Review Article

Water - Based Polyurethanes for Antibacterial Coatings: an Overview

Kaan Aksoy[1*]

[1] R&D Department, Betek Boya Ve Kimya Sanayi A.Ş, 0000-0001-6830-5538, kaan.aksoy@betek.com.tr

[*] Correspondence: kaan.aksoy@betek.com.tr; Tel.: (0090 536 477 28 18)

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Abstract

The spread of bacterial infections and the resulting loss of life and material have led scientists to research ways to develop knowledge in these disease-causing microorganisms. Usage of antibacterial polymer coatings is an important part of this area. Among the polymers, water-based polyurethanes (WPU's) have received a lot of attention in biomedical fields such as antibacterial coatings, biological products and wound dressings due to their unique properties such as reduced use of volatile organic compounds (VOC), biocompatibility, the possibility of using a variety of raw materials. In this review, the methods of creating antibacterial properties in polymers, the synthesis of WPU's and WPU-based antibacterial coatings are reviewed. The products produced as a result of these studies have been recommended for various fields such as the dressing and packaging industries, and the coating of medical equipment.

Keywords: Coating, antibacterial coating, Water-based polyurethane, Volatile organic compounds (VOC), Biocompatibility.

1. Introduction

The spread of infection by microorganisms has become a worrying issue1. Every year, thousands of people die from bacterial infections due to the strong resistance of bacteria to old antimicrobial agents2. Microbes can survive and multiply in the right environment. Since the survival of organisms is possible by controlling the growth of microbes, including bacteria and fungi. It is necessary to destroy microbes or inhibit them by using antibacterial substances3. Also, dealing with bacteria is one of the biggest

challenges in dealing with medical devices, hospital equipment and health products4. A new method in this field is use of antibacterial polymer coatings that prevent the adhesion of a wide range of bacteria to surfaces and thus prevent the formation of biofilm in the early stages after contact with bacteria. Ideal antibacterial coatings have a good activity against the growth of bacteria and otherwise remain as an ineffective coating5. Today, one of the most important applications of antibacterial coatings is use in biomedicine. For example, in the field of medical equipment, the biggest challenge when using artificial prostheses, catheters and other temporary or permanent implants is their microbial contamination and the creation of bacterial biofilms on them. Biofilms are a collection of microorganisms that produce a slimy substance called exocrine polymer (extracellular polymeric substance). The liquid inside the biofilm contains proteins, polysaccharides, DNA and 97% water. There are channels in the biofilm that separate the colony of microorganisms. The first stage of biofilm formation is the adhesion or attachment of bacteria with the help of flagella or electrostatic interaction to surfaces. These surfaces may be living or non-living. Then, microcolonies are formed and begin to mature and form a structure and finally separate from the surface. When bacteria are separated from the surface, each bacterium creates new colonies by producing enzymes. Bacterial cells start producing protein again to form flagella so that the bacteria can be transferred to a new place and the infection can spread4. As an ideal environment, biofilm protects microbes and allows them to continue growing in harsh environmental conditions6. In the biofilm, there is also the possibility of gene exchange, which causes the formation of drug-resistant bacterial species. For this reason, the best way to avoid the spread of infections and diseases is to prevent the formation of biofilms by using antimicrobial surfaces.7. When the active antibacterial substances are placed on the surface, they prevent the growth of bacteria on the surface8. Today, WPU's are widely used in the medical, covering, and textile, and in the production of artificial leather, adhesives, and flooring with their properties such as biocompatibility, non-toxicity, cost-effectiveness, adhesion to different surfaces, good film properties, resistance to chemicals, solvents and water, wear resistance, etc9-12.

Antibacterial polyurethane coatings can be used to prevent the growth of bacteria on different surfaces and also to limit the spread of bacterial infections in many devices such as medical devices, hospital equipment, water purification and cooling systems13 scarred leather cover hospital flooring, food and medicine packaging and health products.

In this study firstly, the different methods of preparing antibacterial polymer coatings are reviewed, then polyurethanes and WPU's are introduced. In the following, the studies conducted in the field of preparation of antibacterial WPU's using solutions such as adding nanostructures, mixing with antibacterial polymers, drug loading, using antibacterial monomers, and modifying the polymer surface are reviewed discussed.

Methods of creating antibacterial properties in polymers

The spread of infections and the growth of bacteria resistant to antibacterial substances have caused researchers to use new methods to create antibacterial behavior. For this reason, in recent years, researchers have tried to create antibacterial behavior in polymer coatings. Today, antibacterial coatings have attracted attention in many fields, especially in medicine, and one of these applications can be mentioned in the production of medical equipment(Ojijo & Ray, 2013).

Various methods of creating antibacterial properties in polymers have been introduced in the following.

Use of nanostructures

Nanotechnology, as a new approach, has widely contributed to the development of aerospace, electronics, environment, medicine, and especially the treatment and diagnosis of diseases(Gu, Hong, & Xiang, 2010; Gurunathan et al., 2018; Laurent et al., 2008; Valsalam et al., 2019). Recent studies have shown that besides these developments, the use of nanostructures presents several challenges. One of them shows that the toxicity caused by nanostructures depends on the type of the substance and its physical and chemical properties. It can also be affected by various factors such as absorption of nanostructured cells and their interaction with cells(Gurunathan et al., 2018). Metallic nanomaterials have surface charge and have the ability to interact with protein and DNA of microorganisms and inhibit them.

Another important mechanism of nanostructures in inhibiting bacteria is the production of reactive oxygen species (ROS, species oxygen reactive). These small, unstable and highly reactive molecules can oxidize proteins, lipids and DNA(Rizzello, Cingolani, & Pompa, 2013). One of the challenging issues in the use of nanostructures in polymers is their quality and distribution in the polymer matrix. The large surface-to-volume ratio of nanostructures increases their surface energy and, as a result, their tendency to become agglomeration in the polymer matrix. Usually, by modifying the surface of nanostructures, the interaction between polymer and nanostructure increases and as a result, dispersion of nanoparticles in polymer matrices is improved(Nguyen, Tran, Xu, & Lee, 2021).

Silver nanostructures, as one of the most widely used nanoparticles, have been widely used for the production of various biomedical products and to prevent the spread of infections due to their very strong antibacterial property and low toxicity for human body cells(Gurunathan et al., 2018). Studies have shown that the antibacterial property of silver

is caused by its high toxicity with different mechanisms, especially the excessive production of reactive oxygen species and stress to the cells and finally the death of the cells(Gurunathan et al., 2018; H. Park et al., 2007). By modifying the surface of silver nanoparticles, their cytotoxicity can be reduced by reducing the contact surface with cells. Also, in subsequent studies, researchers found that silver nanostructures can enter cells and affect DNA by releasing silver cations(Rather et al., 2021). In this regard, it has been determined that the antibacterial activity of silver nanostructures depends on the amount of silver cations released(Rather et al., 2021). In general, by reducing the size of silver nanostructure, its antibacterial effect increases due to the increase in the concentration of released Ag^{+} ions(Rather et al., 2021). Silver ions can stop the growth and reproduction of bacteria by binding to compounds containing phosphorus and sulfur in the membranes and DNA of bacteria(Tsou et al., 2016).

