Antimicrobial sustainable biopolymers for biomedical plastics applications – an overview

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Abstract: The Covid-19 pandemic has increased the need for personal protective equipment (PPE), especially for medical personnel: face masks, full protective clothing, gloves and goggles. To date, they are usually made of thermoplastic polymers, such as polypropylene (PP). To reduce the risk of secondary infections it is essential to enhance the antimicrobial (especially antibacterial and antiviral) properties of the materials used in PPE. There are some attempts to modify materials by, for example, silver nanoparticles or zinc oxides. The increasing demand for personal protective equipment, mostly masks, leads to an increase of environmental problem of non-biodegradable wastes. Therefore some researches on use of safer for user's health sustainable antimicrobial and biodegradable biopolymer fibers, such as cellulose, starch, chitosan, poly(lactic acid) (PLA) or poly(glycolic acid) (PGA), have been done. These biopolymers and their properties are discussed in this article.

Keywords: biopolymer, sustainability, antimicrobial properties, biomedical applications, personal protective equipment.

Biomedyczne zastosowania biopolimerów o właściwościach przeciwbakteryjnych i przeciwwirusowych – przegląd literatury

Streszczenie: Pandemia Covid-19 zwiększyła zapotrzebowanie na środki ochrony osobistej (PPE), zwłaszcza dla personelu medycznego. Dotyczy to przede wszystkim maseczek, ale również odzieży ochronnej, rękawic, czy gogli. Obecnie wykonuje się je najczęściej z termoplastycznych polimerów, np. polipropylenu (PP). W celu poprawy właściwości przeciwbakteryjnych i przeciwwirusowych stosowanych materiałów, dokonuje się prób modyfikacji ich za pomocą np. nanocząstek srebra lub tlenków cynku. Zwiększenie zapotrzebowania na środki ochrony osobistej, zwłaszcza na maseczki, prowadzi do zwiększenia ilości odpadów, w dużej mierze nie biodegradowalnych. W celu rozwiązania tego problemu oraz poprawy właściwości przeciwbakteryjnych i przeciwwirusowych materiałów z użyciem bezpieczniejszych dla zdrowia użytkowników substancji, prowadzi się badania nad wykorzystaniem włókien z biopolimerów, takich jak celuloza, skrobia, chitozan, poli(kwas mlekowy) (PLA) lub poli(kwas glikolowy) (PGA). Właściwości antybakteryjne i antywirusowe, a także zagadnienia biodegradowalności tych biopolimerów, zostały omówione w niniejszym artykule.

Słowa kluczowe: biopolimery, zrównoważony rozwój, właściwości przeciwbakteryjne i przeciwwirusowe, zastosowania biomedyczne, środki ochrony osobistej.

There has been a great deal of research on the sustainable materials to make them environmentally friendly, green, and affordable but still having the same or improved features as the existing product [1, 2]. In the health sector, the demand for biobased polymer products increases along with the raising infection rate of pandemic Covid-19 [3, 4]. The usual type of personal protective equipment (PPE) during this pandemic is the face mask, and it is still in high demand and will be needed for at least another five years [5]. The ongoing pandemic has still obliged many countries worldwide to wear face masks and practice safe social distances. Other PPE applications are for example full clothing used by healthcare personnel, like aprons and gowns, gloves, masks and goggles. Most of the equipment is made of plastics or polymers, which are easy to produce and cheap [6]. The medical mask consists mainly of non-degradable non-woven polypropylene, which allows for filtering of the particles. According to Henneberry, filtration performance and air permeability of non-woven fabrics are more excellent and they are less slippery than the woven cloth [7]. Therefore, non-woven textiles made of thermoplastics such as polypropylene (PP) are frequently used to produce face masks. Such face masks are for single

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use, hence, they generate wastes. Besides PPE, biobased polymers have been used in other applications such as tissue engineering scaffolds, biosensing, wound healing, obstetrics and gynecology, and drug delivery to opt for the new and sustainable way [8].

