

## Research Progress of Fully Biodegradable and Antimicrobial Materials Applied in Personal Protective Equipment

Jingqiu Feng<sup>1#</sup>, Yiwen Zeng<sup>1#</sup>, Zhe Li<sup>2#</sup>, Gaoling Huang<sup>1</sup>, Dong Liang<sup>3</sup>, Enchi Zhou<sup>1</sup>, Chunhong Zhang<sup>2\*</sup>, Dan Li<sup>2\*</sup>, and Linfang Mo<sup>2\*</sup>

<sup>1</sup>Naval Medical University, China

<sup>2</sup>Naval Medical University, Navy Special Medical Center, China

<sup>3</sup>Translational Medical research Center, Naval Medical University, China

#These authors have contributed equally to this work.

\***Corresponding author:** Chunhong Zhang, Naval Medical Center of PLA, Naval Medical University (Second Military Medical University), Shanghai 200433, China, Tel: +86-13001007606; E-mail: [956308151@qq.com](mailto:956308151@qq.com)  
Dan Li, Naval Medical Center of PLA, Naval Medical University (Second Military Medical University), Shanghai 200433, China, Tel: +86-13816577758; E-mail: [13030734@qq.com](mailto:13030734@qq.com)  
Linfang Mo, Naval Medical Center of PLA, Naval Medical University (Second Military Medical University), Shanghai 200433, China, Tel: +86-18916873095; E-mail: [molinfang@126.com](mailto:molinfang@126.com)

### Abstract

Due to the outbreak of the COVID-19, a large number of disposable personal protective equipment (PPE) wastes were generated. It has caused great harm to the ecological environment, even in the future may endanger human health. Therefore, it is of great significance to research biodegradable materials that can be used in the field of medical protective equipment. This article reviews the application of biodegradable materials in personal protective equipment. First of all, the classification, characteristics and general application of biodegradable materials are described. Then, the application of biodegradable antibacterial materials, which can improve the degradability, antibacterial and comfort of medical protective articles, is analyzed. Finally, the significance and challenges are discussed, and some prospects in this field are put forward.

**Keywords:** Biodegradable; Antimicrobial; Personal Protective Equipment; Protective face masks; Medical protective clothing; Nasopharyngeal swabs

### Introduction

Due to the COVID-19 pandemic, frontline workers around the world use about 44 million non-woven Personal Protective Equipment (PPE) everyday, resulting in about 15,000 tons of waste generated every 24 hours. China produces about 25-50 million waste face masks every day, most of which end up in landfill and only a small part

is recycled [1]. Most of these wastes PPE are made of polypropylene, and the highly repetitive methylene group in the carbon chain of polypropylene can produce a highly hydrophobic structure. Meanwhile, there are repetitive methyl side-chains in each monomer, whose structure prevents microorganisms from attaching to the polypropylene surface, making it less prone to biodegradation [2]. Many polypropylene products are incinerated, producing large amounts of carbon emissions and aggravating the global warming, or sent to a landfill, in which case nanoscale microplastics are produced during its degradation process because polypropylene is a non-degradable material that is difficult to remove and can remain in the soil for years. It imposes a huge burden on the environment and even has toxicity effect on human and animal health [3]. The impact of antimicrobial textiles on the environment has also received increasing global attention. At present, the main problem of antimicrobial materials is that their antimicrobial ability is insufficient or not durable. An ideal antimicrobial agent should be efficient with low doses, resistant to washing, and easy to remove --- primarily to avoid contamination when discharged into the wider aquatic environment. Silver, for example, is one of the most popular antimicrobial agents. It is immobilized by forming stable sulfide complexes, which are insoluble in water, and their toxicity and bioavailability are far lower than that of dissolved silver. In addition, in order to assess the safety of antimicrobial compounds for animals and humans, their impact on health should be considered, i.e., the impact of the interaction type, the concentration in textiles, the route of exposure, and the frequency of use, etc. For example, silver may interact with the body's normal microbiota, weaken skin defense barrier, and cause silver metal/silver sulfide particles to deposit in the skin, causing discoloration of the skin and even the eyes [4]. Furthermore, metal ions and their oxides are expensive, and residual metal particles may also be potentially harmful to the environment. At present, in the antibacterial field, bio-based materials such as polyurethane and nano cellulose have come to be valued. In the post-pandemic era, in order to make the protective equipment have higher protective effect and restrain the spread of white pollution, the development of fully biodegradable and antimicrobial materials applied in PPE is of great significance to solve the problem of PPE pollution. This paper mainly discusses the application prospect of biodegradable materials in PPE field.

### **Types of Biodegradable Materials (Table 1).**

Bio-based fully degradable polymer materials are divided into different natural polymers according to the production mode, mainly including polysaccharide polymers such as starch, cellulose, chitin, etc.; and synthetic polymers, mainly including aliphatic polyester containing ester bond, ether bond, amide bond, etc. that are easy to be decomposed, such as polylactic acid and polycaprolactone. Different materials play different roles in protective materials according to their structural characteristics [5].

**Table 1:** Types and characteristics of fully biodegradable materials.

Type	Name of bio-based materials	Source	Advantages	Disadvantages	Range of application
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Natural material	Polysaccharide	Chitosan	The exoskeleton of crustaceans (crabs, shrimp, crayfish) and the cell wall of fungi	No toxicity, no side effects, no rejection reaction, good affinity for human cells, good biocompatibility and degradability; antimicrobial, antiviral, anti-tumor properties and strong adsorption capacity	-	Medical products such as hemostatic agents, absorbable surgical sutures, artificial skin, wound dressings, separation membrane materials, etc.
		Cellulose (Lyocell fiber, acetate fibre, nanofiber)	Agricultural wastes (corn straw, rice straw, sugar cane bagasse), wood, flour, beet, potato tuber, ramie, algae and other plants	excellent biocompatibility, low density, high strength, low cost, favorable mechanical properties, tasteless, odorless, highly crystalline, fibrous, insoluble, thermal and chemical stability, inherent antimicrobial properties	-	Wound dressing, Facial mask substrate etc
		Starch	Corn, potatoes, wheat, cassava, rice	Low price, compatible with antioxidants and antimicrobial agents, good	Poor water vapor barrier and mechanical properties,	-

				film-forming and gas barrier property, hydrophilicity, etc.	etc.	
protein	collagen protein	Pork, beef bone, pig skin, fish skin		Good biocompatibility, low immunogenicity and biodegradability	Poor mechanical performance	Preparation of biodegradable suture, hemostatic agent and wound dressing, biological patch, bone repair material, hemodialysis membrane, hemostatic agent, drug release carrier, tissue engineering scaffold, various ophthalmic treatment devices, etc
	soybean protein	Soybean, soybean chips		Insoluble in water, soluble in acid or alkaline medium, gas barrier performance, acid film shows better Antibacterial activity	The mechanical properties of the films prepared in acid medium are weak	-