Figure 1 shows the interaction mechanism of silver nanostructure with bacterial cell membrane. As shown, the possible reactions between the nanostructure and the cell walls of living organisms have been carried out. First, silver ions are released from silver nanostructures. The difference between the negative charge of the microorganism and the positive charge of the silver ion acts as an electromagnetic absorber between the microbe cell wall and the nanostructure and it causes binding of silver ion to the cell surface, then during the reaction with membrane proteins, it finally leads to the death of the cell(Azam, Ahmed, Oves, Khan, Habib, et al., 2012). It is also possible that the ions released from the silver nanostructure react with the thiol (SH) groups of the surface proteins of the bacterial wall. A number of these bacterial membrane proteins are responsible for the transfer of minerals, and silver ions, by acting on these proteins, cause membrane inactivation and impermeability and eventually cause cell death. Also, a large number of these contacts cause the oxidation of surface molecules of microbes and their rapid death(H. Liu, Song, Shang, Song, & Wang, 2012; Marambio-Jones & Hoek, 2010; Valappil et al., 2007).

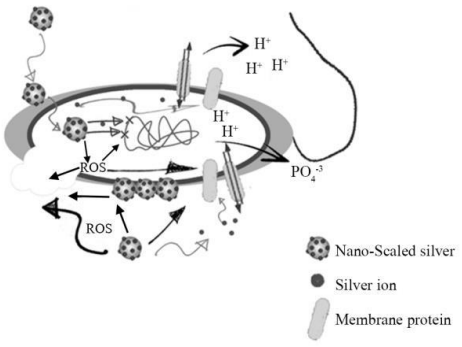


Figure 1. Mechanism of silver interaction with bacteria cell (Azam, Ahmed, Oves, Khan, Habib, et al., 2012).

Zinc oxide (ZnO) nanostructures have received much attention due to their favorable biocompatibility, high antibacterial properties, catalytic power, anticancer properties, easy availability, and affordability(Priyaa & Satyan, 2014; Velmurugan et al., 2014; N. Yang et al., 2017). The nanostructure of zinc oxide with hydroxyl groups is hydrophilic, but by modifying the surface of zinc oxide, it can be used in corrosion protection layers. Antibacterial property of zinc oxide nanostructure depends on the particle size and its concentration. These nanostructures have dual antibacterial properties. This means that it has an effect on gram-positive and gram-negative bacteria and stops the growth cycle of these microorganisms(Hezma, Rajeh, & Mannaa, 2019).

Titanium dioxide (TiO_2) nanostructures also have photocatalytic and antibacterial properties(Zimbone et al., 2015). With ultraviolet light, these nanostructures are activated and generate electrons. Also, these materials produce ROS by absorbing water. Due to their high oxidizing power, by sticking to the bacterial membrane and penetrating into it, they inhibit or kill bacteria.

This nanostructure is used in coating materials that create antibacterial and non-sticky self-sterilizing properties after ultraviolet light irradiation(Ashkarran, Hamidinezhad, Haddadi, & Mahmoudi, 2014; Haider, Jameel, & Al-Hussaini, 2019). Hybrid nanostructures such as Silica nanosphere–graphene oxide (SiO_2-GO) can control the polymer properties and also create a synergistic effect in the polymer. In addition to antibacterial properties, these structures also affect mechanical properties(Fan, Li, Cai, & Li, 2017). Table 1 shows some examples of important nanostructures with antibacterial properties.

Mixing with antibacterial polymers

Mixing the polymer matrix with natural polymers that have antibacterial properties creates antibacterial properties in the final polymer. The superiority of these compounds is reducing environmental problems, reducing the toxicity of waste materials and non-volatile materials, and increasing their efficiency(Arora & Mishra, 2018; Olmos & González-Benito, 2021). In Table 2, examples of antibacterial polymers are introduced.

Table 1. *Example of antibacterial nanoparticles.*

Antibacterial Nanostructure	Type of Polymer Matrix	References
Silver (Ag)	*in situ* synthesis of AgNPs and photocatalytic property of TiO_2 in waterborne polyurethane emulsion	(Chitichotpanya, Inprasit, & Chitichotpanya, 2019)
Polyaniline-Copper@Zinc oxide (ternary nanohybrid)	WPU-based coatings	(Mirmohseni, Azizi, & Seyed Dorraji, 2019)
Titanum oxide (TiO_2)	Orthopedic and spinal implants	(Eltorai et al., 2016)
Magnesium oxide (MnO_2)	High surface area, biocompatible, easy preparation	(Kunkalekar, 2019)
Copper oxide (CuO)	Sol-gel synthesize of $Cu(NO_3)_2{\cdot}3H_2O$ and citric acid	(Azam, Ahmed, Oves, Khan, & Memic, 2012)
Carbon nanotubes(CNTs)	Carvacrol loaded halloysite nanotubes and their waterborne polyurethane nanocomposite coatings	(Hendessi et al., 2016)
Layered double hydroxide clay	Drug/clay complexes in poly(lactic-co-glycolic acid	(Chakraborti, Jackson, Plackett, Gilchrist, & Burt, 2012)

Table 2. *Example of antibacterial polymers.*

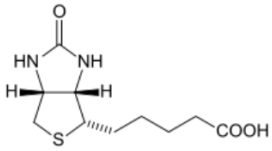
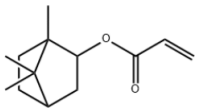
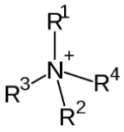
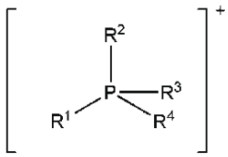
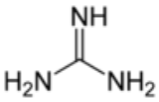
Polymer	Title	References
Chitin	Synthesis and Antibacterial Activity ofWater-soluble Chitin Derivatives	(C. H. Kim, Kim, & Choi, 1997)
Chitosan	Synthesis of novel chitosan-PVC conjugates encompassing Ag nanoparticles as antibacterial polymers for biomedical applications	(Gaballah et al., 2019)

Use of antibacterial monomers

The monomers with antibacterial functional groups, polymers with nitrogen, guanidine, halogen, sulfur, phosphorus, phenol and alimetallic compounds and positively charged species (Quaternary ammonium salt, phosphonium salt) have

intrinsic antibacterial properties(Imazato, Chen, Ma, Izutani, & Li, 2012). Among other antibacterial monomers, we can mention the compounds with triazole ring obtained from the click reaction between azidoalkynes(Hotha, Anegundi, & Natu, 2005). In Table 3, some monomers with antibacterial properties are introduced.

