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Review on the Modification Methods and Application Prospects of PHA and PLA Materials

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Abstract:

Plastic pollution worldwide is in trouble with regular plastic piling up in the ocean and fresh water. Biodegradable bioplastics like polyhydroxyalkanoates(PHA), polylacticacid (PLA) etc have been receiving great attention because of their ecofriendly properties. PHA, which is formed by bacteria and other kinds of microorganisms, has good biodegradability, biocompatibility, and environment-friendliness. It can also be used for water purification via filtration membrane, adsorption media, or biofilter support. PLA is biodegradable, biocompatible and sustainable, this can be applied for water purification. Adsorption capacity, Mechanical strength, Hydrophilicity, all can be modified and both are hurting on land and in water, helping with the world's plan to make less plastic mess. Using renewable sources can be broken down under certain circumstances reducing long term water pollution. Second, they have a smaller carbon footpring, because the production and disposal also match the standards of the circular economy. For water purification, they must possess adequate mechanical strength and chemical stability, tunable hydrophilicity or hydrophobicity, and biodegradability so as to avoid secondary pollution. These property can be improved / compounded I look at how they have changed stuff and what people may use it for to clean up water, I write about what problems they might run into right now, and also give some clues about what might happen in the future.

Keywords: Polyhydroxyalkanoates (PHA); polylactic acid (PLA); water purification; biodegradability; modification methods.

1. Introduction

With the worsening problem of global plastic pollution, the accumulation of traditional plastics in marine and freshwater environments has caused serious environmental hazards. To tackle these risks, biodegradable bioplastics including Polyhydroxyalkanoates (PHA), Polylactic acid (PLA), etc., attract global attention because they are eco-friendly.

PHAs which are produced by certain bacteria as a result of biogenic synthesis is called, and this type of polymer has very good degradability, biocompatibility as well as environmental non-toxicity. PHA can be applied for purifying water. PHA can be made into filters for filtration membranes, made into adsorbers or can be used to support bacteria in biofilters. and PHA is it could potentially be made into surfaces that can get rid of some types of impurities on an active level by using it. Current research mainly includes: improving the production of PHA, improving the mechanical and functional properties of the phospholipid-based materials, and designing materials for specific pollutants (heavy metals, pesticides, organics) Biopolylatex acid(POL)materials are biodegradable, biocompatible, and sustainable, and therefore has a wide application in the field of water purification treatment. PLA's performance when it comes to cleaning water can get better through some changes, and that might mean making it have a better way to stick to stuff, getting tougher so it can withstand more, or having an easier time soaking up water.

For these 2 types of materials, the potential for biodegradation isn't limited to land, since they can break down in sea and water as well, it could help decrease the huge problem on earth about plastic waste. They are made from renewable resources like bugs or plants and you can break them up under some conditions and with a little bit of time. It would reduce water pollution in long term. Additionally, they have fewer carbon emission outputs in both production and disposal which is also in line with the basics of sustainable development within the circle economy.

In wastewater cleaning area, the PHA and PLA should have enough mechanical strength and good chemical stability, can resist all kinds of chemical erosion in water, and have no decomposition to release harmful substances after being used. Tunable property of hydrophilic or hydrophobic for good pollutant elimination. and be biodegradable, so that it would break down on its own once we were done with it, and wouldn't cause anymore pollution. In reality these properties can be changed to some extent by changing or mixing with another material.

This paper will review the modification methods and future development of these two types of material and the potential difficulties under current conditions. and the prediction of future.

2. PHA Materials

PHA is made out of hydroxyalkanoyl monomer. The type and composition of this monomer is what makes its structure differ from one kind to another [1, 2]. Most common types of PHA are short-chain-length (sCL - PH A) and medium-chain length (mCL - PHA). they have different side chain lengths of course they have different physical and chemical properties [2]. PHA materials have multiple mechanisms: it can adsorb pollutants in water as an adsorbent, due to its surface properties [3, 4] ; PHA materials have the characteristics of being degraded by microorganism, reducing the environmental pollution[5, 6]; It can fix and carry some enzymes in water to eliminate specific pollutants from the water [7] ; It can fix and supply Carbon source to promote Denitrification process and degrade nitrogen in the water [8] ; It can be used as carrier of enzyme in water purification and be used to form composite membrane with special nanomaterials to adsorbed or removed water by membrane separation mechanism [4]. Despite its superiority like being biodegradable, compatible with living tissues and good for environment, PHA also faces some restrictions like not tough enough, only somewhat resistant to high temperatures and hard to set speed of wearing out [9 - 11]. By changing it, the mechanical properties, thermal stability, biodegradability, hydrophilicity and antibacterial properties of PHA can also be improved, and it has been widely used in many scientific and technological fields[12].

