



Review on the Use of Nanofillers in Polyurethane Coating Systems for Different Coating Applications

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Abstract: Polyurethane (PU) is the most common, versatile and researched material in the world. It is widely used in many applications such as medical, automotive and industrial fields. It can be found in products such as furniture, coatings, adhesives, construction materials, Paints, elastomers, insulators, elastic fibres, foams, integral skins, etc. because it has extraordinary properties and the facility to tailor-made various formulations according to property requirement using different raw materials which are available. Though the material is having fascinating properties the material is also associated with various problems such as inferior coating properties. Inorganic pigments and fillers are dispersed in organic components and binders to improve different properties of the coating. This paper is intended to review the various nanofillers used in different PU coating systems. It gives a general introduction about the various fillers and its classification, Mechanism by which the filler enhances the mechanical properties of the materials, various factors which affect the properties of the coatings. Various methods of incorporation of fillers in the coating systems are discussed. Various nanofillers such as SiO₂(Silicon Dioxide), TiO₂(Titanium Dioxide), Al₂O₃(Aluminium Oxide), antimony doped tin oxide (ATO), BaSO₄(Barium Sulphate), Fe₂O₃(Ferric Oxide) as well as carbon nanotubes, graphene derived fillers and nano-diamonds are discussed in detail. The importance and effect of surface modification of fillers to enhance coating properties are also discussed along with challenges associated with polyurethane coatings and future trends.

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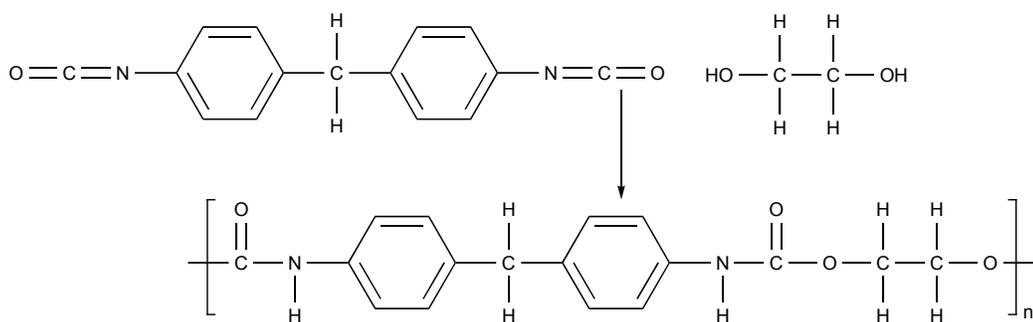
1. INTRODUCTION

One of the most common, versatile and researched materials in the world is polyurethane(PU) [1]. Polyurethane polymer is a reaction product of di/polyisocyanate and di/polyols having a repeating unit –NH-CO-O- made by polyaddition reaction [2]. The reaction is shown in Scheme 1.

PU material was invented by Dr. Otto Bayer and his coworkers in the year 1937 at the I. G. Farben laboratories in Leverkusen, Germany to deal with the competitive challenge arising from the Carother's work on polyamides or nylons at E. I. Dupont. Initial PU product obtained was polyurea which was the reaction product of aliphatic diisocyanate and diamine. The commercial production of PU started after world war 2 when the polyisocyanates became commercially available [3]. PU found widespread applications in medical, automotive and industrial fields. polyurethanes can also be found in products such as furniture, coatings, adhesives, construction materials, Paints, elastomers, insulators, elastic fibres, foams, integral skins, etc. [4].

Because of the versatility of this material, it can be incorporated in different applications. It can be used for corrosion-resistant coatings as well as chemically resistant coatings for wood, masonry, metals etc. The material also finds application as high gloss finishes for aeroplanes [5]. The reason behind the wide use of PU material that it possesses interesting properties because of the presence of Hard and soft segments and these segments are having micro phase-separated structure because of thermodynamic immiscibility [6]. The material can be tailor-made by choosing the appropriate type of isocyanate and polyol components and suitable chain extenders amongst the abundant amount of raw materials that are available for the synthesis of different PU'S [7]. Other than various synthetic raw materials extensive research has been done and going on to produce durable PU's by using renewable sources as a raw material for PU synthesis [8]. Another reason is that it is the most malleable class of material as this class can be moulded, cast and recycled [9]. The key role of various coatings systems is to improve aesthetic appeal of the substrate, it can also help to protect the substrate from a wide range of abuses such as damage due to scratches or impact, corrosion long term weathering and bio-fouling and to provide specialized

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Scheme 1: The reaction of diisocyanate and diol.

functionality to the product e.g., conductivity, insulation, water repellency, and heat reflection [10]. One of the most useful classes of polymers in the coating sector is polyurethane [11].