Table 3. *Antibacterial monomers and their molecular structures.*

Monomer	Structure	Reference
Biotin		(Yao, Li, Neoh, Shi, & Kang, 2008)
Isobornyl acrylate		(Tijing et al., 2012)
Quaternary ammonium salts		(Saeedi et al., 2019)
Quaternary phosphonium salt		(Sabitha & Rajiv, 2015)
Guanidine		(X. Chen et al., 2017)

Drug loading

Loading the drug in the polymer matrix and creating antibacterial properties has been one of the solutions for preparing antibacterial coatings(Borgquist, Körner, Piculell, Larsson, & Axelsson, 2006). Several studies have investigated drug loading in nanofibers prepared by electrospinning method. Electrospinning is a ordinary method to produce nanofibers from polymer solution or polymer melt using an electric field created by difference voltage(X. Chen et al., 2017). The obtained nanofibers have unique properties

such as very low weight, high contact surface, and porosity, which have possessed the consideration of researchers in the field of membranes, wound dressings, and textiles(Chu, Chen, Wang, & Huang, 2002; Strobel, Lyons, & Mittal, 1994). The entrapment of antibacterial drugs in these nanofibers has advantages such as rapid drug release and continuous release at the wound site(Lehocký et al., 2003). Table 4 shows examples of drugs with antibacterial properties.

***Table 4**. Sample of antibacterial drugs.*

Drug	Polymer matrix	Application	References
Curcumin	Polyurethane	Coting	(Marković et al., 2019)
Doxorubicin	Waterborne polyurethane	Micelles containing drug	(W. Huang et al., 2013)
Ampicillin	Polyurethane	Wound dressing	(Petrović et al., 2004)
Mupirocin	Polyurethane	Wound dressing	(Jain et al., 2014)
Cis-platin	Waterborne polyurethane	Drug-containing polymer matrix	(J. Wan, Cai, Feng, Meng, & Liu, 2007)
Streptomycin	Polyurethane	Drug-containing polymer matrix	(Unnithan, Gnanasekaran, Sathishkumar, Lee, & Kim, 2014)

Polymer surface modification

Surface modification is defined as methods that change the chemical and physical properties of the surface, such as surface tension, polarity, and surface hydrophilicity or hydrophobicity. Surface modification methods include X-ray, electron and gamma radiation, laser, plasma and grafting(Morent, De Geyter, Desmet, Dubruel, & Leys, 2011).

WPU's

Polyurethane polymer contains carbonate units, which was first prepared by a German scientist Otto Bayer, in the 1930s. Polyurethanes during polyol reaction (for example, of polyether or polyester type), isocyanate (for example, aromatic or aliphatic)

and chain extenders (for example, alcoholic or amine type) are produced from bulk or prepolymer polymerization(Akindoyo et al., 2016). In terms of morphology, polyurethanes are made of thermosetting pieces, soft parts are made from polyols and hard parts are made from diisocyanates and chain extenders. The chemical and physical properties of polyurethanes can be controlled by choosing different monomers from diisocyanates, polyols and chain extenders. Due to their high flexibility, strength and toughness, good abrasion and chemical resistance, polyurethanes can be used as fibers, elastomers, coatings, sealants, adhesives and sponges in industries such as construction, automobile, medical engineering and textile(Honarkar, 2018). Due to the better process, conventional polyurethanes generally contain solvents and VOCs. Therefore, the presence of these substances in their formulation causes serious damage to the environment and human health. In recent years, WPU's have received a lot of attention due to their low viscosity, high abrasion resistance, strong adhesion to various surfaces, and the ability to spread various additives(Y.-C. Wu & Kuo, 2010).

Polyurethanes do not disperse well in water. Therefore, in order to distribute them with optimal stability, it is necessary to modify their basic structure(Arshad et al., 2018). WPU is a colloidal system in which hydrophobic polyurethane particles are dispersed in an aqueous phase. The reason for the dispersion of these hydrophobic particles in the aqueous phase is the use of emulsifiers. Emulsifiers stabilize hydrophobic polyurethane particles in water. These emulsifiers are divided into internal and external categories(Shendi et al., 2017). Usually, by increasing the amount of emulsifier, the size of polyurethane particles dispersed in water decreases(B. Kim, 1996). In order to justify this observation, different reasons including the increase in hydrophilic properties and as a result, the reduction of particle size have been presented(Barikani, Valipour Ebrahimi, & Seyed Mohaghegh, 2007). Internal emulsifiers that are placed in the main chain of polyurethane can be non-ionic (such as polyethylene oxide) cationic (such as alkylated tertiary amines) and anionic (such as carboxylate or sulfonate groups). Also, high molecular weight polyurethanes can be made stable in water with external emulsifiers(T. Wan & Chen, 2017). However, this method leads to the deposition of particles and the lack of proper stability are not of good quality due to which the integrity, chemical resistance and properties of the prepared films(Francolini et al., 2010; Javaid et al., 2018; Naz et al., 2018).

Different methods have been introduced for the synthesis of WPU's. The most common of which is the prepolymer method. In this process, first the prepolymer with isocyanate ends is prepared from the reaction of suitable dials or polyols with excess amounts of diisocyanates, and then chain extenders and emulsifiers are added to make the dispersion of the polymer in water(Fei Liu, Lin Guan, Zhi Yang, Li, & De Yao, 2001). Other methods can be called acetone, melt, and ketamine-ketazine methods. Among the mentioned

methods, the acetone process is the most common method for the synthesis of WPU. In this method, acetone is used as a solvent to control the viscosity during the chain extension stage. Finally, polyurethane with high molecular weight is prepared and acetone is removed by evaporation(X. Fu, Shen, Jiang, Huang, & Yan, 2011).

Synthesis of antibacterial coatings based on WPU

Easy preparation method, low price, high long-term stability, good adhesion to surfaces, tensile strength, flexibility, ability to spread on surfaces, biocompatibility, fatness and antibacterial property are among the advantages of WPU-based antibacterial coatings(Shin & Choi, 2018). Bacteria strongly adhere to the surface of the polyurethane film and grow quickly and form colonies(Zia, Zia, Zuber, Kamal, & Aslam, 2015). In order to prevent the growth of bacteria on surfaces, many researches have been done. Researchers have expressed various solutions, including the use of polymers, monomers and antibacterial structures, drug loading and polymer surface modification, in order to prepare antibacterial coatings based on WPU.