There have been numerous recent studies on using biopolymer to replace synthetic products achieving the United Nations Sustainable Development Goal of 2030. As mentioned, to this date most of the products used in biomedical field are made of plastics that are not biodegradable. For example, most of the PPEs are made of PP, which is not enough sustainable and recyclable. PP, a thermoplastic polymer, can withstand a variety of chemical solvents, acids, and bases. Although it is considered as "recyclable," it will take 20 to 30 years to degrade and decompose PP completely [9] and the industrial recycling process is regarded as the best option. However, according to Verma *et al*., PP is one of the least recycled post-consumer plastics with a meagre recycling rate [10]. As a result, researchers have proposed biopolymers as a credible option due to their biodegradability [11]. Besides, researches on enhancement of the consistency and efficiency of face masks have been accelerated by implementing properties such as antimicrobial activity. According to the recent literature, biopolymers can be divided into two categories based on their antimicrobial properties. Chitosan is a hydrophilic biopolymer which is synthesized industrially by *N*-deacetylation of chitin. It has antibacterial properties, whereas other biopolymers, like cellulose, starch, poly(lactic acid) and poly(glycolic acid), have no antimicrobial properties but can be used as carriers for other biopolymers or additives [12]. The use of nanoparticles such as nanocellulose with blended metal oxides, like zinc oxides, enhances antimicrobial activity, so it is helpful in the medical field as personnel face masks and deals with dangerous microbes, bacteria, and viruses every day. However, it seems that the use of metal oxides may be toxic. That's why most recent studies still use metal oxides, especially silver nanoparticles, as an antimicrobial agent, with minimum use to make the product safer.

Antimicrobial products are essential for the biomedical industry because they help prevent germs in shared facilities. Bacteria and fungi can quickly grow in humid environments. Textiles and fabrics that allow bacteria to grow are dangerous in the biomedical field because they can lead to the secondary infections [13]. Microbial growth can also lower the product durability, which is especially problematic for products intended to be used for an extended period. As a result, the product's lifespan will be reduced. Antimicrobial products can keep bacteria and fungi on the surface and prevent products from contaminating them. In addition, there are many infectious diseases with increased resistance to antibiotics, therefore new effective antimicrobial products need to be developed [14].

In this review, the antimicrobial performance and activity in biopolymers will be discussed as well as the degradation process to show the difference between fossil-fuel-based polymers and biopolymers in terms of sustainability. We also will discuss the use of the biopolymers in development of more sustainable and green PPE products. Overall, we will focus on biomedical applications and industry but biopolymers can be used in various applications, including coating, food packaging, and civil engineering.

TYPES OF BIOPOLYMERS AND THEIR APPLICATIONS IN BIOMEDICAL FIELD

Biopolymers are natural renewable substances and are often naturally decomposed in the environment. Natural biopolymers are critical in today's biomedical field because of their biodegradability, safety, and antibacterial qualities [15]. Regarding environmental considerations, numerous efforts are being made to replace materials from natural resources that do not rely on oil-based products [16]. Xu *et al.* also reported that biobased polymers are ideal for replacing oil-based polymers due to their renewability, biodegrability, and environmental friendliness [17]. The biopolymer can be used alone or in combination with other polymers to form new composite materials. It can be used in many applications in various fields as the latest composite materials have more enhanced properties [18]. The usual organic biopolymers used in industry are polysaccharides such as cellulose, starch, and chitosan. Additionally, biodegradable synthetic polymers such as poly(lactic acid) (PLA) and poly(glycolic acid) (PGA) are in use in the biomedical field.

Cellulose and bacterial cellulose

Cellulose is considered the most abundant biopolymer source, found in various sources, including plants [19] and fruits [20], as the main structural component of the plant's cell wall. Cellulose can be derived into cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs), which is helpful in nanotechnology applications [21, 22]. The other type of cellulose is bacterial cellulose (BC), which is usually synthesized by bacteria (such as *Acetobacter xylinum*) in a pure form, without impurities [23]. It can also be synthesized by some microorganisms, for example, from the *Komagataeibacter* genera [24]. To be exact, BC is produced by various strains of *Acetobacter* species and strains of pseudomonas, *Achrobacter, Alcaligene, Aerobacter* and *Azotobacter* [25]. Due to its characteristics BC can be developed into various shapes, like films, hydrogels, microspheres, and fibers [26].

Cellulose is a linear polysaccharide with a structure of β-D-glucopyranose that also has a covalent bond connected between C4 hydroxyl groups and C1 carbon atom [27]. According to Dehnad *et al*., nanocellulose, due to its hydrophilic and fibrous state, has been suggested as a reinforcement material [28]. Ludueña *et al*. reported

that the size of the filler particles would affect the interaction of filler matrix, which stated that the smaller the size of the particles, the better the interaction [29]. The studies have confirmed that the nanosized cellulose has better interaction than the microsized cellulose because it can form a crystallized network connected by hydrogen bonds [30, 31].

