{2+}, and $Cu2^{+}$ are also expected to be absorbed by Nano cellulose [7].

4. Lignin

4.1 Extraction Methodology of Lignin

Lignin, another nature fiber with sufficient resources originating from the earth, for example sugarcane, ash trees, peanut shell and etc. The common procedure to extract lignin start by drying the resource until the moisture rate drops to about 10%. Next, depending on the resource, it is either scattered into a powder or added proper solution to make a mixture. Then, the product is treated with sodium hydroxide and a black liquid is obtained. Following that, either acid or ethanol is added to the liquid to precipitate lignin. The precipitated lignin will then be washed by ethanol and water. Finally, it is dried in a vacuum oven and stored for application [8, 9].

4.2 Properties of Lignin

Lignin is a biopolymer with network structure. It possesses abundant aromatic rings and benzo-quinonyl, leading to its high rigidity which can help delay the decomposition in wood. The xylem of a tree is rich in lignin and lignin's high mechanical strength is what helps to bear the weight of the tree from the very bottom. Lignin came in second in terms of the total amount of resources among the biopolymers (cellulose ranks first as mentioned). In addition, it is rare that a species with such enormous amount of aromatic structure can be renewable and biodegradable. Contrary to cellulose, lignin can dissolve in ambient condition in alkaline and sulfite solution.

4.3 Applications of Lignin

4.3.1. Renewable energy

Energy demands has surpassed the past and the future because people's demand for electricity in life and in industries is soaring. Renewable and sustainable solar and wind energy substitute have been found and they can produce adequate electricity. However, the two energies cannot be provided constantly so they may not be producing electricity whenever people need to use electricity. Therefore, finding super capacitors to store energy are an urgent matter. Lignin based activated carbon has already been applied in energy storage in super capacitors. The activated carbon is manufactured from extracted lignin which is obtained in the black liquid. Then, it is treated in KOH under heat. The capacity of lignin based activated carbon could reach values close to 400 F/g, which is sometime twice the volume of regular capacity [10].

4.3.2. Wound dressing

Lignin is not only the biodegradable and biocompatible fiber, but also it is known for its antioxidant and antimicrobial properties. Therefore, it is considered a good choice for wound healing process. Curcumin also exhibits wound healing potential capabilities. The combination of lignin and curcumin with the addition of poly caprolactone, which is a biocompatible material, is aimed to fabricate wound dressing with antibacterial property. Using the 3D printing method, no solvent will be wasted so that no harm will do to the environment. Semi-solid extrusion fabrication method produces filaments that can load with rather a large amount of drug without preparing the polymer. 2, 2-diphenyl-1-picrylhydrazyl (DPPH) assay is carried out to test the lignin composites' antioxidant property. The addition of lignin alone or lignin and curcumin to the poly caprolactone matrix can increase the antioxidant rate to both about 70%. Similarly, for the antimicrobial property, the addition of lignin alone or lignin and curcumin to the poly caprolactone matrix can increase the antimicrobial rate to 88.8% and 89.9% respectively. Therefore, statistics revealed that the addition of lignin to the composites can inhibit the infection of the wound so that it could heal more efficiently. The wound closure test illustrating that there is no observation of infection and supported the view firmly as well [11].

5. Conclusion

The annual production of plastic has reached more than 300 million tons by the year of 2019, so the phenomenon calls for immediate actions on finding renewable materials. This paper discussed how nature fibers and sustainable polymers can be the replacement for environmental-unfriendly plastics, such as PE, PET. Abundant researches have validated biobased polymers and nature fibers' promising future for their critical bio-compatible properties. With people's more attention to sustainable production and to protect the environment, the issue will be addressed with the joint efforts of both the manufacturing companies, governments and citizens.

However, it is true that the preparation and polymerization methodologies for those renewable species are not yet mature and the procedure of manufacturing can also cause environmental problems such as wasted solvents slipping into rivers and the sea. The sustainable polymers are not taking over plastic once and for all, even though some of the renewable polymers have already been put into massive production, like drinking straws made from PLA. In addition, due to lack of certain properties like insufficient mechanical strength, the development of bio-compatible polymers needs to be taken to the next level to broaden their applications. Moreover, the safety of the bio-based polymers products, namely the cytocompatibility and the cytotoxicity should be strictly tested and validated with the help of the supervision of governments. Most importantly, the degradation of the biopolymers should be seriously taken into account to secure every one of them is degraded until it is clean before discharge. Meanwhile, it is still a problem that way too much chemical manufactured polymers are still piling up and the conventional way of burning them all up is even more hazardous

to the ecosystem than producing them in the first place. Researches need to be extended on this subject as well.

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