Use of antibacterial polymers

Chitosan is a linear biopolymer and deacetylated n-form of chitin, which has NH_2 and hydroxyl groups(Saikia, Gogoi, & Maji, 2015). The antibacterial activity of chitosan against bacteria and fungi has been confirmed and their effect in reducing biofilm formation by bacteria has been reported. Chitosan has the ability to react with isocyanate groups due to its alcohol and amino groups(C. Huang, Chen, & Pan, 2000; Wang, Wu, Li, Mu, & Lin, 2020). However, due to its poor solubility, chitosan shows its antibacterial activity only in the acidic range(Fei Liu et al., 2001; Qi, Xu, Jiang, Hu, & Zou, 2004). In this regard, El- Sayed(Atef El-Sayed, El Gabry, & Allam, 2010) and colleagues used chitosan as a chain extender in the manufacture of WPU and investigated the antibacterial activity (Fig. 2).

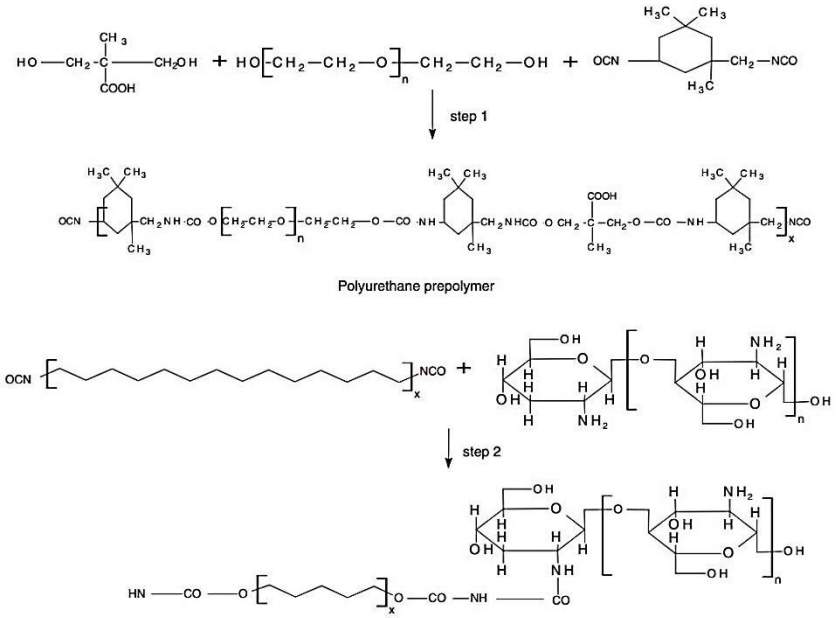


Figure 2. The synthesis of waterborne polyurethane with chitosan (W. Zhang et al., 2021).

Arshad et al.(Arshad et al., 2018) have also used chitosan with different weight amounts (2% and 4% by weight) as a biological additive in order to create antibacterial properties in WPU coatings. The results of this study showed that after placing chitosan in the main structure of polyurethane chains, remarkable results have been achieved in improving the antibacterial activity. In addition, the gradual increase in chitosan concentration shows a significant increase in bacterial activity, which is due to the presence of positively charged NH_2 groups and the interaction with the negatively charged bacterial cells walls. These synthesized antimicrobial coatings are also environmentally friendly. One of the limitations of using chitosan is its solubility in acidic environment. The major disadvantages of chitosan is the loss of its antibacterial properties in alkaline conditions, which causes the cationic nature of chitosan to be lost and it is no longer able to stick to the walls of bacteria vessels(Wang et al., 2020). Also, other biological compounds can be added to it in order to increase the biocompatibility of chitosan. Among these compounds is alginate, which is also biocompatible. Therefore, biocompatibility can be improved by modifying the surface of chitosan with alginate(Zhang, Li, Gong, Zhao, & Zhang, 2002). Zhang and colleagues prepared a set of composite materials with carboxymethyl chitosan in WPU based on castor oil and formed semi-interpenetrating polymer networks (semi-IPN_s)(W. Zhang et al., 2021). In this study, the effect of the amount of carboxymethyl chitosan on zeta potential, particle size distribution, thermal stability, mechanical properties, hardness and surface wettability of composite films were investigated and discussed. By increasing the amount of carboxymethyl chitosan (from 0 to 10% by weight), the crosslink density increased from 11.97 m^3mol^{-1} to 178.67 m^3mol^{-1} and the Young's modulus increased from 1.24 MPa to 6.7 MPa. Also, the tensile strength,

hardness, hydrophilicity and adhesion of the prepared films increased by increasing the amount of carboxymethyl chitosan due to the introduction of a large number of hydrophilic groups.

Zhang and colleagues(M. Zhang et al., 2021) were prepared hydrogel films with high mechanical resistance from water-based polyurethane-gelatin carboxymethyl chitosan (CMCS/WPU/-*g*-GH). This structure was confirmed by XPS and FTIR. Strong hydrogen bonding between CMCS and WPU-*g*-GH molecules has been established. In addition, the prepared hydrogel films show water absorption ability, favorable swelling behavior in phosphate buffer solution (PBS) and controllable biodegradability. Also, these films showed good antibacterial performance against *E. coli.* and *S. aureus*. When the amount of CMCS in the hydrogel was 6% by weight, the inhibition zone of *E. coli.* and *S. aureus* reached 16 and 20 mm. Also, the lower the pH and the higher the concentration of H^+ in the solution, the more the prepared hydrogel films show antibacterial activity, which is in accordance with the natural process of wound healing. GH-g-WPU/CMCS hydrogel films have a controllable degradation process that meets the standards of wound dressings in modern medicine.

From WPU's, due to the presence of water solvent and the production of low or zero volatile organic compounds, non-toxicity, biocompatibility, barrier property, oxygen permeability, optimal adhesion to the wound surface, proper control of wound moisture, the ability to absorb and control wound secretions, and also it can be used in the preparation of semi-permeable wound dressings(Buchan et al., 1981). The presence of water in the WPU structure makes the cells more inclined to stick to the wound surface. If the wound dressing is more similar to the structure of the skin, the process of wound healing, angiogenesis, cell adhesion and growth will accelerate(Banks, Bale, Harding, & Harding, 1997).

In another study, Bankoti et al.(Bankoti et al., 2017) were introduced nn-toxic WPU-chitosan porous hydrogel scaffolds with optimal adhesion to the wound site for the purpose of healing skin wounds. Based on these studies, the best considered sample is the C3P7 sample (Fig. 3) with a molar ratio of chitosan to WPU of 3:7. According to the results, the manufactured C3P7 sample showed a faster process in wound healing than the Tegaderm commercial dressing.