Chemical syntheses		PLA	Chemical synthesis or microbial fermentation, pure sugar and food crops, agricultural residues of starch and cellulose, by-products of the food industry	Excellent biocompatibility, no adverse effects on organisms. Excellent mechanical properties and certain antimicrobial and barrier properties after modification	Uncontrollable degradation rate, relatively brittle, poor impact toughness and heat resistance	Protective equipment at various levels, biomedical materials, food packaging, medical sutures, pharmaceutical excipients, tissue engineering, drug delivery, wound management, implants in biomedical field
	PBS products	PBS	Polymerization of succinic acid and 1,4-butanediol (BDO)	Strong tensile strength and toughness, easy for industrial processing, good stability and heat resistance, mechanical and processing properties similar to PP, good film-forming property, cytocompatibility and histocompatibility, no	Longer degradation time than that of PLA, lower transparency and hardness, inadequate succinic acid supply	Packaging (including food packaging, cosmetic bottles, drug bottles), tableware, disposable medical supplies, agricultural films, pesticides, fertilizer slow-release materials, biomedical polymer

				cytotoxicity		materials and other fields
	PBSA	Copolymerization of succinic acid, 1,4-butanediol (BDO) and adipic acid (AA)	Better toughness, faster degradation rate	-	-	-
	PBST	Copolymerization of succinic acid, terephthalic acid (or its dimethyl ester) and 1,4-butanediol	Good thermal stability and mechanical properties, excellent biodegradability, higher profits than PBS	Difficult processing technologies, low degree of industrialization	-	-
	PU	Polymeric polyol converted from natural polymers such as starch, cellulose, tannin, etc.	Good permeability, ductility, and flexibility, higher fitting degree, higher cost performance, environment-friendly	-	-	Face masks, etc.
	PPC	Carbon oxide and propylene oxide	Biodegradability, biocompatibility, impact toughness, transparency, non-toxicity, excellent barrier property	Poor water resistance, heat resistance and mechanical properties	-	Drug sustained release agent, absorbable sutures, disposable tableware, food packaging materials, film products

						field, plastic wraps for low temperature meat products, gum base material, degradable foam material, sheet, etc.
		PGA	Glycolic acid as the synthetic monomer, mainly from beet, immature grape juice and sugarcane.	Faster degradation rate, especially the fast strength decay rate in a short time	Hard and brittle, difficult to be processed, low strength, fast degradation rate, etc.	Absorbable sutures, tissue engineering, drug control systems, absorbable bone nails and plates, surgical correction materials, etc.
Microbial syntheses		PHA	A member of the polyester family consisting of hydroxyalkane monomers	There are a wide range of polyester families, with properties ranging from low to high flexibility, It can adapt to applications in various fields	Expensive, molecular weight (MW), unstable structure, and unstable thermal mechanical properties	-
		PHB	Polyhydroxybutyrate	Low cost, physical properties similar to PP,	Poor thermal stability, high brittleness, low strength	Biofilm materials, absorbable sutures,

				good biocompatibility, certain piezoelectricity, no toxicity, no irritation, no antigenicity, no hemolysis, no genotoxicity	drug-controlled release carriers, orthopedic absorbable plates and nails that can guide tissue regeneration
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### Natural materials

These materials are processed directly from natural materials and are basically non-toxic. The main sources include cellulose, lignin, starch, gelatin, chitin, deacetylated chitin, chitosan and its derivatives [6].

**Polysaccharide:** Chitosan can be formed by the polymerization of chitin after alkaline deacetylation, which mainly comes from the exoskeleton of crustaceans (crabs, shrimp, and crayfish) and the cell wall of fungi [7]. It has good affinity for human cells, no toxicity, no side effects, no rejection reaction, and good degradability. In addition, it also has antimicrobial, antiviral, anti-tumor properties and strong adsorption capacity. Chitin and chitosan have high chemical reactivity. The amidate of carboxylation, cyanidation, acidification and other modifications are widely used in pharmaceutical industry, and the products include artificial skin, wound dressing, separation membrane materials, etc. Chitosan and its derivatives have been widely used as non-toxic or low toxic antimicrobial materials, among which the quaternary ammonium salt of chitosan is the most widely used. Quaternary ammonium chitosan has significantly enhanced antimicrobial activity compared with chitosan and can be used in anti-inflammatory drugs or as filling fibers in wound dressings [8]. For example, HPTC-2, the product of quaternization of natural polymer chitosan, is used as antimicrobial agent. Multiple antimicrobial systems processed by HPTC-2 can have a sterilization rate of 99.8%~100% against staphylococcus epidermidis after one month of use. When HPTC-2 is used to treat cotton fabric, it still maintains more than 80% antimicrobial activity after 20 times of washing, and gives the fabric excellent permanent non-ironing property [9].

**Cellulose:** It can be obtained from agricultural wastes such as corn stover, straw and bagasse, or from plants such as ramie and algae. Cellulose has excellent biocompatibility, low density, high strength, and has the most favorable mechanical properties at a small cost. It is tasteless, odorless, highly crystalline, fibrous and insoluble, and has thermal and chemical stability, inherent antimicrobial properties, etc. Some bacteria can also produce extracellular bacterial cellulose. For example, acetobacter xylinum can be synthesized with Bacterial Cellulose (BC) under aerobic and glucose conditions, and can also be fermented with different media containing glucose. BC can be used to producing wound dressings with good elasticity and strength, which can effectively defend against pathogenic microbial infection [10].

**Soluble fiber:** It refers to the regenerated cellulose fiber using N-methylmorpholine-N-oxide as solvent and used for wet spinning. Its waste can be naturally degraded, and 99.5% of the oxidized amine solvent in the production process can be recycled [11]. It has "very low toxicity, and does not pollute the environment".



