Chapter 6

Water-Borne Polyurethane Based Composites and Their Applications in Functional Textile Coatings

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Abstract

Polyurethanes have gained great attention owing to their biocompatibility, biodegradability, excellent mechanical strength, tailorable chemical, and physical forms in the industrial field in recent years. While the performance properties of the polyurethane material can be improved with the composite structure formed by reinforcing different types of nano particles (3D fillers, nanofibers, nanotubes, and plate-like filler) into polyurethanes, it can also pave the way for different application areas. Fillers can be used to modify the crystallinity, molecular arrangement, crosslinking, and functional chemical groups of the water-based polyurethane (WPU) based composite structure. Polymer nanocomposite coatings are a subject of study that requires the engineering of composite materials that combine the advantages of different components. In this study, researches and recent developments in the design and preparation of WPU-based composite coatings that can be used in the development of functional textiles and positive impact of WPUs composites on the future prospects of this field are presented. While this study enables researchers to gain awareness of the potential applications of functional textiles designed with WPU composite coatings, it can encourage researchers for new research in terms of diversifying the application forms with different materials.

1. INTRODUCTION

Polyurethanes (PUs), discovered by Otto Bayer in 1937, are one of the most widely used polymers on the global market[1–3]. PU material is a functional material with its high mechanical flexibility, biodegradability, and

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physicochemical properties. Increasing environmental awareness in recent years has led to the search for green materials compared to traditional solvent-containing environmentally hazardous materials, and therefore water-based polyurethanes (WPUs) have emerged as an alternative material to solvent-based polyurethanes[4]. WPUs are an environmentally friendly material with a low volatile organic compound (VOC) content. The low VOC ratio and the possibility of using precursors from renewable sources have made WPUs an attractive material from a sustainability perspective[5]. The properties of PUs such as flexibility, elongation, high impact and abrasion resistance enable them to find applications in textile, leather, aerospace, furniture, fibers, elastomers, adhesives, sensors, electronic components, paints, coatings, biomedical and other industries[6–11]. WPUs are preferred in leather finishing, synthetic coating and textile lamination due to their non-toxic, VOC-free, soft, high-strength film-forming properties[12]. As a functional material, with properties such as good corrosion resistance, high acid and alkali resistance, mechanical properties and wear resistance, PU is widely used in military, defense, construction, transportation, and other fields. However, in recent years, researchers have been investigating various ways to develop new PU coatings in line with the requirements of the new age. Especially with the development of nanotechnology, researchers are trying to use nano materials together with traditional PU coatings to increase the performance of PU coatings[13].

PUs are segmented polymers consisting of a hard segment (HS) containing isocyanate, which provides strength and durability to the material, and a soft segment (SS) containing polyol, providing flexibility[14]. By changing the material types and segmented structure ratios included in the PU structure, materials with different properties can be obtained. Water-solvent WPUs are similar in performance to conventional solvent-based PUs and have a wide range of applications (Fig. 1). such as coatings, textiles, biomedical applications, adhesives and foams[15–17].

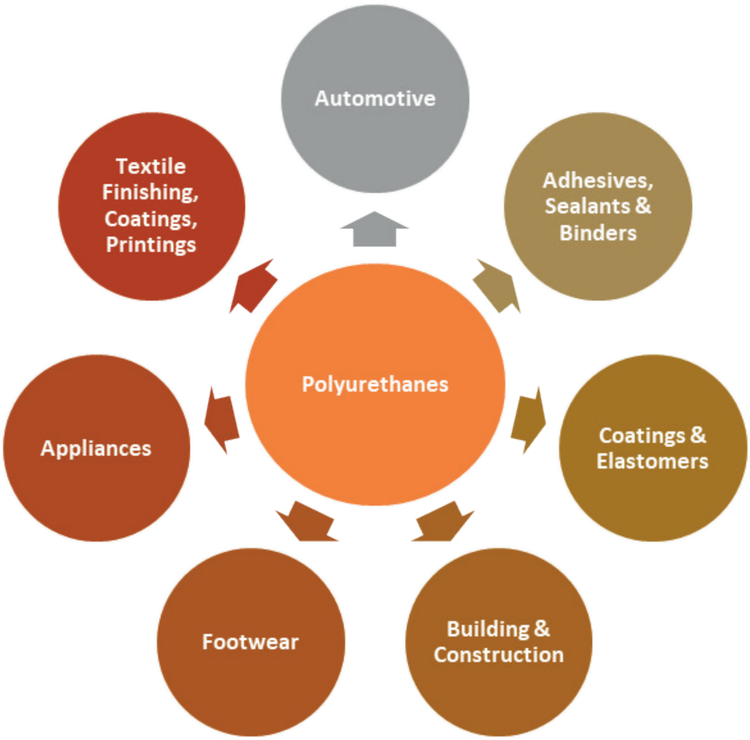

Figure 1: Potential application areas of polyurethane.