Though the material is having fascinating properties it also has problems such as yellowing, low adhesion, low thermal resistance, low anticorrosive properties and low mechanical properties [12]. Properties of polyurethane coatings can be improved by routes such as developing a new class of macromolecular architecture, called dendritic hyperbranched polymers (HBPs) and a combination of organic and inorganic components in a coating. Inorganic pigments and fillers are dispersed in organic components and binders to improve optical, mechanical and thermal properties [13]. This paper is intended to review the various nanofillers used in different PU coating systems and its effect on their properties.

2. FILLERS AND ITS CLASSIFICATION

The particulate materials that are added to the polymer matrix to enhance the material properties and/or to reduce the cost are called fillers. Size, dimensions, origin, function, and/or morphology are the criteria's for the classification of fillers. According to size fillers are classified as macro, micro and nano and according to the dimension they are classified as 1D, 2D and 3D [14]. According to the origin, the fillers are classified as synthetic and natural fillers [15]. Initially fillers added to the polymeric material to reduce the cost of the composite, however, they were found to be more useful than just as a cost-reducing material. The fillers which provide properties other than cost reduction are called as functional fillers. Improvement in processing, density, thermal expansion, thermal conductivity, flame retardancy, optical

changes, electrical and magnetic properties and mechanical properties like stiffness can be changed by using functional fillers [16,17]. According to the morphology of fillers, they can be classified as a cube, sphere, block, plate, flake, fibre. The examples of fillers having different shapes and aspect ratio are tabulated in Table 1:

Fillers also can be categories as organic and inorganic fillers these fillers further can be classified according to their chemical family [18]. Various organic and inorganic fillers along with their examples as tabulated in Table 2.

3. MECHANISM OF FILLERS TO ENHANCE PROPERTIES OF POLYMER MATRIX

According to Nunes *et al.* when elastomer needs to have higher tensile strength there should be the energy dissipation near the edges of the growing fracture by viscoelastic processes. When fillers are loaded the dissipation of energy occurs via viscoelastic processes, preventing fractures reaching sizes at which they become unstable which leads to the cracking of a polymer. Therefore when polymers are reinforced with fillers the growing fracture meets the filler particle, energy dissipation occurs and increase in tension becomes essential for further fracture growth. This is the reason when the filler concentration increases the rupture is delayed because of the increase in the number of barriers which prevents the fracture growth [19].

The crystallinity of a polymer has a strong influence on various properties of the polymeric systems [20]. The reinforcing fillers such as talc act as a nucleating and crystallizing agent in amorphous polymers such as polylactic acid and increases its crystallinity [21,22]. According to Liu *et*

Table 1: Morphology, Aspect Ratio and Examples of Fillers

Shape	Aspect ratio	Example
Cube	1	Feldspar, calcite
Sphere	1	Glass spheres
Block	1 – 4	Quartz, calcite, silica, barite
Plate	4 – 30	Kaolin, Talc, hydrous alumina
Flake	50 -200++	Mica, graphite, montmorillonite Nano clays (MMT)
fibre.	20-200++	Wollastonite, glass fibres, Carbon nanotubes, wood fibres, asbestos fibres, Carbon fibres

Table 2: Chemical Class and Examples of Organic and Inorganic Fillers

Category	Chemical Family	Examples
Organic	Carbon, graphite	Carbon fibres, graphite fibres and flakes, carbon nanotubes, carbon black
	Natural polymers	Cellulose fibres, wood flour and fibres, flax, cotton, sisal, starch
	Synthetic polymers	Polyamide, polyester, aramid, polyvinyl alcohol fibres
Inorganic	Oxides	Glass (fibres, spheres, hollow spheres, flakes), MgO(Magnesium Oxide), SiO ₂ , Sb ₂ O ₃ (Antimony Oxide), Al ₂ O ₃
	Hydroxides	Al(OH) ₃ (Aluminium Hydroxide), Mg(OH) ₂ (Magnesium Hydroxide)
	Salts	CaCO ₃ (Calcium Carbonate), BaSO ₄ , CaSO ₄ (Calcium Sulphate), phosphates
	Silicates	Talc, mica, kaolin, wollastonite, montmorillonite, Nano clays, feldspar, asbestos
	Metals	Boron, steel

a.l. one of the reasons for the increase in mechanical properties of the polymer composites is that the inorganic fillers enhance the crystallinity of the polymers and since the crystallinity leads to high tensile strength [23]. After the application of external force in the coating containing inorganic fillers, the fracture of the coating occurs because of the reduced energy dissipation [24].