Fabrics made of lyocell fiber are characterized by good skin affinity, water absorption and air permeability. Currently, lyocell fiber is mainly used in face mask substrates. In the field of medical protection, lyocell fiber can be used in the inner layer of face masks to improve the comfort of face masks and other PPE [12].

**Cellulose acetate:** The degradability of cellulose acetate, a derivative of cellulose, has been confirmed by many studies. Regenerated Cellulose Fiber (RCF), represented by cellulose acetate, can be prepared into some microfibers by special processes, and then through electrostatic spinning, physical bonding and other processes, it can be compounded into PPE filter elements sufficient to achieve filtration effect [13]. However, compared with lyocell fiber, which also belongs to RCF, the production of cellulose acetate discharges more pollution, which limits its commercial scale production [11].

### **Nanofibers**

Nanofiber membranes with fiber diameters ranging from tens to hundreds of nanometers are suitable for fine aerosol interception. The nanofiber membranes prepared by electrospinning technology can achieve high filtration performance through smaller fiber diameter and pore size [14]. By using electrospun nanofibers, the diameter of the fine fibers is helpful to increase the specific surface area of the filter medium, so as to improve the filtration ability of the nanofiber layer [15]. Nanofibers have a large specific surface area, which has obvious advantages in loading active substances in nanofiber face mask. In addition, nanofibers can also achieve the slow-release effect of composite active substances. Nanofibers have good retention capacity for the antimicrobial drugs compound on them, so that a longer antimicrobial protection effect can be achieved [16].

**Starch:** Mainly derived from corn, potato and other crops, this kind of material is compatible with antioxidants and antimicrobial agents. It has good film-forming and gas barrier property, hydrophilicity, and poor water vapor barrier and mechanical properties [3].

### **Protein**

**Collagen:** Mainly derived from pork and beef bone, pig skin, fish skin, it is a flexible polymer with a complex structure, the barrier property of which decreases with the increase of Relative Humidity (RH). Due to its good biocompatibility, low immunogenicity and biodegradability and other characteristics, it has become the most popular raw material for biopolymer packaging. The mechanical properties of collagen are poor, but can be improved by cross-linking modification or combining with other biomaterials. At present, collagen has been widely used in the preparation of biodegradable sutures, hemostatic agents, wound dressings, biological patches, bone repairing materials, hemodialysis membranes, hemostatic agents, drug release carriers, as well as tissue engineering scaffolds, various ophthalmic treatment devices, etc. [10].

**Soy protein:** Mainly derived from soybean and soybean flakes, it is insoluble in water, but soluble in acid or alkaline media. Its flexible film has good gas barrier property, and its acid film shows better antimicrobial activity, but weaker than the mechanical properties of the film prepared in alkaline media [3].

### **Chemical synthesis**

Compared with natural polymers, biodegradable polymer materials synthesized by chemical methods can be designed and adjusted to achieve the goal of synthesizing target materials by selecting appropriate monomers, controlling reaction conditions in the synthesis process, or carrying out simple, low-cost physical or chemical

modifications, according to the needs of practical applications. At present, the main chain of chemically synthesized biodegradable polymers generally contains hydrolyzable ester group, acyl amino group or urea group. So far, aliphatic polyester is the most widely studied and used chemically synthesized degradable polymer material in clinical biomedical practice.

### **Poly(lactic acid (PLA, polylactide)**

As a representative biodegradable polymer, PLA is considered as a promising material candidate. It is biodegradable thermoplastic polyester produced by the polycondensation of lactic acid, which can be fermented from carbohydrates such as corn, sugar cane or cassava [17]. Due to its low cost, excellent mechanical properties, ease of processing, hydrophobicity, and antimicrobial activity [18,19], PLA has been widely used in biomedicine field for tissue engineering, drug delivery, wound management, implants, and food packaging, etc. At the same time, with its natural precursor, PLA is also susceptible to biodegradation such as thermal decomposition, enzymatic hydrolysis, oxidation or photolysis [20]. As a kind of PPE, PLA also shows excellent mechanical properties and certain antimicrobial and barrier properties after modifications, so it is widely used in various kinds of protective equipment. For example, in face masks, PLA is used in different layers by taking advantage of different functional characteristics of PLA after different processing. The filter layer generally adopts melt blowing technology to reduce the material gap and improve the filtration performance [21]. The inner and outer layers can adopt the electrospinning technology, which not only ensures softness, but also improves the air permeability of the fabricated fiber film, making the face mask fluffier and more plastic. Thus, it can improve the fit degree between the mask and the face, making it comfortable to wear with good antimicrobial and filter performance. In addition, the PPE prepared by electrospinning technology has good degradability, and the composite fiber membrane of face masks made of such materials can be directly composted or incinerated after use. There will be no chemical pollution in the incineration process, and the PPE can be completely degraded into CO<sub>2</sub> and H<sub>2</sub>O within a few months after landfill. However, this technology is not mature at present and the cost is high, so it is not suitable for application or mass production [22]. In addition, although PLA itself is a brittle polymer, the toughness of PLA material can be greatly improved after blending it with toughening agents, and can even be toughened. Therefore, PLA mixture is also an ideal material for non-fabric protective equipment such as protective face masks. As far as the barrier property is concerned, the antimicrobial property of PLA material mainly comes from other materials compounded with it. However, PLA has good biocompatibility and is easy to be compound with other materials. For example, it can be used as the packaging of disposable medical supplies after being compounded with polybutylene succinate [23].

**Polybutylene succinate (PBS):** PBS is a linear degradable aliphatic polyester formed by the polycondensation of 1,4-butanediol and succinic acid. It has strong tensile strength and toughness, and is easy for industrial processing. It has good stability and heat resistance, and mechanical and processing properties similar to polypropylene (PP), which make it a leader in biodegradable plastics. The biodegradable nano-filter element made of PBS is hygroscopic, breathable, comfortable and antibacterial, and it is widely used in packaging, daily use, agricultural film, textile industry and other fields. Furthermore, due to its good cytocompatibility and histocompatibility and no cytotoxicity, it is also widely used in biomedical polymer materials and other fields. However, the degradation rate of PBS is slower than that of PLA [24].

### **PBSA**

It is formed by the polycondensation of succinic acid, 1,4-butanediol and adipic acid. Compared with PBS, it has better toughness and faster degradation rate [25].