Although they find different usage areas, independent use of PUs may not provide sufficient mechanical and thermal properties in some cases[18]. On the other hand, in addition to good physical properties, properties such as high mechanical performance, UV resistance and flammability should be further improved in terms of resistance to harsh conditions[19]. WPU is a high performing polymer in coatings, composite materials, adhesives, foams, elastomers and etc. WPU coatings have chemical and heat resistance, mechanical and physical durability properties. In recent years an important research area to obtain functional WPU coatings is the experimental design and formulations of nanocomposite coatings containing nanocarbon particles (carbon nanotubes, graphene, graphene oxide (GO), graphene, etc.) and inorganic nanoparticles (metal, metal oxide nanoparticles, etc.)[3,20]. Over the past decades, by adding these functional nano-reinforcement materials in small contents have been used to improve the corrosion resistance, mechanical and thermal properties of coatings by incorporating them into coating formulations[21]. The incorporation of functional fillers into polymer matrices is an effective method that increases the performance of PU composites[22].

These systems, which are formed by dispersing nanoparticles into a polymer matrix, are used to improve the properties of the composite material such as optics, conductivity and abrasion resistance[23]. WPUs produced in this way owing to the incorporation of nanoparticles exhibit outstanding advantages such as good elasticity, weathering resistance, solvent/chemical resistance, pH and thermal stability, mechanical strength and biodegradability, along with surface properties that can be modified or improved[3]. Functional WPU polymer is a high performance polymer that can be used in fields such as composites, medicine and electronics[24]. Recently, many articles have been published on WPU-based composites containing carbon nanotubes or graphene platelets to develop high-performance and electrically conductive WPU coatings[25]. Recently, the current trend is to design new materials that offer antimicrobial protection by coating or making surfaces functional by reducing the adhesion of microorganisms to surfaces or biofilm formation of pathogens[26].

Applications of WPU nanocomposite coatings to various technical fields such as textile, biomedical and defense industries have been reported. Therefore, research has turned to more sophisticated WPU nanocomposite coatings that can be used in application areas where higher value-added products can be obtained instead of neat WPU-based materials[20]. With research and technological developments, there is a great interest in the design and production of functional textiles today. It is among the expectations that textiles, which are protective substances between humans and the environment, protect users from harmful factors. These special needs require the modification of textiles and the expansion of their usage areas. There is a need for UV protective, waterproof-breathable, NIR shielding and antibacterial textiles especially for outdoor applications[20,27]. This study mainly covers the major developments in the field of functional textile coatings prepared with WPU composite coatings, with special emphasis on the coating material and processes, application areas and related challenges for future advancement.

2. THE STRUCTURE OF POLYURETHANE AND COATING PROCESSES OF WATER-BORNE POLYURETHANE

The Structure of Polyurethane

There are various ways of using polyols and isocyanates, which are the essential components included in the structure, to obtain a water-based polyurethane with the desired properties. Generally, in the synthesis reaction, the first step is polyaddition polymerization resulting in a gradual growth of polyol containing the stabilizing hydrophilic moiety (OH/NCO<1) with the excess isocyanates. This polymerization process results in isocyanate-terminated prepolymers in the presence of a solvent (such as acetone or methyl ethyl ketone). This reaction is followed by the interaction of excess isocyanates with amines. In the last step, the chains of the prepolymers are extended by adding diamines and diols[4].

PUs are the only class of plastics obtained by extensive changes in one property such as thermosetting or thermoplastic, rigid or flexible, rigid, or open cellular type. The location and structure of -ol and isocyanate included in the PU structure is very important in determining the properties and final applications of the polymer. In the segmented PU structure, the hard segment is composed of isocyanate and chain extender, while the soft segment is composed of polyols. The reaction of the prepolymer with the chain extender increases the molecular weight, while the hard and soft segments used in different proportions form a block copolymer. Polyols allow PUs to have good tensile properties with high Tm, while isocyanates allow them to degrade without causing toxic problems. Diols or diamines are chain extenders used to form the Mw of the polymer and to increase the length of the hard segment[18].