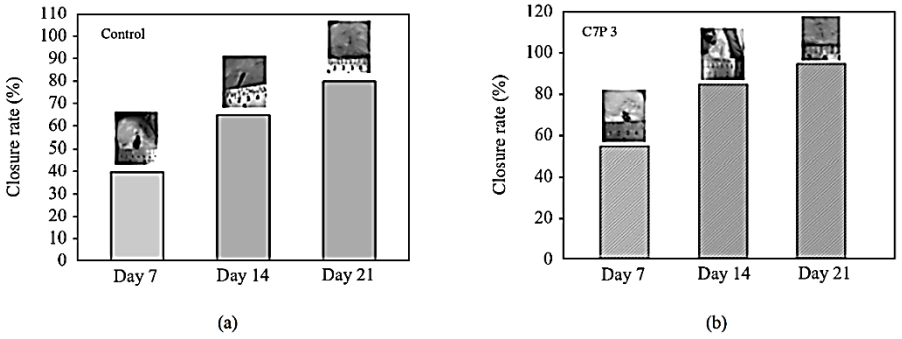


Figure 3. a) Tegaderm (control) and (b) C7P3, wound healing process for 21 days (Agnol, Dias, Ornaghi Jr, Sangermano, & Bianchi).

Zo et al.(Zo, Choi, Kim, Shin, & Han, 2020) investigated the activity of osteoblast cells on WPU/CMCS (5:5) scaffolds. As shown in Fig. 4, the activity of cells increased continuously until the seventh day and this activity on the scaffolds was more than the control sample (2D). These results were consistent with SEM micrographs. In the SEM micrographs of Fig. 4, it was found that the cells started to shed the extracellular matrix (ECM) on the scaffold during the seventh day, which means the high metabolic activity of the osteoblast cells. Also, osteoblast cells are well attached and multiplied. The observed high adhesion and proliferation of osteoblast cells show that WPU/CMCS scaffolds are potential bone tissue engineered structures.

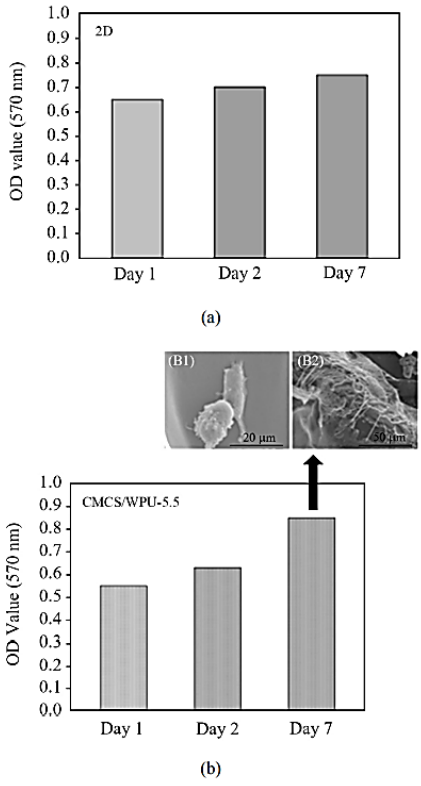


Figure 4. Metabolic assay on 1st, 2nd, and 7th day and SEM images on 7th day after seeding osteoblast cells onto CMCS/WPU-5:5 scaffolds (Anthierens, Billiet, Devlieghere, & Du Prez, 2012; Sajomsang, Gonil, & Tantayanon, 2009).

Use of antibacterial monomers

Most antibacterial coatings are applied by adding antibacterial agents such as peroxides and silver nanostructures. However, antibacterial coatings have many disadvantages, such as toxicity, high cost, and unstable antibacterial activity, which limit their scope of service and application(L. Chen, Suh, & Yang, 2018). A new method whose antibacterial properties have been proven is the use of antibacterial monomers, positively charged species (quaternary ammonium salt, phosphonium), such as guanidine compounds, in the main chain of urethanes(Y. Chen et al., 2018). Li et al.(X. Chen et al., 2017) prepared an antibacterial WPU coating modified with chitosan-guanidine hydrochloride. Because of guanidine has the ability to establish hydrogen bonds with bacterial membranes. Researchers used polymers containing guanidine to make antibacterial coatings. The antibacterial test results of these coatings against *E. coli* and *S. aureus* were 87.2% and 90.1% respectively.

In the past decades, quaternary ammonium salts have been intensively investigated due to their antibacterial activity for a wide range of bacteria and low toxicity(Anthierens, Billiet, Devlieghere, & Du Prez, 2012; Sajomsang, Gonil, & Tantayanon, 2009). Fan et al.(Fan et al., 2017) prepared a new WPU coating that was modified with the quaternary ammonium chain extension. Ammonium-based polymers of the quaternary have favorable antibacterial properties against a wide range of microorganisms, including gram-negative and gram-positive bacteria. The antibacterial mechanism of these compounds has not been proven yet, but, according to the researchers, this function is probably due to the binding of the ammonium group to the bacterial membrane with electrostatic attraction and membrane deformation, and finally the death of the bacteria(Anıl, Berksun, Durmuş-Sayar, Sevinis, & Ünal, 2020; Kowalczuk & Pitucha, 2019).

Liang et al.(Liang, Liu, Lu, Chen, & Zhang, 2018) used castor oil and N-methyldiethanolamine (a type of ammonium salt of the quaternary) to prepare cationic polyurethane aqueous dispersion in order to improve the mechanical, thermal and antibacterial properties of WPU. The results showed that by adding N-methyldiethanolamine as a chain extender due to strong interaction with urethane groups, a stable dispersion was formed. Also, by increasing the weight percentage of N-methyldiethanolamine (from 0.69 to 1.19 molar), the antibacterial activity of the films changed (The bacteria containment area increased from 11.4 mm to 11.94 mm). Because due to the increase of this compound, which indicates the increase of ammonium groups of the quaternary type, the antibacterial activity of WPU has improved. This cationic polyurethane aqueous dispersion based on castor oil, with good mechanical and antibacterial properties, can be used as a coating in medical instruments and food.

Another application of ammonium compounds of the quaternary type in polyurethane aqueous dispersions is the preparation of antibacterial polymeric wound dressings(Patil, Jirimali, Paradeshi, Chaudhari, & Gite, 2019). Kim et al.(Yoo & Kim, 2008) have designed a WPU-based polymer dressing with ammonium compounds of the quaternary type. The purpose of using polyurethane (PU) is to achieve a flexible wound dressing with favorable and non-toxic adhesive properties. In this research, the antibacterial property of fourth type ammonium compounds increased the amount of growth and proliferation of fibroblast cells and decreased the wound healing time. To prove the antibacterial properties of these compounds, an experiment was conducted on mice to compare the wound healing process using sterile gas (without antibacterial agent) and wound dressing containing N-vinyl pyrrolidone (quaternary ammonium) within two weeks. According to the observations, the treatment of the wound with the quaternary type of ammonium coating improved faster within 14 days and the wound site was well repaired.