Khalil *et al.* mentioned that due to their large aspect ratio and ability to shape interconnected network structures through hydrogen bonding, nanosized cellulose could impart greater stiffness to the nanocomposites even at small concentrations when incorporated into the polymer matrix [32]. In nanocellulose, hydroxyl groups -OH are abundant, allowing hydrogen bonding and surface modification ability [33]. From these studies, for the sake of the development of biodegradable materials having properties similar to those of fully synthetic products, nanocellulose can be used with or without blending into another biopolymer. The schematics of the cellulose structure can be seen in Figure 1 [34].

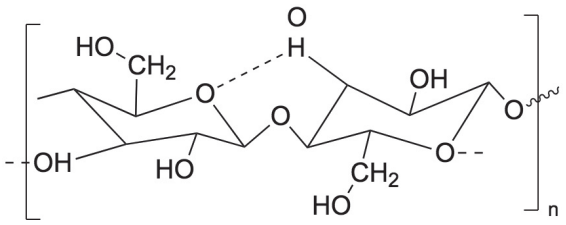


Fig. 1. Schematics of single cellulose chain repeating unit with interchain hydrogen bonding (dotted line)

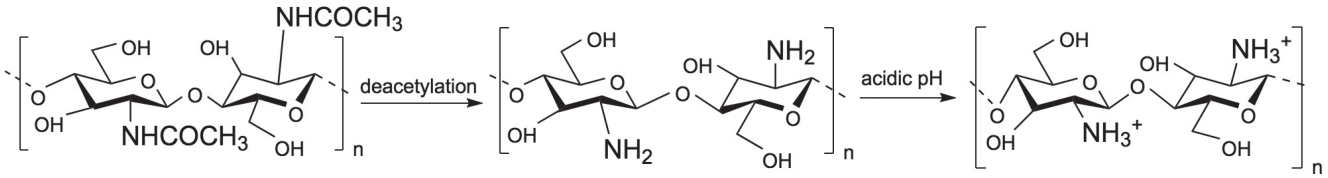
Based on their biocompatibility, biodegradability, and low cytotoxicity, nanocellulose is a promising candidate material in the biomedical industry [35]. According to the studies, cellulose was widely utilized in medical implants, tissue engineering, drug delivery, and injury healing [36]. To date, there are studies on using nanocellulose in biomedical field in the form of membranes, hydrogels, and composites with bioactive compounds or conductive polymers [37–39]. Nanocellulose must be combined with another antimicrobial biopolymer to impart antimicrobial properties because the materials do not have antimicrobial properties on their own. For example, the study by Sun *et al.* showed the incorporation of cellulose network with *N*-halamine by electrospinning technique [40]. The composite positively showed antimicrobial activity against *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative). This led to Fernandes *et al.* study, who developed antimicrobial nanocellulose membranes through chemical grafting by incorporating amino alkyl groups into the nanocellulose (NH_2). The study found a reduction in bacterial growth for both Gram-positive and Gram-negative bacteria [41].

Recently, nanocellulose has been used in drug delivery applications. Kupnik *et al.* showed that nanocellulose is a carrier for drug delivery by mixing nanocellulose with other biologically active molecules with antimicrobial properties such as chitosan, curcumin and others [14]. The presence of antimicrobial properties of the composite has shown growth inhibition for *E. coli* and *S. aureus*. Other exciting studies are the derivation of cellulose from fruit plants, such as sugar cane bagasse [42], fruit bunch [43], and durian rind [20]. A recent study by Lubis *et al.* showed the incorporation of cellulose fiber from the durian rind with quaternary ammonium salt group such as 2-[acryloyloxyl]ethyltrimethylammonium chloride (CIAETA) by grafting method. Grafted CIAETA was reported to release Cl^-, which can be absorbed by bacteria and eventually kills them. As a result, it was demonstrated that grafted CIAETA successfully increased antibacterial activity.