### **PBST**

It is prepared by the copolymerization of succinic acid, terephthalic acid (or its dimethyl ester) and 1,4-butanediol. It has good thermal stability, mechanical properties and excellent biodegradability, and is widely used in disposable daily necessities, packaging materials, agricultural films and other fields. The huge domestic polyester production capacity can be used for transformation, but the process technology is difficult and the industrialization degree is low. At present, only Sinopec Yizheng Chemical Fiber Company has achieved 10,000 tons of industrial production.

**Polyurethane (PU):** PU is a kind of polymeric polyol organic polymers, which can be converted from natural polymers such as starch, cellulose, tannin, etc. The internal structure of the face mask made of PU is a three-dimensional mesh, ensuring a dust barrier rate as high as 99.5%. It can be cleaned for many times. According to relevant studies, the dust barrier rate after 4-10 times of cleaning is still 99%, which improves the reuse efficiency. The diameter of PU fiber is much smaller than that of ordinary material fiber, and the three-dimensional mesh filter structure makes it more breathable, extensible, softer and fitter. Degradable PU is more cost-effective and suitable for the production of face masks as an environment-friendly material.

**Polypropylene carbonate (PPC):** PPC is a kind of completely degradable and environment-friendly plastic synthesized from carbon dioxide and propylene oxide, which is also one of the most promising environment-friendly plastics at present. It has biodegradability, biocompatibility, impact toughness, transparency, a virulence, and excellent barrier property. It is mainly used for blending with polyolefin to improve the solvent resistance and oxygen barrier property of products, or with degradation materials such as PLA, PBAT and PBS, etc.

**Polyglycolic acid (PGA):** PGA uses glycolic acid as the synthetic monomer, mainly derived from beet, immature grape juice and sugarcane. Its degradation rate is fast, the strength decay is especially fast in a short time. But it is hard and brittle, and is difficult to process with a low strength and a fast degradation rate [6]. Therefore, it has been modified by many methods to optimize its physical and chemical properties to expand its application field. At present, modified PGA has been widely used in absorbable sutures, tissue engineering, drug control systems, absorbable bone nails and plates, and surgical correction materials, etc. [10].

### **Microbial synthesis**

It means that some organic matter (such as glucose or starch) is used as food source, and the carbon source organic matter is synthesized into polyester or glycan polymer with differentiable characteristics under the action of a series of complex reactions such as fermentation of micro-organisms. At present, polyhydroxybutyrate in polyhydroxyalkanoate is the widely used biodegradable polymer materials synthesized by microorganisms in clinical practice. Both of them are thermoplastic polyesters synthesized by a series of microorganisms, but their use is currently limited by the high cost and the complex biological processes.

### Blended biodegradable materials

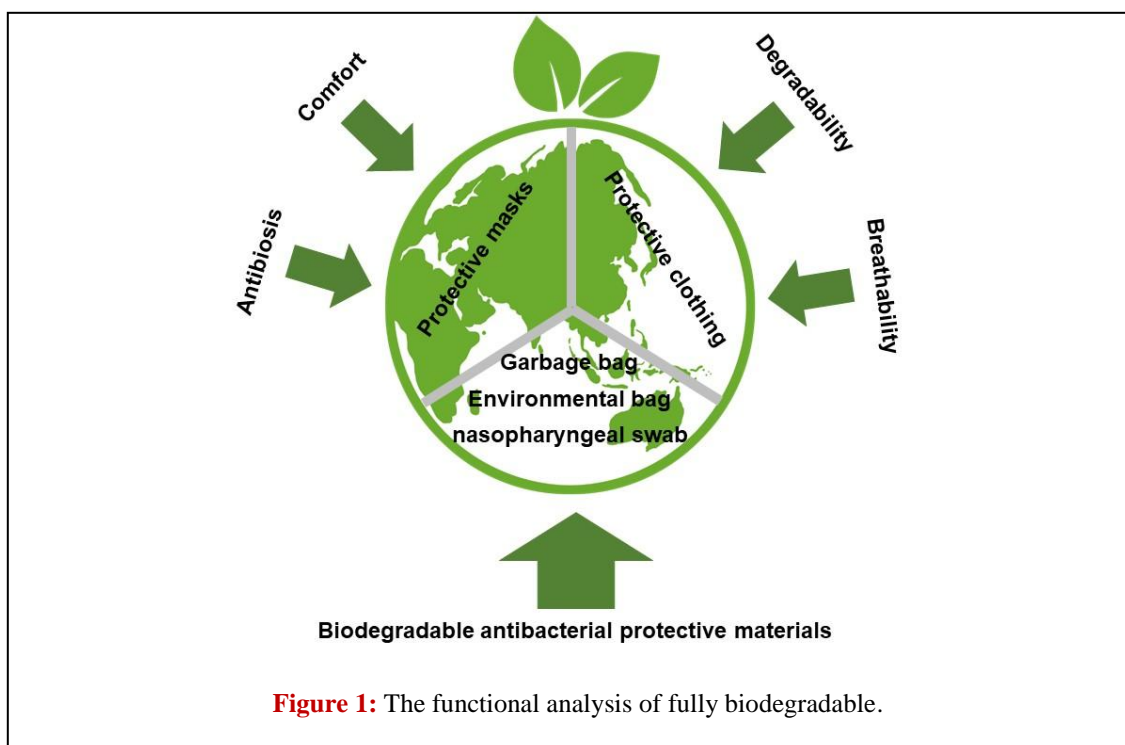
It mainly refers to the mixing of materials with good mixing ability and synergistic effect for improving some shortcomings of the material, so as to meet the application needs. The inherent disadvantages of some biodegradable polymers, such as poor mechanical, electrical and thermal properties, and the narrow range of process parameters, can be overcome with various nanofiller reinforced composites. Biodegradable polymers are used as the base materials, and appropriate reinforcing fillers are added through the use of advanced technologies to meet the practical needs [18]. In the context of the COVID-19, for personal protective equipment, we pay more attention to the polymer's defense ability against bacteria, COVID-19, etc., that is, antibacterial. At present, a large number of metal ions and metal oxides have been proved to have antibacterial and antiviral activities, especially, Nano sized copper (I), iodide (CuI), silver (Ag), and gold (Au) particles. Charan demonstrated the antiviral activity of arsenic oxide (As<sub>2</sub>O<sub>3</sub>) and antimony oxide (Sb<sub>2</sub>O<sub>3</sub>) against bacteriophage viruses. These metals and metal oxides can be used to integrate antiviral activity into the surface of personal protective equipment. During fiber processing, method of embedding antibacterial agent or surface coating or modification is applied to make the fiber antibacterial, so as to reduce the risk of infection with novel coronavirus. For example, the addition of metal ions in chitosan Cu (II) and chitosan Zn (II) complexes improves the ability of chitosan to destroy bacterial protein shells and kill bacteria [26,27]. Metal nanoparticles, such as Ag, Cu and Au (less than 100 nm in size) [28-41], have antiviral and antiviral activities against a variety of viruses and can reduce the infectivity of viruses; For PPE, silver nanoparticles are easy to composite and have excellent antibacterial properties silver nanoparticles can maintain antiviral activity by inhibiting respiratory enzymes, thus controlling the binding between viruses and host cells. Melting and mixing the nano silver ion coated with the drug with the main material of PPE can make the mask have antibacterial and bacteriostatic effects with relatively long aging [42]. For example, Mori et al. [43] found that the concentration of silver nanoparticles in the nanoparticles/chitosan complex is proportional to the antiviral drugs, and the nano silver/chitosan composite hydrogel also has antibacterial effects on Escherichia coli and Staphylococcus aureus [44]. ujimori studied the antiviral activity of nano Copper Iodide (CuI) particles with an average size of 160 nm, and found that Cu<sup>+</sup>in aqueous solution may play a catalytic role in similar Fenton reaction, playing an antiviral activity. This antiviral property will enable CuI nanoparticles to be applied to filters, masks or protective clothing by mixing with polymer based materials. In addition, the classical antibacterial metal/metal oxides (such as copper oxide, zinc oxide, titanium oxide, silver oxide, etc.) of nanometer/micrometer scale are dipped/coated on the disposable N95 respiratory mask layer, indicating that the mask layer has antiviral activity against human influenza A virus (H1N1) and avian influenza virus (H9N2). In addition, the mainstream Polyhexamethylene Biguanide Hydrochloride (PHMB) in the market has become a new generation of antibacterial materials due to its unique molecular structure and superior antibacterial activity. Its advantages are mainly reflected in: high efficiency, safety, stability, long-term effect and no corrosion on various treated surfaces [45]. Cationic antibacterial polymer containing guanidine group, is similar to the structure of natural antibacterial peptide. And it has high antibacterial activity and excellent biocompatibility [46]. For example, when Polyhexamethylguanidine (PHG) and Neomycin Sulfate (NEO) are jointly used as antibacterial agents, the prepared Bactericidal Cellulose Nonwovens (BCNWs) can inactivate 99% of SARS CoV-2 in a few minutes. Beside the above mentioned, there are many other polymers as follow. PLA/PHBV/GO melt blown nonwovens developed by Xiao Aiju et al. have higher filtration efficiency and inhibit Staphylococcus aureus compared with