Recently, natural compounds named borneol have been introduced as ideal antibacterial adhesives due to their excellent adhesive properties. Borneoles have four configurations that correspond to different positions of the hydroxyl group. In this regard, Wu et al.(J. Wu, Wang, Mu, & Lin, 2018) have produced a new antibacterial WPU using isobornyl acrylate and thiol additive (as a chain extender) by Michael addition reaction and condensation polymerization (Fig. 5). Their goal is to develop a simple method for preparing polyurethane coatings compatible with the environment, with antibacterial and durable properties. Their antibacterial activity showed that isobornyl acrylate improves the antibacterial performance of polyurethane films. According to Fig. 5, when the weight amount of isobornyl acrylate reaches 25%, these films have better antibacterial properties with an inhibition ratio of 80.4 and 89.3% against *S. aureus* and *E. coli* and show very good resistance. Despite this, little research has been done on polyurethanes with borneol compounds and its derivatives. In addition, designing an efficient approach for borneol compounds, while maintaining their high antibacterial activity, is a challenging issue.

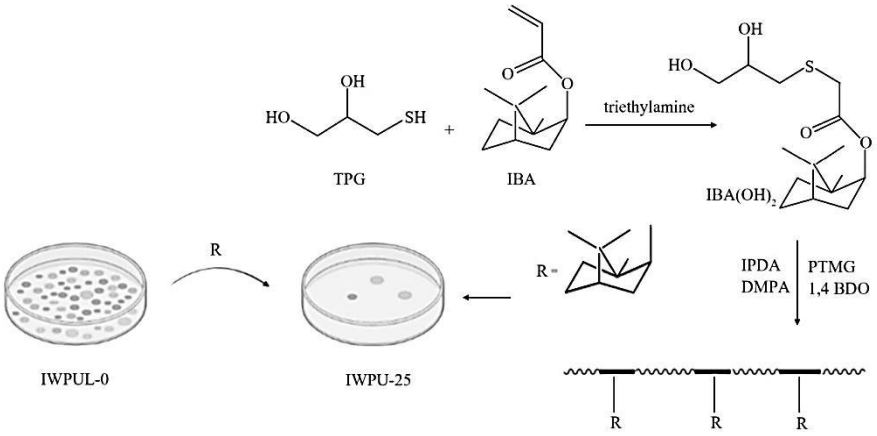


Figure 5. Synthesis scheme of antibacterial WPU with isobornyl acrylate ((Hasnain & Nishat, 2012; Zhou, Teo, & Srinivasan, 2014).

Recently, structures with properties similar to quaternary ammonium salts have been introduced using quaternary phosphonium salts(Hasnain & Nishat, 2012; Zhou, Teo, & Srinivasan, 2014). It has been shown in many reports these salts show better antibacterial activity than ammonium salts. Therefore, it is expected that by adding phosphonium salts of the quaternary type to polyurethanes, the antibacterial property can be transferred to the polymer matrix. In this study, Wang et al.(Anthierens et al., 2012) proposed an easy approach to prepare antimicrobial WPU with type IV phosphonium groups. Also, their thermal stability and antibacterial effect were evaluated. By increasing the weight percentage of quaternary phosphonium salts (from 0 to 20% by weight), the bacterial inhibition value of the WPU20 sample increased up to 85%. A lower inhibition ratio (81%) was obtained for resistance against Gram-negative bacteria *E.coli*. The results showed that WPU films with type IV phosphonium salts show broad antibacterial activity and inhibit the growth of *S. aureus* (gram positive bacteria) to a greater extent.

Use of antibacterial nanostructures

Metal nanostructures with low toxicity, heat resistance and antibacterial effect against Gram-negative and Gram-positive bacteria are known**(J. H. Park et al., 2011)**. Inside the biofilms, there is a possibility of exchanging antibiotic genes, which causes the formation of very resistant cells to many bacterial species and creates drug resistance(Eltorai et al., 2016). In the activity of antibacterial nanocomposite coatings, antibacterial activity usually increases by increasing the content of nanostructures to the desired level, which depends on the characteristics of the nanostructure. Hydrophilicity and hydrophobicity of the surface are the important factors that ensure the anti-bacterial properties of the coatings**(Ma & Zhang, 2009)**. The combination of nanostructures with antibacterial properties in WPU's especially in medical and textile applications has

attracted a lot of attention. The homogeneous dispersion of such nanostructures in the WPU matrix can significantly improve the antibacterial efficiency of the resulting nanocomposites including anti-inflammation probes for various applications.

Silver nanostructures

Silver nanostructures (AgNPs) are used in polymer composites to increase antibacterial properties(Mohammadi et al., 2018). It is also reported that silver increases mechanical properties(J. Chen et al., 2019). There are two types of solutions for making Ag/WPU nanocomposites; 1) Use of AgNPs in making nanocomposite and 2) making AgNPs in situ in WPU(H. Fu, Wang, Li, & Chen, 2016). Recently, the second method has received much attention. Because, it can overcome the coagulation and gelation problems caused by the connection of WPU chains by Ag^+ ions. It also provides the possibility of adding a larger amount of Ag^+ ion. The use of silver salts to make silver nanostructures requires the use of reducing agents to reduce the amount. It is worth noting when adding silver nanostructure to polyurethane water dispersions, the color of the polymer solution changes from milky to dark brown. Reduction of silver ions is done with one of the components used in WPU, such as polyol component, or the use of substances capable of reducing silver ions, such as $NaBH_4$, DMF(H. Fu et al., 2016), dopamine(Mirmohseni, Azizi, & Dorraji, 2019).

Tsou et al.(Tsou et al., 2016) were able to reduce silver ion by synthesizing a pyridine compound. Pyridine compounds reduce silver by coordination interaction with silver ions, then during the reaction with urethane prepolymer, they enter the main chain of the polymer as a chain extender. Pyridines are hydrophobic and antibacterial compounds and prevent adhesion and biofilm formation by bacteria. The results have shown that with increasing content of pyridinium compound, Young's modulus, glass transition temperature, hydrophobicity and contact angle increased and initial degradation temperature and tensile strength decreased in these films. In addition, films have very good antibacterial activities compared to *S. Aureus* and *E. coli* (% 99.9) showed. The amount of antibacterial property increases in pyridine content.