On the other hand, scientists extensively studied BC, which seems to be a promising candidate for several biomedical applications among many potential nanocellulose. Compared with plant-derived cellulose, BC is low cytotoxic, has high porosity and 3D network structure, by which BC is used for tissue engineering purposes [44]. BC has higher crystallinity than cellulose, which may be due to the network structure of BC [45]. Surface modifications such as protein coatings, plasma treatment, and introduction of surface charges were explored to improve the attachment of the cell [46–49]. Barud *et al.* studies showed the antimicrobial BC membrane that was mixed with silver nanoparticles by *in situ* preparation of silver nanoparticle BC with the hydrolytic decomposition of silver nitrate using triethanolamine (TEA). Although the result exhibited antimicrobial activity, the amount of silver contents in BC was controlled [50]. The research resulted in recent work by Luo *et al*., who developed a carboxyl BC membrane by assembling nano-zinc oxide *in situ* with maleic anhydride. The antibacterial activity of nano-zinc oxide is dependent on photocatalytic bacterial disruption and reactive oxygen species (ROS) bacterial attack. These studies could help with wound healing. The content of nano-zinc oxide is being controlled due to the use of metal oxide [51]. Companies like Biofill™ and Dermafill™ developed bacterial cellulose wound dressings as temporary skin substitutes to treat burns [52]. Gengiflex™, on the other hand, is a treatment for dental implants or grafts that claims to reduce inflammation and pain after surgery. Axcelon Biopolymers Corporation recently developed a Nanoderm Ag, an antimicrobial wound dressing with silver ions incorporated into the product [53]. The research for more advanced products is still ongoing.

Chitosan

Chitosan has similar structure to cellulose with a slight difference in the C2 carbon atom, which has amino groups attached. It is a linear copolymer of *n*-acetyl-D-glucosamine and D-glucosamine, which has been derived from chitin [54, 55]. Chitin is the second most abundant bio-



Chitin Chitosan Protonated form of chitosan

Fig. 2. Process of deacetylation from chitin to chitosan and the structure of protonated chitosan

polymer in nature, after cellulose. It is present in crustacean's shells, for example, crab, lobsters, and shrimp and can also be found in cell wall of fungi and yeast [56]. The process of enzymatic deacetylating of chitin under alkaline conditions produces chitosan soluble in aqueous acidic media [22] and the degree of deacetylation is more than 50%. The report shows that deacetylated chitin needs more than 60% of D-glucosamine residues to be called 'Chitosan' [57, 58]. Additionally, the study demonstrated that a high degree of deacetylation (DDA) facilitates mixing of nanocellulose in an aqueous medium [21]. Figure 2 shows the process of deacetylation from chitin to chitosan. Chitosan is a protonated polysaccharide (that makes the chitosan cationic) that can easily be linked or bonded to other anionic molecules in an acidic medium and this is crucial to its surface activity properties. According to Pavinatto *et al*., chitosan is the naturally positive charged polysaccharide due to its amino groups in the structure. The amino groups can be protonated and become a polycation, forming ionic complexes with various anionic molecules. Besides that, chitosan can also be considered environmentally friendly and easy to recycle as it can be biodegraded into non-toxic residues [59]. Chitosan has unique properties and can be used for biomedical purposes.

Studies showed that chitosan is biocompatible, biodegradable and non-toxic, similarly to cellulose. Chitosan differs from cellulose in antimicrobial and antibacterial characteristics [60–62]. Due to these properties, chitosan can be used for wound dressing, cancer diagnosis, distribution of medication, tissue engineering, bioimaging, wound healing, and many more [63–65]. In tissue engineering scaffolds applications, for instance, the study by Dutta *et al*. explained the usage of chitosan as a promising biomaterial for the application [63]. Chitosan has three properties that make it suitable for applications: (1) possibility of low-cost production, (2) positive charge and reactive functional groups that enable its composition with anionic polymers, and (3) its antimicrobial properties. The fact that chitosan does not cause any inflammatory nor allergic reactions (opposed to silver nanoparticles) made it a very appealing material [66]. However, due to the low mechanical strength of chitosan, it has to be incorporated with inorganic material to improve the mechanical properties for the scaffold's application [67]. Chitosan is also used in drug delivery applications because it can form a stable complex, making it an excellent applicator for drug encapsulation and controlled release. The self-assembly chitosan, occurring in the water phase under normal conditions is also produced and could be used in generation of materials with a wide range of properties and functions [65]. In dentistry and oral medicine, Decker *et al.* investigated the use of chlorhexidine (CHX) as a chitosan-treated antiplatelet material, which can help increase antimicrobial activity and reduce the antimicrobial activity of plaque formation. The studies also noted that the biofilm model of Chitosan-CHX would be a promising material in the biomedical industry [68]. In addition, Wichai *et al*. synthesized alginate with BC-chitosan composite by hydrogen treatment. As a result of the study's findings, the product can be used for wound dressing and medication release applications because of its antibacterial capabilities against both *S. aureus* and *E. coli* [69]. In a recent study by Cabañas-Romero *et al*., chitosan has been produced as a nanocomposite, along with the bacterial cellulose (BC). The BC-chitosan composite showed impressively inhibited bacterial growth due to the antimicrobial properties of chitosan. It was also stated in the study that the antibiofilm could be helpful in the biomedical field [24].