Coating Processes

In order to be effective on the physico-chemical properties of WPU products, it finds application as a coating material in different forms such as fibers, foams, and films. The coating process can be applied by methods such as spraying, dipping/wetting, powder coating, roller coating. The coating can provide smoothness, corrosion resistance, hydrophobicity, resistance to acidic or basic environments and thermal stability to the applied surface. Surfaces coated with WPU-based composite can be used in the fields of biomaterials, textiles, and defense technologies. In this context, high performance WPU coatings are an important research topic for the development of domestic automotive and other technical coating materials in recent years[27].

3. COMPOSITE COATINGS FOR FUNCTIONALIZATION OF TEXTILES

The design of the surfaces of textile materials as nano-structured and their application potential in the field of biomedicine have revealed that films produced from biopolymers and coatings containing nanoparticles are an important alternative in terms of improving the surface modification of textiles. Basic coating process of textiles with functional agents is given in Fig. 2.

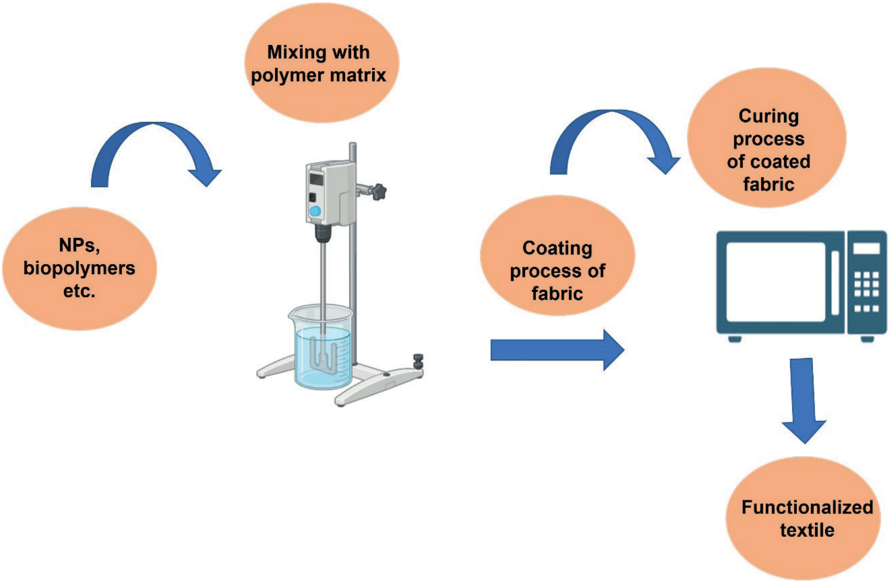

Figure 2: Basic coating process of textiles with functional agents.

There are methods in which functional textile surfaces are obtained by using nanocomposite coatings, which consist of direct functionalization methods where the nanocomposite coating is transferred directly to textile fibers, and indirect methods where the composite is produced and then applied to textile materials. Metal nano oxides ((copper oxide (CuO), zinc oxide (ZnO), titanium dioxide (TiO_2), magnesium oxide (MgO), silver (Ag), copper (Cu), Ag/TiO_2, Zn/CuO, etc.)) have large surface and also are suitable for coating of fibers. Therefore, they are used to form functional composites to use for surface modification of textile materials[28]. Recently, nano-silica, titanium dioxide, graphene and nanoclay coatings have gained importance to improve the properties of polymer nanocomposite (PNC) coatings and mechanisms for create effective surfacial mitigations. The nano fillers used are classified according to their size as 0D (nanoparticles), 1D (nano rods, nanotubes, or nanowires), 2D (nano films, nanosheets or nanoplatelets). On the other hand, PNCs can be classified according to the nanofiller sizes included in the structure[29]. With the increase in research on polymer nanocomposites, it is possible to develop new material classes with unique structure-property relationships. Although these materials are generally started to be obtained by using inorganic fillers, studies on the superior potential of these materials are quite new. Recently, studies on the development of protective coatings for high-contact surfaces in healthcare institutions have increased[30].