2.1 Modification

2.1.1 Physical blending modification

Physical Blending Modification: Incorporation of some other polymers or inorganic material and degradability will be improved the mechanical properties and thermal resistance properties of PHA as well. Take mixing PHA into PLAl and PCL as an example. Since pha, pla, pcl, they all have different degradation characteristics, thus the degradation speed of pha is influenced by its chemical constitution and environmental situation[13]. PLA mainly degrades by hydrolysis, and the degradation rate of PCL is slower. Shuffling around different types of polymer, how much of each you use and getting different types of crystal structure (how ordered their molecules are) or letting them become more of less compatible can help control breakdown rate as you want. Besides, blending PHA with nanoparticles like (titanium dioxide, nano-zinc oxide etc.)

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can yield composite materials which display photocatalytic performance for degrading organic contaminants from water [14]. Amphiphilic block copolymers formed from reversible addition-fragmentation chain transfer RAFT polymerization have been mixed with PVDF to form modified membranes.

2.1.2 Chemical modification

Chemical Modification: To add new functional groups into the PHA polymer chain by chemical reaction, thus changing the surface properties and reactivity. For example, by introducing hydroxyl, carboxyl groups, etc., the PHA chains are made with hydrophilic groups through esterification and thus increasing affinity for water [15]; Moreover, methods such as graft copolymerization and cross-linking can also be used to change the molecular structure and degree of aggregation of PHA, so as to change the mechanical properties and biodegradability of PHA.Acid washing can also improve the formaldehyde removal rate by activated carbon[15].

2.1.3 Surface modification

Coating a thin functional film over the surface of PHA substances can provide it with some new properties: for example,after plasmato use chemical vapor deposition to put antibacterial layer in PHA surface, so PHA's antibacterial effect will get improvement.[16] besides, we could adopt self - assembly technique to make nano structured film on PHA's surface, this would boost the surface area additionally the adsorption capacity. PVDF membrane's degree of hydrophilicity and antifouling ability are changed by the plasma treatment of the PVDF membrane surface[16].

2.1.4 Nanocomposite modification

When nanomaterials are introduced into the PHA matrix, it greatly improves the overall performance. To take an instance, the addition of carbon material like graphene and carbon nanoparticles, would give the PHA better mechanical strength, electrical conductivity and thermal stability [17]. Moreover, adding metal nanoparticles like gold nanoparticles, silver nanoparticles, etc. into the PHA matrix, it can endow the PHA with antibacterial and photocatalytic performance.

2.2 Applications of PHA Materials in Water Purification

2.2.1 Microbial removal

PHA can be made into nanofiber membranes or open pore structures to filter bacteria and viruses from water For instance, with the electrospinning method, one can create PHA nanofiber membranes with both high porosity and a big surface area so as to catch up with the bacteria in water [18]. We could also make the PHA be good at fighting off germs by putting stuff on it that fights off germs, like silver tiny bits.

2.2.2 Pollutant adsorption

Put PHA together with adsorbents such as activated carbon and zeolite, we could create things that can stick to the yucky stuff - organic and heavy metal - found in water. like how activated carbon powder gets all mixed in to make that PHA making composite stuff which sticks stuff up and can also catch some too. And the surface modification can add some functional group to the surface of pha material with certain adsorption capacity, so as to make the pha material more selective to absorb some kinds of pollutants.

2.2.3 Photocatalysis

It is also combined PHA can be coupled with photocatalysts such as titanium dioxide nanoparticles, which is used then in the photocatalytic degradation of organics in water. Take titanium dioxide nanoparticles disperse into PHA matrix, then prepare composite with photocatalytic activity as an example [14]. Under the illumination of ultraviolet or visible light, titanium dioxide nanomaterials produce electrons and holes that can oxidize and decompose organic pollutants in water into harmless small molecules.