Zang et al.(Zhong, Luo, Yang, Wu, & Ren, 2017) were successfully prepared high-performance anionic WPU/Ag nanocomposites with excellent antibacterial property by an in situ method. Anionic carboxylate groups in WPU act as stabilizing agents for silver nanostructures. The results showed that the formed spherical silver nanostructures were uniformly distributed in the WPU matrix and showed good dispersion without aggregation. In addition, the presence of silver nanostructure, remarkable antibacterial behavior against *E.coli* bacteria showed. Also, by increasing the amount of silver nanostructures, the antibacterial property of the films has also increased.

The problem of WPU coatings with nanoparticles prepared from the in-situ reduction of silver ions is the coagulation of polyurethane micelles. Because, the interaction of silver ions with carboxylate groups of polyurethane chains leads to cross-links. Therefore, studies have been conducted in this field to solve the mentioned problem(Tao, Zhang, Zhang, Yuan, & He, 2006). The researchers found out during research that, this problem can be overcome by coordinating silver and then reducing it. Also, the use of this approach improves the stabilization and protection of nanostructures. Polyol is used as a reducing agent for silver ions and Schiff's base ligand as a stabilizing agent for silver nanoparticles. According to the results, silver ions are well distributed in the polymer matrix due to the coordination interaction.

According to Fig. 6, two types of WPU films have been prepared. One of which has Schiff base ligand and the other Schiff base ligand with silver nanostructure. Their antibacterial behavior has been investigated against gram-positive and gram-negative bacteria. Based on previous research that indicates the strong antibacterial behavior of silver nanostructure against two strains of bacteria, this matter is well shown in this figure. The film containing only the Schiff base ligand did not show any antibacterial behavior. But the film that has Schiff base ligand and silver nanostructure has a very favorable zone of non-growth of bacteria (zone inhibition).

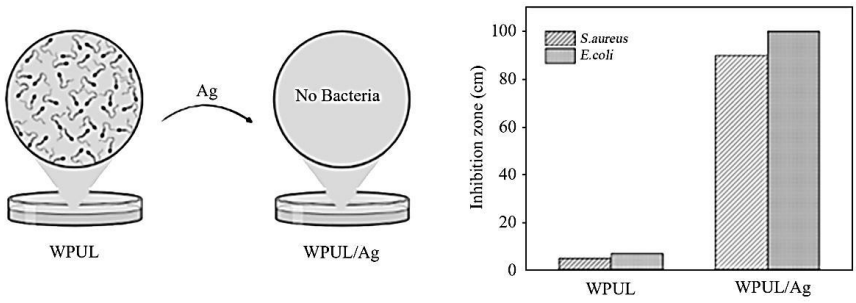


Figure 6. Antibacterial attitude of WPU film against gram-negative and gram-positive bacteria (Mohammadi et al., 2018).

Liu(H. Liu et al., 2012) et al. prepared another sample of WPU-silver nanocomposite. Their goal was to simultaneously improve the mechanical and antibacterial properties of WPU. Rod-shaped cellulose nanocrystals (CCNs) have a great ability to absorb metal cations and due to the strong interaction between the hydroxyl group and the silver cations. They cause the uniform dispersion of the silver nanostructure in the polymer matrix. Such interactions reduce the mobility of silver cations, prevent the formation of large particles and stabilize the silver nanostructure. The results showed that tensile strength of WPU films increases by 33.7 MPa with adding 10% by weight of rod-shaped cellulose nanocrystals. On the other hand, the tensile strength of WPU films decreases

with increasing amount of silver. The increase in the length to tear with the increase of rod-shaped cellulose nanocrystals is greatly reduced (from 2041% to 1740%). Increasing amount of silver causes increases slightly (from 1814% to 1857%). Most importantly, WPU/CCNs/AgNPs nanocomposite films showed strong antibacterial activity against *E. coli* and *S. aureus* (99.5% and 87.7% respectively). According to the results, nanocomposites can be used as antibacterial coatings.

In another study, Park et al.(J. H. Park et al., 2011) reported the electrospinning production of poly (vinyl alcohol)/WPU/silver composite nanofibre mats in aqueous solution for anti-bacterial exploits. According to the results, the mechanical, thermal and antibacterial properties of WPU/PVA/Ag nanofibers are improved compared to PVA nanofibers. By increasing the weight amount of silver nanostructure up to 1%, the nanofibers have become more fragile. The results of TGA also indicate that the thermal stability of the nanocomposite containing 1% by weight of silver nanostructure has been improved by reducing the weight by 4%, about 50°C compared to the pure PVA/WPU mixture. Also, its antibacterial activity increased by increasing the amount of silver from 0 to 1% by weight, and no bacteria grew.

Zinc oxide nanostructures

In addition to thermal, optical and semiconducting applications of nanostructured zinc oxide (ZnO), these nanostructures are well known due to their antibacterial properties by producing reactive oxygen species, hydrogen peroxide, and mechanical destruction of the cell membrane(Ma & Zhang, 2009). Zang et al.(Y. Yang, Xiong, Huang, Shi, & Zhang, 2019) synthesized ZnO nanowhiskers by hydrothermal synthesis method and modified them with aminopropyl triethoxysilane (APTES) to improve the interaction between nanowhiskers and urethane groups. The properties of ZnO/WPU nanocomposite such as mechanical resistance, thermal stability and antibacterial effect were all affected by ZnO nanowhiskers. WPU/ZnO films have strong antibacterial effect against *E. coli* and *S. aureus* showed. According to the results, with the increase in weight percentage of ZnO nanowhiskers, the survival percentage of bacteria decreased and the best antibacterial activity was reported with 4% by weight of ZnO nanowhiskers. It was found that the synthesized WPU/ZnO nanocomposites are useful as effective coatings due to their favorable mechanical and antibacterial properties.

Halloysite nanotubes

Halloysite nanotubes (HNTs, halloysite nanotubes) are a special type of nanotubes that have a crystalline structure. The external surface of these nanotubes consists of O-Si groups, and its inner surface consists of OH-Al groups, which gives them the ability to carry drugs and other nanomaterials. Halloysite are very similar to carbon nanotubes in

terms of structure and are a good alternative to carbon nanotubes due to their cost-effectiveness(Du, Guo, & Jia, 2010). In a research by Fu et al.(Hu, Yuan, & Shi, 2012) they made antibacterial coatings based on WPU's by modifying the surface of halocytes with the help of chitosan and silver nanostructures. Improved thermal and mechanical properties were attributed to HNT-Ag nanostructures. In the direct mixing of WPU and silver nanostructure (without HNT), silver nanostructures tend to accumulate, are not uniformly distributed, and show weak antibacterial properties (69.5%). While in HNT-Ag/WPU samples, silver nanostructures are placed on the surface of HNTs and HNT-Ag particles are uniformly dispersed in the WPU matrix. Antibacterial activity of Ag/HNT films against *E. coli* and *S. aureus* is 91.8% and 99.9% respectively.