4. RESEARCHES ON APPLICATIONS OF WATER-BORNE POLYTURETHANE BASED COMPOSITE COATINGS FOR FUNCTIONAL TEXTILES

One of the areas where polyurethane coatings are extensively used is to protect the applied surface against corrosion. This protection feature of polyurethanes has been enhanced by adding additives and nano-fillers to the polyurethane. These nano-fillers included in the structure can improve the barrier property of the coating by increasing the microscopic areas. Polyurethane composite coatings are frequently preferred in biomedical device and other commercial surface systems. Because these coatings, which are resistant to bacteria and microbes, and reduce infections, have decontamination properties. On the other hand, it is used as a top-coat camouflage material in defense technologies, in aircraft and strategically armed vehicles. These coatings exhibit improved physical properties, high mechanical strength and chemical resistance against high temperatures and adverse environmental conditions. In the literature, the relationship between the mechanical properties and strength of the coatings used in the production of high-performance materials is examined. Polyurethane/graphene coating systems, one of the research subjects, have been used to impart properties such as electrical and thermal conductivity and antibacterial activity to the textile surfaces on which they are applied. In this context, various nanofillers have been used in the development of nanocomposite coatings. The inclusion of these materials in polyurethane coating formulations can cause structural modification of the polyurethane. The nano-fillers included in the coating formulations have a decisive role in the resistance of the coating to chemicals, heat, and moisture with their improved surface properties. Therefore, studies on polyurethane nanocomposite coatings have shown that high performance coatings can be obtained with desired properties[27]. With the increase in the demand for technical textiles in recent years, multifunctional coated fabrics are among the products that attract attention[20]. In this paper, the researches made in the last five years regarding the potential applications for water-based polyurethane-based composite coatings and functional textiles were determined and these researches are given below according to the fillers used in the resin matrix.

4.1. Metals and Metal Oxide Nanoparticles-Incorporated Water-Borne Polyurethane Composites

Shen et al. designed and prepared functional inorganic ZnO nanoparticles (ZnO NPs) used as reinforcement material with UV protection property for use in water-based polyurethane acrylate (WPUA) composite coating.

PUA@ZnO NP composite coatings with silane coupling agent modified ZnO NPs with different morphologies were prepared and their structural characterizations were made. WPUA@ZnO NP emulsions were applied to cotton, PET, and PP fabrics then, mechanical, and interfacial properties of coated fabrics were investigated. ZnO NPs achieved efficiently UV initiation and improved the UV absorptions and thermal properties of the waterborne polyurethane acrylate composite coating to which they were added. In addition, improvements were observed in the mechanical properties, abrasion resistance, water, acid and alkali resistance of the fabrics[31].

Zhang et al. firstly prepared the silver/water-based polyurethane-acrylate (Ag/WPUA) coating by combining a new and easy method, reduction, and polymerization reactions. In this study, antibacterial finishing was carried out with Ag/WPUA coating under UV radiation. The characterizations of the obtained coatings were made by transmission electron microscopy (TEM), Fourier transform infrared spectra (FTIR) and X-ray diffraction (XRD). According to the results of the analysis, 99.99% antibacterial activity was obtained for E. coli and S. aureus. On the other hand, the applied coating preserved the tensile strength and thermal stability properties of the fabrics[32].

Xu et al. prepared a mixture by adding SiO_2 particles and multi-aperture silica aerogel (SA) modified with silane coupling agent to water-based polyurethane acrylate (WPUA) and applied to cotton fabrics to obtain a thermally stable water-repellent protective surface. The results showed that the thermal stability of the coated fabric was improved with SA and SiO_2. It has been determined that the SA concentration increases the hydrophobicity of the surface, and the contact angle reaches 120° when the SA concentration is used as 4%. In this study, the test data obtained as a result of the combination of SA and SiO_2 with WPU in the coating of cotton fabrics were promising for developing physical and chemical protective clothing[33].

4.2. Carbon Materials-Based Water-Borne Polyurethane Composites

4.2.1 Water-borne polyurethane/carbon nanotube composite coatings

Nyugen et al. prepared a multifunctional conductive composite ink by incorporating a mixture of carbon nanotubes (CNTs) and heat-treated $Ti_3C_2T_x$ MXene into the WPU matrix. Composite films with high electrical conductivity and mechanical flexibility were produced with this mixture. This composite was reported as a practical approach in terms of providing superior electromagnetic shielding and thermal performance in ink-printed wearable electronic applications[34].

Dai et al., used a green method to produce 70/30 polyester/cotton fabric with the properties of hydrophobicity and electromagnetic shielding. For this purpose, two-component water-based polyurethane dispersions modified with hydroxyl-terminated polydimethylsiloxane were synthesized and 80% CNT and 20% graphene were included in this polymer matrix. The contact angles of the fabric coated with this polymer matrix containing woven materials were obtained as 103.4° and 153.6, respectively. It has been determined that the coated fabrics produced with a green and simple method exhibiting high electromagnetic shielding (EMI) performance have high potential in EMI applications[35].