pure PLA melt blown materials. Cai Cheng et al. [47] found that with nano SiO<sub>2</sub> as an electret, and the composite formed by surface modification and polylactic acid can significantly improve the PLA filtration efficiency, up to 99.69%. Through mixing electrospinning of composite Polyvinyl Alcohol (PVA), Polyethylene Oxide (PEO), Cellulose Nanofibers (CNF), and then esterified and nitrogen doped TiO<sub>2</sub> (N-TiO<sub>2</sub>) and TiO<sub>2</sub> mixture deposition, a reusable, biodegradable and antibacterial mask can be formed [10]. The polylactic acid/graphene composite antibacterial film showed good antibacterial activity against E. coli cells, B. subtilis cells and S. aureus cells, and the number of bacterial colonies decreased by 80%. At the same time, they showed low toxicity to mammalian cells, such as mouse fibroblast (L929) and macrophages. Moreover, the elongation at break of the composite was significantly increased from 3% to 30%, showing better flexibility [48]. Chitosan polylactic acid membrane has very high inhibition efficiency against common bacteria such as Escherichia coli, Staphylococcus aureus, Vibrio parahaemolyticus, etc. Besides, the addition of chitosan can significantly improve the tear strength of PLA. The water permeability and water content of polylactic acid membrane increase, and 2% chitosan polylactic acid membrane has the best water permeability and water content [49].

## The Functional Analysis of Fully Biodegradable and Antimicrobial Materials Applied in Personal Protective Equipment (Figure 1)

### Protective face masks

At present, fully biodegradable materials used in protective face masks include PLA and chitosan.



### Antimicrobial property

For environment-friendly face masks made of Chitosan/Ag@AgCl-TiO composite materials, chitosan can destroy the bacterial cell wall and hinder the free movement of bacteria, so as to play an antimicrobial role. Chitosan is a kind of active substance with positive charge. It has the following antimicrobial mechanisms: (1) Adsorbing the substances containing anions in the cell body and disrupting the normal physiological activities

of the cell; (2) Ammonium ions in chitosan molecules adsorb on the cell surface to form a high molecular membrane, which can prevent the transport of nutrients into the cell and make the negative charge distribution on cell wall and cell membrane uneven, destroying the balance between cell wall synthesis and lysis; (3) Chitosan activates chitinase, degrades chitin, and destroys fungal cell wall; (4) Chitosan directly interacts with the RNA and DNA of the strains, affecting RNA transcription and protein synthesis; (5) The positively charged azyl in chitosan binds to the bacterial cell wall and hinders the bacterial proliferation [26,27]. PLA: for biodegradable face masks made of PLA, the environment-friendly PLA melt-blown cloth is used to replace the polypropylene melt-blown cloth, which not only solves the environmental pollution problem, but also further improves its antimicrobial property. For the improved electrospinning face masks made of PLA, the mesh electrode is used as the electrospinning receiving device to prepare PLA nanofilm, which is harmless to human body. The two kinds of fabricated nano membranes with different weight are respectively coated on KN90 and KN95 face masks, and the filtering efficiency of the masks increased from 93.61% and 96.74% to 98.83% and 99.07%, respectively. The improvement of filtration efficiency means that of antimicrobial performance [28].