Starch

Chemical structure of starch is linear amylose with a highly branched amylopectin formed by a large number of D-glucose units linked by α-1,6-glycosidic bonds [12]. It is made from many plants, including corn, potatoes, and wheat [70]. It is pretty popular in the food industry, especially in food packaging applications, as it is abundant and edible. Like cellulose, starch has no antimicrobial properties, so it usually acts as an antibacterial biopolymer carrier [71].

In the food packaging industry, starch is also used as a composite material in the biomedical field. For example, there was a research on creating of collagen-based scaffolds impregnated with sago starch and capped with silver nanoparticles. According to that study, the product increased its thermal stability and tensile strength. Furthermore, the silver nanoparticles made the product antimicrobial [72]. Adeli *et al*. used an electrospinning method to create nanofibrous mats from poly(vinyl alcohol) (PVA)/chitosan/starch composite for wound dressing applications. The crosslinking properties of the material made it suitable for the applications, as it demonstrated good wound breathing and the ability to provide an appropriate moist environment. Again, incorporating

chitosan into a composite rendered the material antimicrobial [73]. Also, a similar work of Ounkaew *et al.* showed the use of nanocomposite of carboxymethyl starch/PVA/silver nanoparticles for the wound dressing application [74]. The study focused on using the optimal amount of silver nanoparticles and citric acid to reduce green silver nanoparticle synthesis. It was demonstrated that AgNPs could be used after all, but they could be treated with specific materials to create a greener synthesis method. According to a recent study, the nanocomposite hydrogel of carboxymethyl starch and CuO nanoparticles could be used as a wound-healing material. Citric acid was also used as a crosslinking agent to create the hydrogels [75].

Poly(lactic acid) (PLA) and poly(glycolic acid) (PGA): biodegradable synthetic polymers

Poly(lactic acid) (PLA) comes from lactic acid, obtained from sugar fermentation from renewable resources such as sugar cane [76]. Lactic acid has a structure of two enantiomeric forms, a starting point for poly(lactic acid) synthesis, named L- and D-lactic acid. Poly(lactic acid) can be also considered as a biopolymer that substitute environmentally harmful petroleum-based plastic products since it is a highly versatile biodegradable polymer and compatible biologically [77, 78]. However, the synthesis process of poly(lactic acid) involves very high energy consumption, according to Savioli Lopes *et al*. The use of catalyst is necessary and strictly controlled and has a long time to polymerize [79]. Therefore researchers studied the reaction and kinetic reaction behavior of synthesis of PLA. PLA biomedical applications include producing of sutures (stitches) and medical implants. Apart from that, it can be used in tissue engineering scaffolds and delivery system materials [80]. Hu *et al*. showed the grafted chitosan with PLA. The grafting process started with a poly(L-lactide) (PLLA) or poly(D-lactide) (PDLA) precursor that was grafted to the backbone of chitosan using *N,N'*-carbonyldiimidazole as a coupling agent. They discovered that hydrogels with a high equilibrium swelling ratio were obtained due to stereo complexation between enantiomeric PLLA and PDLA. These findings conclude that the materials are appropriate for delivering bioactive molecules or drugs, such as insulin [60].

PLA was also used with chitosan and cassava starch in a recent study [81]. The nanocomposite material exhibited strong evidence of hydrogen bond formation. Because bentonite is a renewable material, its presence could aid in the material's decomposition. Antimicrobial properties due to chitosan were observed as well, which could be helpful in the biomedical industry.