Graphene oxide nanosheets

Graphite is a three-dimensional structure consisting of millions of graphene layers. When graphite is oxidized by strong oxidizing agents, oxygenated functional groups enter the graphite structure, which not only separates the layers from each other but also turns into hydrophilic substances. The structure of graphene oxide (GO) includes carbon layers with hydroxyl, epoxy and carboxyl groups with random distribution on the surface and edge of the plates. Due to the presence of oxygen groups and the fusion of the main structure of graphene, this material does not have the main properties of graphene such as good electrical and thermal conductivity(Perreault, De Faria, Nejati, & Elimelech, 2015). However, due to the presence of these groups, it has a better ability to react with materials, which allows it to be linked to polymers or other materials through covalent bonding(Xiong, Zhang, Shi, & Mai, 2015). When the nanostructure of graphene oxide (rGO) is reduced, properties such as high specific surface area, excellent electrical conductivity, high mechanical resistance and antibacterial properties can be achieved. Reduced graphene oxide affects the bacterial membrane by producing reactive oxygenated species and leads to the death of the bacteria(Krishnamoorthy, Umasuthan, Mohan, Lee, & Kim, 2012).

Double layered hydroxides

Electrolyte double hydroxides (LDH) are known as nanostructures with positive charge of electrolytes and binary anions. These nanostructures have physical and chemical properties very similar to hydrotalcite(Bai, Zhang, Dai, & Li, 2006). The basic structure of LDH layers is based on the structure of brucite, $Mg(OH)_2$ and it is formed by the substitution of a part of divalent cations of the brucite network with trivalent cations, which creates a positive charge in the plates(K. Liu, Su, Miao, Ma, & Zhang, 2016). Among the unique features of LDH, we can mention its toxicity, cheapness, good biocompatibility, favorable thermal, mechanical and antibacterial properties, large

contact surface and high capacity of interlayer anion exchange. According to the mentioned properties, these materials have shown great ability to be used in the fields of catalysis in chemical reactions, anti-corrosion coatings, polymer additives and drug release(W. Zhang et al., 2021). In this regard, Yang et al. used Mg_3Al_2- LDH interlayered with parahydroxybenzoic acid (*p*-BzOH) to make antibacterial WPU. Their aim was to improve mechanical properties, water resistance and create antibacterial properties by releasing para-hydroxybenzoic acid from Mg-Al- LDH layers. They synthesized WPU/LDH nanocomposite with favorable thermal and mechanical properties by in situ polymerization method. The resulting nanocomposite films with the highest weight percentage of filler (2% by weight) showed very strong antibacterial activity against *E. coli* (97.8%) and *S. aureus* (81.5%). Hu et al.(M. Zhang et al., 2021) modified Mg-Al-LDH with IPDI and then synthesized WPU/LDH nanocomposite with improved thermal and mechanical properties by in situ polymerization method.

Hybrid nanostructures

Hybrid nanostructures are obtained by combining two or more nanostructures. A polymer with a hybrid nanostructure has the properties of each of the existing nanostructures. Xiong et al. deposited ZnO nanostructures on double layered hydroxides and then modified it with a part of isoforene diisocyanate (IPDI). Finally, they synthesized WPU/LDH-NiAl/ ZnO aqueous dispersion. Compared to pure WPU, the tensile strength of the resulting composites increased to 13.5 MPa due to the formation of a network structure by increasing the weight amount of LDH-NiAl/ZnO till 13.5%. Composites made have a strong antibacterial effect against *E. coli* (99.9%) and *S. Aureus* (98.1%) showed(Bankoti et al., 2017). Also, Jiang et al.(Jiang et al., 2019) used rGO/GO hybrid nanostructure to make WPU nanocomposite that was confirmed by FTIR, TEM and XRD tests. Antibacterial tests showed that nanocomposites rGO–CuZnO were very sensitive to *E. coli* and *S. aureus* and they had the ability to seriously destroy the structure of their cells. When the weight percentage of rGO–CuZnO in the preparation of WPU/CuZnO-rGO coating was 2%, antibacterial activity and corrosion inhibition efficiency against *E. coli* and *S. aureus* improved to 94.35 and 93.30%.

Drug loading

Loading antibiotic substances in antibacterial coatings is also one of the developing approaches. Coatings that contain drugs can release the drug in a controlled manner and prevent the toxicity resulting from a one-time release of the drug(Zo et al., 2020). Chang et al.(Chang et al., 2017) produce an antibacterial coating based on WPU for leather coating. They prepared a low molecular weight copolymer containing the antibacterial drug ciprofloxacin and acrylic acid. The purpose of using this copolymer with WPU was its favorable compatibility with WPU and its slow release, biocompatibility and creating

long-term antibacterial properties on leather. Based on the results, the water-soluble antimicrobial copolymer led to an increase in the antimicrobial performance of WPU coatings and also increased the lifespan of leather products.

Polymer surface modification

There are different methods to modify the surface of polymers. One of these methods is correction with ultraviolet (UV) rays. This approach has been shown to be an advanced technology for improving the performance of WPU systems. In recent years, the demand for effective, cost-effective and environmentally friendly coatings has led to the improvement of WPU-UV production processes(Masson, Decker, Jaworek, & Schwalm, 2000). In this regard, Liu et al. synthesized WPU-acrylate based on castor oil as an environmentally friendly agent. Also, the loading of modified lysozyme enzyme with double bond in WPU coating by UV curing shows a way to develop highly effective antibacterial surfaces. These coatings are able to destroy E. coli and S. aureus as soon as they come into contact with the antibacterial enzyme and they can be efficient in long-term use. The inhibition efficiency of bacteria increased from 10% to 68% by adding 1.5% by weight of lysozyme enzyme compared to the control sample. On the other hand, the mechanical and thermal properties of the enzyme coating are better than the control coating(Adler, Messerle, Wagner, & Koszinowski, 2000). WPU coatings modified with UV rays are currently widely used as antibacterial, antistatic and flame retardant coatings to protect the surface of wood, plastic and metal with the appropriate selection of nanostructures, additives, monomers and chain extensions(Agnol et al., 2021). Table 1 Test for Table Name

2. Conclusion

In this review, various methods of creating antibacterial properties in polymers; raw materials, synthesis methods and advantages of WPU's compared to polyurethanes based on organic solvents were investigated. In addition, the studies conducted in the field of preparation of antibacterial WPU's using solutions such as adding nanostructures, mixing with antibacterial polymers, loading drugs, using antibacterial monomers and modifying the polymer surface were reviewed. Considering the biocompatibility and favorable mechanical properties of WPU-based antibacterial coatings, it is expected that the results of these researches can help to introduce new products with the possibility of application in sectors such as covering medical equipment, general equipment, packaging industries, and preparing wound dressings.

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