### **Comfort**

**Chitosan:** A Chitosan protective face mask, which uses chitosan spun-lace cloth to greatly improve the skin friendly effect, is suitable for people with skin sensitivity. At the same time, it adopts a special ear band structure, which can be worn for a long time without pinching the ear. The cotton or cotton gauze material in the mask can effectively prevent dirt in the air and oral saliva immersion, and avoid increasing respiratory resistance, so that the wearer can breathe smoothly for a long time, and the comfort of the mask can be maintained [29,30].

In cold winter, the circulation of inspirations and exhalations produces water droplets, which can affect the filtration performance and the comfort of masks. In hot summer, sweat also affects the comfort of the mask. However, PLA itself contains a large number of hydrophobic groups (lateral methyl group) and lacks of hydrophilic groups, showing good hydrophobicity. Therefore, the improved PLA electrospinning masks can provide additional comfort in humid environments. Since the gas permeability of the mask can also affect its comfort, the improved PLA electrospinning masks uses PLA resin particles as spinning materials, and improves the receiving substrate to prepare a filter membrane with uneven structures to achieve the balance between filtering efficiency and resistance. Low resistance means good permeability, so that users can breathe more smoothly and are not easy to feel suffocated when wearing these masks [28,31].

### **Full degradability**

Since most of the bio-based materials have excellent degradability, they are selected as the theme materials of PPE. For example, PLA can achieve full degradability through biodegradation, transesterification thermal degradation, hydrolysis degradation and free radical degradation. As a non-toxic, non-irritating synthetic polymer with good biocompatibility and biodegradability, PLA will produce no harmful substances during incineration or biodegradation. Or chitosan, as a natural polysaccharide organic material, can be biodegraded or be degraded by catalysts such as pepsin, papain, lipase, etc., or by physical methods like microwave, ultrasonic wave, gamma ray radiation, photodegradation. Among these methods, the reaction condition of enzyme degradation is the most moderate, without adding a large number of reagents, which causes the least

environmental pollution. Moreover, the enzyme as a catalyst can be used continuously with low cost and high efficiency, which is conducive to the industrialization of chitosan degradation [27,32,33].

### **Medical protective clothing**

At present, the raw materials used for biodegradable medical protective clothing include polyglycolic acid, polyadipic acid/butylene terephthalate, polybutylene succinate, polyethyl lactone, etc.

**Antimicrobial property:** In some degradable medical protective clothing, polybutylene succinate is added to the biodegradable film, which can accelerate the degradation rate and improve the water vapor barrier property of the material. The combination of polybutylene succinate and poly adipic acid/butylene terephthalate with a specific proportion can further improve the water vapor barrier property, which makes foreign pathogens less likely to invade [34]. The surface layer of some degradable medical protective clothing is subject to antimicrobial and antiviral treatment by dip rolling to form a second protective layer against microorganisms, which can actively kill harmful bacteria and viruses adhering to the outer surface of the protective clothing and provide protective barriers for medical workers at all times. The surface layer completed the above treatment shall be subject to the single side three-proofing treatment, and the outer side fabric of the surface layer will be antimicrobial and antiviral / hydrophobic and hydrophilic with double protective effect [35].

**Gas permeability:** The gas permeability of biodegradable films is generally better than that of ordinary hydrophobic petroleum-based polymer films. The base material support layer of some medical protective clothing has a number of protrusions and depressions, and the appearance has a concave convex longitudinal mesh effect, which is breathable, comfortable and accelerates moisture dissipation. In some medical protective clothing, the melt blown intermediate layer composed of complex inter layers of micro fibers acts as a filter layer, excluding many micro dust particles and water-based liquids. Because these intermediate layers are breathable, air and sweat can pass through the clothing to keep the skin cool, striking a valuable balance between permeability and antimicrobial property [35].

**Comfort:** The inner layer of degradable medical protective clothing is made of cotton spun-lace cloth, which can improve the mechanical properties and softness of the material and enhance the wearing comfort of the medical protective clothing [34]. Part of the inner fabric of the protective clothing has instant hydrophilic effect, and the knitted fabric on the top layer has hydrophobic and hydrophilic function, which ensures that the fabric can absorb the sweat and moisture excreted by the human body to the maximum extent and ensures the comfort of wearing. In addition, the convex surface of the base material support layer is the innermost part of the protective fabric, namely the base layer. The existence of the convex leaves a certain space between the body and the clothing, which is conducive to the heat dissipation. When the human body perspires, the water vapor will bypass the convex part of the hydrophobic layer and gather in the concave part of the hydrophilic layer, and be quickly absorbed by the hydrophilic fiber and transmitted to the other side of the fabric, keeping the skin side dry. Thus, the problem that the inner side of the protective clothing is sticky due to a large amount of human perspiration can be solved and the comfort of wearing can be ensured [35].

### **Application of new materials for disposable medical supplies**

**Medical garbage bags made of degradable and antimicrobial raw materials:** A biodegradable antimicrobial material mainly made of environment-friendly substrate has strong antiviral and antimicrobial performance, and

it does not need to be disinfected after one-time use, which can avoid secondary bacterial and viral pollution. Degradable antimicrobial raw materials can achieve complete biodegradation without producing any pollution to the environment, which have environment-friendly characteristics. A small amount of nano-non-metallic photocatalytic material is added to the raw materials of the garbage bag, which can continue to kill bacteria and viruses after the garbage bag is abandoned [36].

**Degradable environment-friendly bags:** At present, most degradable environment-friendly bags contain acrylic resin, which has good physical and mechanical properties, weather resistance, chemical resistance and water resistance, but it is harmful to the environment. For the environment-friendly bags made of etherified starch and PLA toughening agent, mixing corn oil and PLA in the toughening agent and adding diethylamine and maleic anhydride can enable them not only to have excellent emulsification and dispersion ability, but also to overcome the disadvantage of uncontrollable degradation degree due to poor thermal stability, which is the main problem of degradable plastic bags with polyethylene as the main material, and mineral powders, such as photodegradable agent and calcium carbonate, as the admixtures [37]. There is also a kind of degradable environment-friendly bags with calcium carbonate and polyethylene as the main raw materials. During the preparation process, the specific components of polyethylene can be adjusted to make the bags completely free of propylene resin. The addition of degradation admixtures can significantly increase the degradation rate [38].