The other biomedical polymer includes poly(glycolic acid) (PGA), which is known for its excellent degradation behavior. Poly(glycolic acid) has a simple structure with ester groups in the form. Based on studies of Göktürk *et al*., there are four types of processes to produce poly(glycolic acid): polycondensation method, ring-opening polymerization method, solid-state polycondensation method, and Brønsted acid-catalyzed polymerization of carbon monoxide and formaldehyde [82]. Because of its biodegradable properties, PGA is used for stitches in the biomedical field. Studies showed that PGA stitches had lost nearly half their strength after a few weeks and fully deteriorated in one month. Within six months, the sutures were fully absorbed [83]. The degradation process produces glycolic acid which can later be excreted in the urine [84]. The new study discovered that bacterial-derived polymer poly-γ-glutamic acid (γ-PGA) could be used in biomedical delivery systems. Various *Bacillus* strains can naturally produce the material. Because of its controlled and sustained-release properties, as well as its low toxicity, the material itself acts as an antimicrobial agent for drug delivery [85].

ANTIMICROBIAL ACTIVITY OF BIOPOLYMERS

Antimicrobial properties are now desired in food packaging and biomedical devices, as cross-contamination of dangerous bacteria can cause severe public health and safety problems. The biopolymer can impart the antimicrobial properties on its own or incorporate it with another component that will make a composite [86]. As stated in subsection "Cellulose", cellulose or nanocellulose are acted as reinforcement agents and have no antimicrobial properties. This is because the structure of the cellulose is naturally a place where the microorganisms grow. As a result, modifications are needed to impart the antimicrobial properties, and it could be achieved by incorporating with antimicrobial polymers, such as chitosan [87]. It is also a win-win situation for the chitosan, as it has poor mechanical strength and thermal and barrier properties. The same goes for starch, which has poor mechanical performance and no antimicrobial properties; hence it needs to blend with another biopolymer [88].

As mentioned before, chitosan, in contrast with cellulose, starch, and poly(lactic acid), is the most promising biopolymer with antimicrobial properties. Structural properties such as molecular weight or deacetylating degree (DDA), as well as surrounding conditions such as pH, temperature, and ionic strength, strongly affect antimicrobial activity [13]. The limit of the usage of chitosan is that its solubility is reduced in neutral pH conditions. Hence, chitosan must be chemically modified primarily to produce derivatives that improve the properties that expand its applications [89, 90]. Modifications need to be involved into the amino group or hydroxyl group, increasing the surface activity. Studies show that establishing quaternary ammonium groups for permanently positive charge in chitosan chains would improve their antifungal and antibacterial characteristics because the amino groups affect the biological activity of chitosan. Sahariah *et al.* [91] developed more efficient method for the selective alteration of the amino group by up to 100% substitute for chitosan. In contrast, Wang *et al.* recently

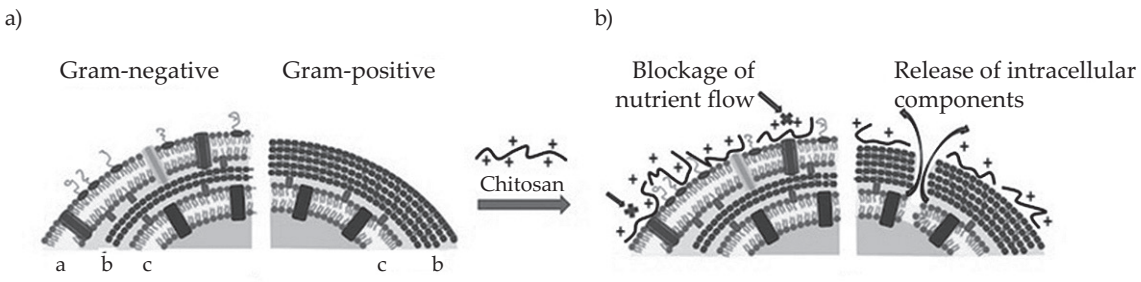


Fig. 3. Proposed mode of antimicrobial action of chitosan: a) is the original structural composition of Gram-negative and Gram-positive bacteria, b) is the effect of chitosan binding to the outer envelope of Gram-negative and Gram-positive bacteria

have obtained *O*-quarternized chitosans improving the chitosan solubility in water and their antibacterial activity against Gram-positive bacteria [92].