2.3 Future Prospects

Even though PHA materials are full of prospects in water purification sector, there are still some problems. Chemical transform method will introduce some bad elements, it may lead to secondary pollution. Modified PHA materials might not maintain high performance when used over an extended period of time, for examples, antibacterial chemicals may "leak out" or adsorbents can lose their ability to adsorb. Also, there are some new types of modification materials that are quite expensive at present. Future studies about PHA materials for water purifying might focus on these parts: Development of new eco-friendly modification methods, Improvement of the stability and service life of the modified materials, Reduction of the production costs of the modified materials, Wider application range of PHA in water purification Through repeated improvements to modification methods and expansion of application fields, PHA materials are expected to take on a larger part of the water purification field in the future and tackle the current global water resource crisis.

3. PLA Materials

Polylactic acid (PLA) is a biodegradable thermoplastic polyester produced using renewable resources like lactic acid extracted from corn starch or sugarcane [19-24]: In water purification field, mainly used is various membrane forms of PLA. Nonwoven Fabrics [25, 26]. The membrane material can achieve controlled wettability so as to obtain good oil-water separation performance, and it can also be used for the photocatalytic degradation of pollutants [25]. However, PLA iteself is not perfect, there are problems such as brittle and hydrophobicity which should be modified in terms of water treatment. [23] The mechanical strength, heat resistance and biodegradability of PLA can be improved further by compounding it with other materials such as metal nanoparticles or carbon-based materials. This would result in better removal of pollutants from water [27]. The application of using modified PLA-related materials for water purification is mainly achieved through the utilization of the biocompatibility, biodegradability, and synergistic effect between it and other functional materials. Thus to allow for the adsorption and decomposition of environmental pollutants [25, 27-30].

3.1 Modification

3.1.1 Blending modification

And also PLA can be combined with other kind of biodegradable polymers like poly(butylene adipate-co-terephthalate) (PBAT) and polycaprolactone (PCL). Blending modification also involves the various mechanisms like compatibility, and formation of microphase separation structures, change in Crystallinity, Stress transfer and Processing rheology all these make it possible to enhance the toughness and processability of PLA [31-34]. Take PLA co-polymerized with bio-based poly (pentylene 2,5-furandicarboxylate), it is improved in PLA toughness [31]. PLA blended in TPS, costs can be reduced but the modification is necessary to improve compatibility. [32,35] And it also uses the bamboo charcoal which is activated and combined with polyethylene glycol in a twin - screw extruder for improving the mechanical properties of PLA [36].

3.1.2 Nanocomposite modification

Add some nanomaterials like silica(SiO2), zinc oxide(ZnO), titanium dioxide(TiO_2) and GO to PLA, and the strength of PLA will be stronger, heat resistance will be better and adsorption will be better. [27, 35, 37-39] like we take in SiO2 nanoparticles as we introduce them to the PLA film and we post thermo treat the membrane to see if we can get an improvement to the membranes desalination [38].

3.1.3 Surface modification

PLA's wettability is also able to change using surface treatment, so it would be more capable of adsorbing nonpolar compounds: For example, improving the oil-water separation ability of PLA nonwoven fabric by grafting with TMPS and TiO_2 nanoparticles[40].

3.1.4 Graft modification

Grafting the biobased polyamide (PA) to bamboo charcoal, which is a carbon based flame-retardant. when the material encounters combustion, bamboo charcoal can generate a char layer which serves as a thermal and oxygen barrier so as to prevent the spread of flames. The porous structure of bamboo charcoal improves the flame resistance of bamboo charcoal. Bamboo charcoal can also be used as filling material for high-stable thermal property of composite materials and reduce the thermodecay. to make it so that the PLA/PCL composite material can still increase its flame retardancy in this way, but without sacrificing degradability [34].

3.1.5 3D Printing technology

3D printing technology can be applied to produce filters equipped with particular structures as well as functions using PLA technology for water filtration [30, 41]. For example, 3Dprinted MOF(metalorganic framework)monolith is customised, highperforming material that can be used for treating water and adsorbing gas [42].

3.1.6 Examples of PLA modification

PLA/PCL/BC-NPA: Surface modification of biochar, then mixing this biochar with PLA and PCL composites for flame retardant. [34] Improved BC-NPA makes combustion improvement better with PLA/PCL composites.
PLA/GPOE-MPOE blends: In order to increase the PLA's friction toughening, the POE which is modified with chemical modification is added to the PLA [43].