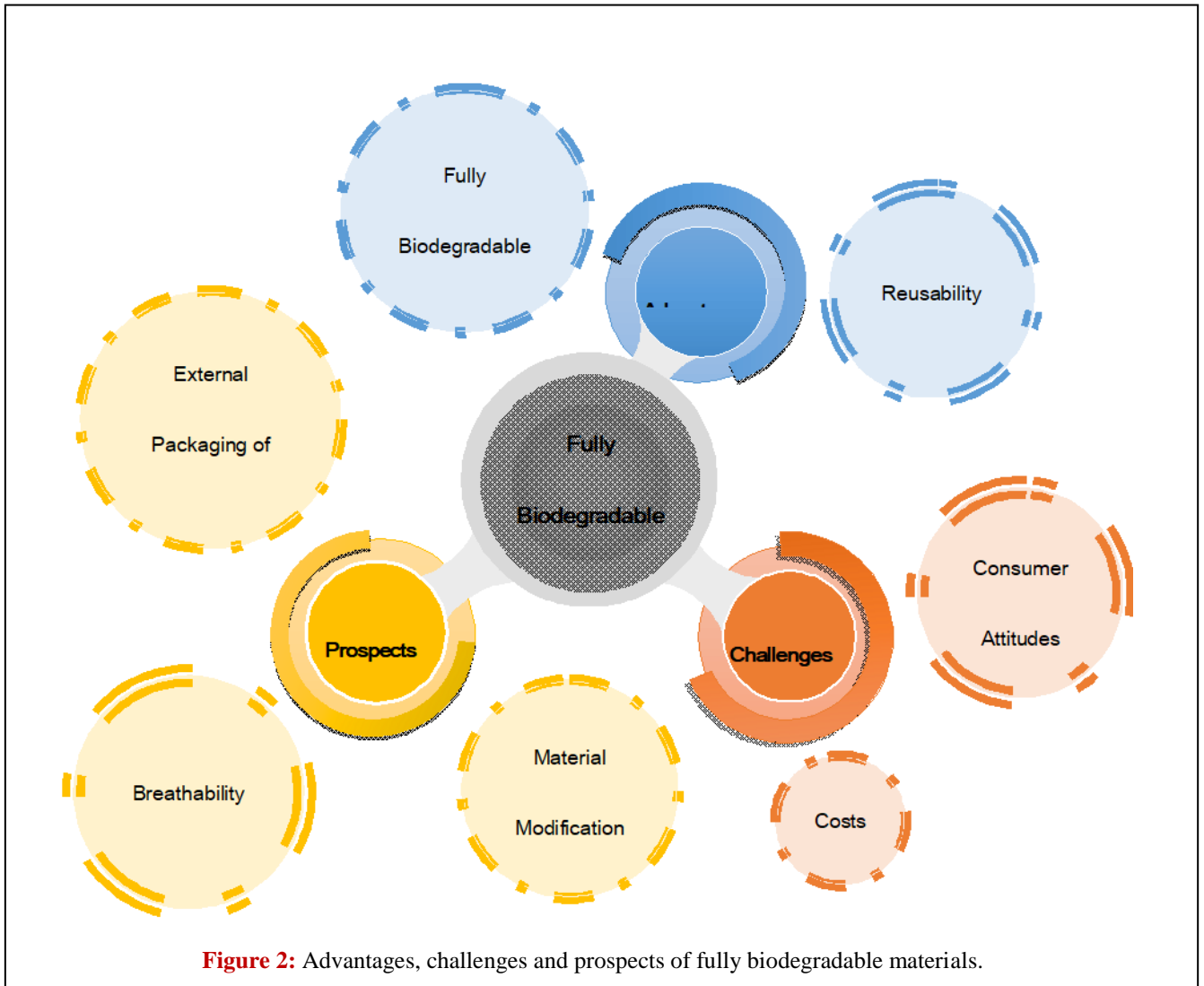
**Environment-friendly degradable nasopharyngeal swabs:** A nasopharyngeal swab consists of: a sampling head, an environment-friendly degradable swab rod, and swab glue applied around one end of the swab rod. The raw material of one kind of sampling head uses the modified pomelo peel fiber, and thus the pomelo peel which is originally used as garbage is recycled. The modified pomelo skin fiber is obtained by the esterification reaction between organic acid and pomelo skin fiber, and it has higher water absorption, cell release rate and connection strength, which is environment-friendly and degradable, meeting the market demands [39].

## **Advantages and challenges of Fully Biodegradable Materials (Figure 2).**

### **Advantages**

**No residual plastic particles, less environmental pollution:** For non-fully degradable plastics, especially the microfibers extracted from petroleum-based polymers, their biggest harm to the environment is that the plastic particles produced in the degradation process will pollute the surrounding water or soil for a long time, and enter the ecological cycle. However, the fully biodegradable materials will not produce secondary microplastic pollution in the environment during the biodegradation process. For example, although PLA will produce a small amount of PLA fragments in the degradation process, the fragments can be completely mineralized into carbon dioxide in the end [40]. Therefore, it can be said that the fully degradable material is the best solution to solve the microplastic pollution.





**Antimicrobial property can prolong the service life of the product and even enable it to be reused:** With the improvement of mask quality, the service life of new masks has been greatly prolonged. The enhanced mechanical and antimicrobial properties make it possible for disposable masks or protective clothing to be reused. For example, a mask made of electrospun PVA, CNF, and PEO has superior mechanical strength and abrasion resistance. It can achieve 100% self-disinfection when exposed to sunlight, and maintain stable filtration efficiency over a long period of time, thus reaching the standard of reuse [10].

### Challenges

The main challenges facing biodegradable materials include cost, consumer attitudes, antimicrobial agent treatment, etc.

**Costs:** Due to defects in production methods, the cost of bio-based polymers has always been a key barrier to their commercial applications. At present, the development of microbial synthesis routes and the availability of cheap carbon-rich precursors have expanded the commercial application scope of degradable materials. The mixed cultures have low prices but poor yield and volumetric productivity [5]. According to our investigation, polypropylene and polyethylene have all been localized. And the price of mainstream polypropylene products is about 8.00 yuan/kg or 9.00 yuan/kg, while the price of mainstream polyethylene products is about 8.00 yuan/kg. This price is very low. But generally speaking, the price of degradable materials is higher than that of

polypropylene and polyethylene. Even the cheapest PPC costs 15.00 yuan/kg, nearly twice as much as polyethylene and polypropylene. Other promising materials in the field of PPE, such as PLA, PBS and PU, are much more expensive than polypropylene and polyethylene, among which PLA is cheaper. Therefore, the price is still a huge constraint to the development of biodegradable antibacterial materials.