To date, the exact mechanism of antimicrobial activity in chitosan remains uncertain. Tang *et al.* reported that the mechanism is based on interactions of the positively charged microorganism membrane with the negatively charged chitosan. The protonated chitosan contained a positive load in the amino group [93]. Figure 3 shows the mostly proposed mode of action of chitosan on Gram-negative and Gram-positive bacteria. Electrostatic interaction between metal ions on the bacteria surface is binding with polyanions. According to the research, in the case of Gram-negative bacteria, chitosan can cause changes in the permeability of the outer layer by creating ionic bonds and preventing the transport of nutrients into the cell and building internal osmotic pressure. Hence, the cell will die due to the lack of nutrients. As for Gram-positive bacteria, the peptidoglycans in the cell wall are hydrolyzed, leading to leakage of intracellular components. Hence, it increases the interaction [89]. There are also other types of action mode that have been proposed, as can be seen in Figure 4.

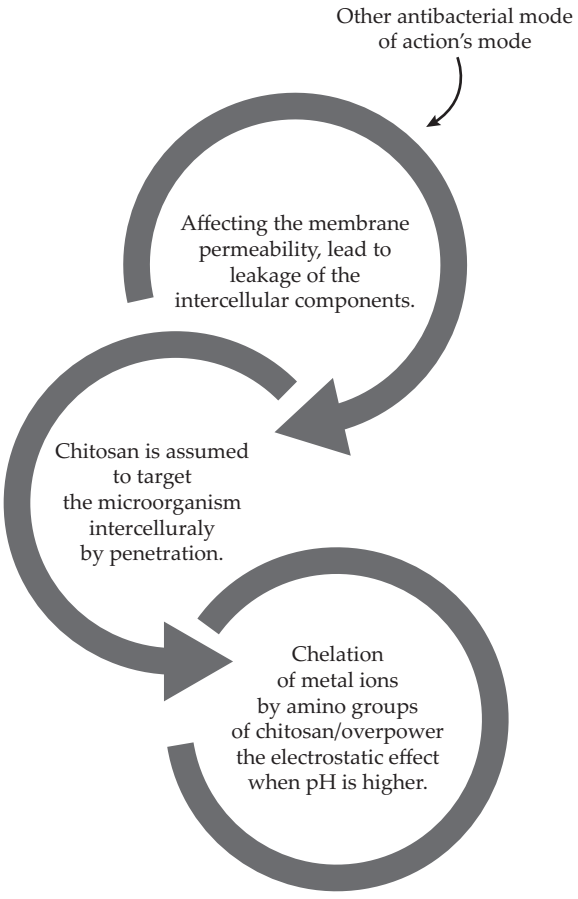


Fig. 4. Another antibacterial mode of action's model

Nanoparticles such as silver nanoparticles (AgNPs) are also used widely as antimicrobial agents, incorporated with chitosan. Studies showed that chitosan/AgNPs nanocomposite agglomeration could be reduced by adding silver nanoparticles because agglomeration disrupts antimicrobial activity. Although the use of silver nanoparticles in biomedical applications is prevalent, the effect of silver nanoparticles on the user's health is increasingly concerned. This is because the metal or metal oxide nanoparticles may exhibit toxicity, which could also be harmful to the environment [94]. Apart from silver, there are many types of other nanoparticles such as titanium oxide (TiO_2) [95] and zinc oxide (ZnO) [96, 97].

The mechanism of the antimicrobial activity for general nanoparticles is detailed in Table 1.

USE OF BIOPOLYMER IN MICROBIAL PERSONAL PROTECTIVE EQUIPMENT (PPE) MANUFACTURING

Recently, because of the Covid-19 pandemic, the idea of incorporating antimicrobial biopolymer into the PPE has been widespread. It is reported that the virus would linger on the fabric for up to six days on the outer layer (for example, the face mask) [102]. Therefore, the idea to implement antimicrobial properties is crucial. Before the pandemic, the researches and development on this matter were ongoing due to producing the antimicrobial PPE specifically for biomedical use, such as doctors and nurses who spend most of their time in the hospital. Recent studies have shown the use of metal oxide nanoparticles as an additive to impart antimicrobial properties [103]. A study showed a 100% reduction in viable *E. coli* and *S. aureus* in the coated mask materials after 48 hours of incubation. In addition to using nanoparticles, biopolymers were also used as an antimicrobial agents in PPE

T a b l e 1. Mechanism of antimicrobial activity for nanoparticles (metal/metal oxides)