3.2 Applications of PLA in water purification

PLA and its composite have been widely researched on the removal of pollutants in water such as heavy metals, dyes, organic pollutants, and microplastics [30, 37, 39].

3.2.1 Heavy metal removal

PLA can be made to soak up lead from water. From the reseach it is found that when molydenum dioxide nanoparticles are added to PLA, it will increase the physical adsorption ability of the water insoluble lead compound to the water.

3.2.2 Dye adsorption

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PLA can be used to take a dye out of water similar to Methylene Blue [39]. PLA-Znob.TiO nanocomposites formed by ultrasonic assisted melt extrusion shows good adsorption performances of methylene blue.

3.2.3 Microplastic separation

3D-printed PLA with polysaccharide nanofibers used to trap metal ions and remove microplastics from the water [30]. They are multi-valued, strong, recyclable, can withstand a lot, and are conducive to sustainable water treatment.

3.2.4 Oil-water separation

Modified PLA nonwovens for oil-water separation [40]. Using the simple and low-price method of immersing the PLA nonwoven fabric into a xylene and trimethylpropylsilane solution for oil-water separation. The superhydrophobic fiber membrane prepared from PLA blended with PBAT has good mechanical properties and can be used for effective oil-water separation. The PLA/PBAT blend membranes modified with banana peel NPs may improve oily wastewater purification and antifouling performance.

3.2.5 Membrane technology

PLA can also be used as a membrane material [22, 37, 38] People think the PLA nanofiber membrane made of electric spinning does great when it comes to filtering liquids and cleaning them up. Novel post- thermally treated, green, biodegradable PLA @SiO_2 nanocomposite membranes can be utilized for water desalination [38].

3.3 Future Prospects

PLA is a very applicable and applicable biodegradable material in the application field of water treatment: Future research might include a couple of important points: coming up with better and cheaper ways to modify it so it can do even more things to clean water; trying to make it work together with other stuff like new tiny things made from nature and special growing food, which could take out different bad stuff from water; learning how well it stays good over time in big water cleaning places where it is used, so we know it works as it should; looking into using a fancy printer to make it faster to get made from a design, just like when you color with crayons and make fun shapes; studying if making this thing for cleaning is nice for our planet and how long it lasts before going away by itself to know if it's good for the Earth.

4. Blends of PHA and PLA

Combining PHA and PLA is also very much in the water purifi cation field. We can mix and match the good traits out of each, for example the strong plastic called PLA and the degradable PHA. In general, it is necessary to add a compatibilizer to improve its compatibility and achieve better comprehensive performance [43]. On the other hand, they also could be effective and long-standing drinking water' s disinfectants by PLA membrane modification grafted chemically QAS monomers. Preparation of water-purification membranes by electrospinning, in order to take advantage of the phase separation of PLA and PHA, prepare membranes with the desired structure (such as spindle-knot type) and improve the degradation Rate. Filtration efficiency [29].

5. Conclusion

PLA and PHA, they are kinds of degradable substances that will help lessen the environment pollution created by discarding plastic. PLA comes from renewable source, it usually made from corn starch which is plant based resource, PHA comes from microorganisms. both materials have wide application range and can be increased by modification or compounded with other materials to increase the materials application range Meanwhile, PLA and PHA also exhibit distinct differences in chemical structure and properties. PLA is a polyester, it has moderate mechanical strength and rigidity, but low toughness. PHA is different from other polyester materials, where there are many types differing greatly from each other, short-chain PHA are harder and long-chain PHA have a better flexibility Synthetic-wise, the PLA main production method is via the polymerization reaction of lactic acid, but it's the accumulation result of microorganisms at certain conditions for PHA PHA's raw material sources are broader, because it can be made with sugar, oil, and sewage. As for the degradation rate, PLA degrades relatively quickly most of the time, but PHA can degrade quickly under certain circumstances. PHA will be more hydrophobic than PLA in most cases and is used for certain purposes. PLA and PHA have all been used in places such as reducing microplastics, mixing changes, and composite materials. Regarding future research, it would cover new kinds of high-performing PLA and PHA substances and disintegrate in different environments; analyze how the substance can be synthesized in an effective and inexpensive way, study when and how these substances will be used depending on environmental influence and the substances inherent properties On the whole, PLA and PHA as a kind of good degradation material in water purification makes a great contribution to sustainable development.

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