**Table 2:** Raw material quotation.

Price List of Raw Materials						
Serial No	Name	Model	Place of Origin	Price (yuan/kg)	Processing level	Remarks
1	PLA	LX175	Thailand	23.00	Extrusion, rotational molding, blow molding, film blowing	Total, Thailand
2	PLA	4032D	U.S.A	35.00	Extrusion, rotational molding, blow molding, film blowing	Nature Works
3	PLA	-	China	25.00	Extrusion, rotational molding, blow molding, film blowing	The domestic manufacturers differ according to the index requirements, and the price difference is between 4-5 yuan per kg
4	PBAT	C1200	Germany	20.00	Injection molding and film blowing	BASF, Germany
5		TH801T	China	18.00	Extrusion, rotational molding, blow molding, film blowing	Xinjiang Lanshantunhe River
6	PBS	FZ91PM	Thailand	42.00	Extrusion, injection molding, film blowing	Thailand PPT Chemistry

7		TH830S	China	40.00	Extrusion, injection molding, film blowing	Xinjiang Lanshantunhe River
8	PBSA	40440D	Japan	40.00	Extrusion, injection molding	Japan Showa Electric
9		-	-	-	-	vacancy
10	PBST	TH901T	China	25.00	Injection molding	Xinjiang Lanshantunhe River
11		TS159	China	28.00	Injection molding and film blowing	Sinopec Yizheng
12	PU	YS3018	China	450.00	Content greater than 45	dow
13		-	China	60.00	-	There are relatively many domestic manufacturers, and the price can be produced according to the product indicators, ranging from 30 to 100
14	PPC	1010.00	U.S.A	45.00	Blown film	American Dow
15		5660.00	The republic of Korea	15.00	Injection molding	Total, France
16	PGA	-	China	180.00	Active ingredient: 99	Thickener meeting the national standard
17	PHA	3001.00	U.S.A	45.00	squeeze	American Dow
18		-	China	30.00	Blown film	Domestic manufacturers
19	PHB	1001 MD	Germany	90.00	Injection molding and film blowing	BASF, Germany

20		-	China	20.00	squeeze	PP extruded pipe
21	polypropylene	M800E	China	9.50	Injection molding	Shanghai Petrochemical Medical Grade
22		5250T	China	8.00	Injection molding	Zhenhai Petrochemical Medical Grade
23	polyethylene	HDPE	China	8.00	Injection molding, extrusion, blow molding, wire drawing	The price of HDPE produced by domestic petrochemical companies fluctuates between 7-10 according to the market

**Consumer attitudes:** Market research confirms that consumers will not change their purchase decisions based only on ecological factors. Therefore, it is not enough for degradable products to be environment-friendly. They also need to meet the needs of consumers in other aspects, including better performance than the original products, particular functions (such as absorbing ethylene, preventing ultraviolet radiation, eliminating water vapor, and enhancing antimicrobial activity against common bacteria), low prices, etc. But at present, synthetic plastics do not have these characteristics [5].

### Prospects

**A bold new approach to apply nanotechnology to antimicrobial materials:** With the development of nanotechnology, the feasibility and superiority of antimicrobial modification of PPE by drug coated with nanoparticles gradually revealed. As an excellent drug carrier, nanoparticles can be easily compounded into various biodegradable materials, and their coated drugs have various types and good effects, which have a quite broad development prospect at present. The nanocomposite obtained by thermal mechanical blending of antimicrobial materials and degradable bio-based materials has better antimicrobial properties and tensile resistance. Their applications in the PPE field also have promising prospects.

**Improving comfort parameters such as air permeability:** While ensuring that the wearer's skin is not sensitive, spices can be added into biodegradable bio-based materials in the production of face masks, which can improve the freshness of the inhaled air and reduce the odor and discomfort caused by long-term wearing. With the development of composite materials, bio-based fully degradable materials are compounded with other fabrics with strong air permeability and hydrophobicity to make the protective clothing more breathable while maintaining high antimicrobial property, and to ensure that the wearer would not feel sweaty after wearing it for a long time.

**Biomedical field:** For example, PLA is used as nano drug carrier, implantation device, etc. Bio-based materials

generally have good biocompatibility, which are non-toxic and non-irritating, and have long been applied in the field of biomedicine. With the continuous improvement of the properties of new bio-based materials, they have been increasingly applied in medical implants and antimicrobial dressings.

**Problems:** Due to defects in production methods, cost and productivity of bio-based polymers has always been a key barrier to their commercial applications. In addition, the market competition among them is also affected by consumer purchasing preferences. In short, biodegradable products should not only be environment-friendly, but also provide new properties, such as protecting from ultraviolet radiation and eliminating water vapor, to cope with the challenge brought by the same type of products. However, most bio-based materials currently lack these features.

## Conclusion

In this article, it can be found that the application range of biodegradable materials is really wide. They can be used in medical products, including hemostatic agents, absorbable surgical sutures, wound dressings, drug control systems, absorbable bone nails and plates, surgical correction materials, hemodialysis membrane, various ophthalmic treatment devices, medical garbage bag, Nasopharyngeal swab, etc. It can also be applied to other aspects, such as, packaging (including food packaging, cosmetic bottles, drug bottles), tableware, agricultural films, pesticides, fertilizer slow-release materials, tissue engineering (artificial skin, tissue engineering scaffold, bone repair material), and other fields. Most importantly, In the context of the COVID-19, we pay more attention to its application in the field of medical protection, including Facial mask substrate, Surgical suit, Protective clothing, Disposable surgical gloves, disposable bag, Medical garbage bag, Nasopharyngeal swab, Outer packaging of these medical products, etc. Through comparison of various degradable materials, we found that Chitosan, cell, Starch, PLA, etc. have both biodegradability and antibacterial properties, and are more suitable for application in the field of PPE. In addition, antibacterial agents can also be added to the degradable substrate, such as metal ions, metal oxides, metal nanoparticles, PHMB, graphene, etc. If we can develop protective materials with degradability and antibacterial properties as well as other necessary physical and chemical properties and turn them into products, it will be of great significance.

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