Nanoparticles (metal/metal oxides)	Mechanism	Reference
Ag	Cell growth is inhibited, and the cell membrane is disrupted when Ag^{+} is released	[98]
ZnO	The release of Zn^{2+} and photocatalytic generation of reactive oxygen species (ROS) to sterilize	[99]
Cu	The release of Cu^{+} destroys the cell membranes and damages cell	[100]
TiO_2	Photocatalytic generation of ROS to sterilize	[101]

production in many studies, for example Cheng *et al.* studied the performance of using chitosan as an antibacterial agents added to cotton fabrics [104]. They showed that the treatment of chitosan cotton could result in excellent antimicrobial activity when exposed to dilute household bleach. Chlorinated coated swatches can inactivate 100% of *S. aureus* and *E. coli* O157:H7 with a contact time of five minutes. They also found that the shearing properties of the treated swatches increased while the strength of the breakage decreased compared to uncoated cotton. Later, Wang *et al*. developed three antimicrobial face masks consisting of non-woven PP for the exterior layer, medium layer antibacterial and inner cotton medical yarn. The central layer of herbal microcapsules has been taken up from a typical Chinese medicine called *Scutellaria baicalensis* (SB). This study also found that the adhesion of the herbal microcapsules was still excellent after washing the filter layer 100 times [105].

Recently, there is a company that successfully developed a self-decontaminating PPE in response to the Covid-19 pandemic. A thermal process that establishes ionic or covalent bonds would reduce the risk of infection [106]. Duritex™ is the brand name of the product, and it is a self-disinfectant natural biopolymer. They noted in the report that self-disinfection of PPE has significant benefits, particularly for healthcare workers who are likely to wear PPE all day.

Botelho *et al.* in the most recent study introduced the new textile for PPE obtained by using plasma chitosan blended with silver nanoparticles on nylon fabric [107]. The other company that successfully produced the antimicrobial face mask (with N95 feature) is from Vietnam. The exciting part is that they use Vietnamese coffee in production. The product was named AirX. The product has two protective layers; one of them is the biodegradable filter produced using silver nanotechnology and coffee. The other interesting part is that the face mask is reusable and washable [108]. Coffee antimicrobial and Duritex™ face masks are shown in Fig. 5.

Face masks are not the only personal protective equipment (PPE) available on the market. Surgical gloves, commonly used by healthcare personnel, have also been developed as an antimicrobial product. Triclosan (2,4,4′-trichloro-2′-hydroxydiphenyl ether), also known as TCS, was reviewed by Babadi *et al*. as a traditional antimicrobial agent for glove production [110]. Due to its toxicity, however, it was replaced by polymer blend films such as PVA and natural rubber. Riyajan *et al.* reported the use of PVA and natural rubber, which has good antimicrobial activity against *S. aureus* and *E. coli* [111]. The new development turned now to the usage of *Garcinia mangostana* Linn. or mangosteen [112]. According to the report, the mangosteen peel and seed have excellent antibiotic properties. They can be used as biofillers in natural rubber to

Fig. 5. Coffee antimicrobial face mask (Left) [105] and Duritex™ face mask (Right) [109]

produce medical gloves and other rubber health products. Recently, Khanzada *et al*. conducted the development of electrospun nanofibers of Aloe Vera and PVA. Based on its excellent antibacterial activity against *S. aureus* and *E. coli*, the composite established itself as a promising candidate for use in the production of protective clothing PPE [113].

CONCLUSION

The use of biodegradable and renewable biopolymers is crucial. It can be further studied as it has many potential properties useful in the biomedical area, especially for PPE production. Using biopolymers in disposable goods such as personal protective equipment (PPE) is necessary to replace polypropylene (PP) non-woven face masks, since polypropylene is non-degradable. PP face masks generate PPE waste that would damage the environment and ecosystem persistently. To our best knowledge, there are no report on using a blended biopolymer with nanoparticles to produce PPE. Before commercialization, every medical product containing nanomaterials, such as a new type of face mask, must be certified. This is the primary reason for the non-commercialization of the product. Nevertheless, biodegradable woven polymer with antimicrobial properties innovations can assist the improvement needed to fabricate PPE or face masks for the benefit of medical and consumer industries. The development of biodegradable face masks with added antimicrobial features is required by society and the world in fighting diseases due to bacteria and viruses, especially during the Covid-19 pandemic and other infectious diseases such as SARS, *etc*.

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