In another study, Wu et al., developed a new water-processable thermoelectric coating material made of waterborne polyurethane, multi-walled carbon nanotubes (MWCNT) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) composite. The fabricated composite material was coated on commercial cotton and polyester yarns. Compared to cotton yarn, polyester filament showed better coverage and was found to be more preferable as a coating surface than cotton fabrics[36].

4.2.2 Water-borne polyurethane/graphene and graphene derived nanofiller-incorporated coatings

Graphene material is a planar sheet of sp2-bonded carbon atoms. Recently, it has attracted great attention as the basic building block for advanced materials with various application areas. Graphene, which has superior electronic, thermal, and optical properties, differs from other three-dimensional materials. There are studies of functional textiles in which graphene is used as a filling material. For example; Textile fabrics were coated using graphene or graphene composites, and the properties of these fabrics such as electrical conductivity, thermal stability and antibacterial activity were investigated[37]. Graphene oxide (GO) shows high chemical activity due to the presence of oxygen functional groups such as hydroxyl, epoxy and carboxyl groups in its structure, which are important for the modification of graphene[38]. In recent years, GO has been the subject of intense research, especially in anti-corrosion coatings, with its high strength, large surface area, and barrier properties. The presence of oxygen-containing groups on its surface creates active sites, especially for chemical modification[39].

In one study, Song et al. reported the preparation and application of GO/WPU composite paste. The rheological properties of GO/WPU composite printing paste were analyzed because it affects the definition of printed patterns. The UV protection factor and UV transmittance of the RGO/WPU composite printing paste applied to the fabric containing reduced GO (RGO) in different GO contents were investigated. The printed fabric showed super high UV protection properties such as 757 UPF. In addition, in color analysis, the K/S color yields of the printed fabric increased as the GO content increased. While wet and dry rubbing values decreased with increasing GO content, washing fastnesses showed good characteristics[40].

In another study, Hu et al. reported a composite containing graphene and water-based anionic aliphatic polyurethane, as a multifunctional finishing material, which can be applied to woven cotton fabrics with an easy pad-dry process. Radiation emission and UV protection properties of coated fabrics were investigated. It has been reported that coated fabrics increase far infrared emission compared to untreated fabric, and the UPF factor reaches 500 UPF, which is 60 times higher than pure cotton fabric. It has been determined that the functional properties of the fabrics are stable even after 10 washings[37].

Bramhecha et al. applied graphene-doped WPU to cotton fabrics as a coating material and examined them for near infrared (NIR), UV protection, breathability, and antibacterial activity. According to the analysis, the coated fabrics showed UV protection (UPF>50), NIR resistance up to 90%, and antibacterial activity over 99% against E. Coli and S. Aureus bacteria. With these results, it was stated that graphene doped PU could be a multifunctional coating for protective textiles[20].

Wang et al reported the application of a graphene aerogel composite EMI shielding composite to 100% cotton fabric with WPU. The effect of the amount of aerogel in the composite coating on the fabric's EMI function, mechanics and style of the fabric was investigated. As a result, it was determined that the increase in the amount of aerogel had a positive effect on the EMI protection and mechanical strength properties of the fabric. It is predicted that electromagnetic shielding fabrics designed with graphene aerogel, which reduces the consumption of nano carbon materials and provides good electromagnetic shielding properties, will create a good industrial application prospect[41].

5. CONCLUSION AND FUTURE PERSPECTIVES

In recent years, the use of PUs for coating material on different surfaces such textile, glass, metal, plastic etc., has increased greatly due to their superior mechanical properties. WPU coatings attract attention due to their non-toxicity, chemical resistance, and superior mechanical properties. However, studies on improving the thermal stability, UV resistance and strength properties of WPU coatings by incorporating different types of nanoparticles into the polymer matrix have gained great attention. There are several unaddressed research areas of nanocomposite coatings such as automotive, electronics, aerospace, and textiles. The textile sector is a wide sector where such environmentally friendly functional coatings to produce high potential for the development of products with high added value can find application. In the literature, studies on the application of coatings formed by incorporating different nanoparticles (metal/metal oxides, carbon-based nanoparticles) into the WPU structure on textile materials are limited. It is thought that more detailed studies should be conducted to understand the interaction between WPU and nanofillers and to examine the effects of different preparation methods on the material structure.

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