4. FACTORS AFFECTING PROPERTIES OF COATINGS

Various factors affecting the properties of composites coatings are discussed. Coating properties are affected by the size, shape, filler content, filler distribution, aspect ratios and surface characteristics of the fillers [25]. Each factor is discussed in detail in the following section.

4.1. Filler Size

One of the important factors which affect the properties of the composite coating is filler size, as the size of filler reduces the contact surface increases it results in the increased aggregation of the fillers in the system [26]. The viscosity of an uncured polyurethane mixture depends on the particle size of the filler when carbon black, silica, aluminium oxide and zirconium(III)oxide was used as a filler the viscosity of the polymer mixture increases with decrease in the particle size [27].

4.2. Filler Content

Effect of filler content on various properties of PU composite coatings is studied by various authors. When the clay filler content of the coating increases the molecules of polymer merges inside the clay hindering its molecular mobility and makes it more fragile [28]. The increase in clay filler content in the composite affects the impact properties adversely causing the coating film brittle and favours the cracks in the film [29,30]. Youssef *et al.* has investigated the effect on structural and mechanical properties of polyurethane resins based on Cu(II)phthalocyanines, the composite coatings were prepared by varying the amount of Cu(II)phthalocyanines and it is observed that the quantity of

filler affects the filler distribution which ultimately affects the properties of the coating [31].

Series of diglycidyl ether of bisphenol A epoxy modified with organically treated bentonite clay nanoparticles (b-NCP's) were studied for abrasion resistance properties. The concentration of b-NCP's was varied from 0.12% to 5% and its effect on abrasion properties of the epoxy coating system was studied. The smoothness of film signifies that the clay particles are completely and uniformly dispersed into the matrix which was proven by the SEM (scanning electron microscopy) images. The increasing amount of b-NCP's resulted in a decrease in the Tg. The optimum concentration of the nano clay in the matrix found to be 0.75% and it showed the best abrasion resistance. The optimum concentration of the nano clay into the matrix also depends on the curing time and it increases with the increasing curing time. The phenomenon for the higher abrasion resistance is attributed to increased rigidity, compactness and lower molecular mobility [32]. The viscosity of the uncured polyurethane mixture also depends on the filler content in the mixture, the viscosity increases with increasing filler content [27].

4.3. Filler Distribution

Composite properties are affected by filler distribution within the polymer matrix which is explained as follows by various authors. The epoxy/polyester powder coatings containing nanofillers such as muscovite mica and montmorillonite (MMT) affects the thermal properties of a hybrid powder coating because of the improper distribution of fillers [33]. SiO₂ particles generally have a tendency to agglomerate which hinders the homogeneous dispersion of these fillers in the polymer which ultimately results in the inferior mechanical properties [34]. Improper distribution or agglomeration of filler causes diffuse reflection of incident light affecting the glossiness of the coating. Permeability of a coating is one of the important factors which is affected by the distribution of fillers into the polymer the predominantly exfoliated nanocomposite structure shows less liquid and gas permeability. The rheological properties are also affected by the dispersion of fillers. In the case of polyol/organoclay nanodispersion results in an increase in the viscosity [35].

4.4. Aspect Ratio

Composite properties can also be affected by the aspect ratio of clay nanoparticles high aspect ratio restricts the molecular mobility of the polymer because of the increased intercalation into the galleries of the clay fillers and increases its stiffness [28].

4.5. Fibre Orientation

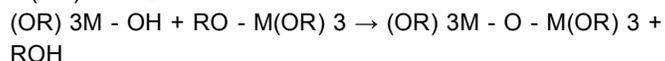
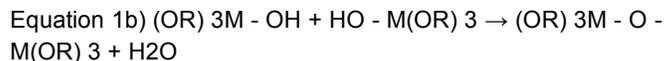
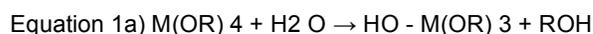
In the case of fibre-reinforced composites, the properties are affected by the orientation of fibres. In the case of sisal fibre reinforced rubber seed oil-based polyurethane composite the better thermal and mechanical properties were obtained in the case of the unidirectional orientation of fibres [36].

5. PREPARATIVE METHODS

Various preparative methods used for the synthesis of PU nanocomposites include sol-gel, In-situ polymerization, solution dispersion method, spray coating, dip coating methods. Some of the important preparative methods for nanocomposites are described as follows.

5.1. Sol-Gel Process

Hydrolysis and condensation are the two main reactions which take place in the sol-gel process. Equation a and b shows hydrolysis and condensation reactions respectively.



Both the reactions involve multiple steps and each reaction occurs sequentially. In the hydrolysis process, organic chain bonds to the metal are cleaved and subsequently, the OH (Hydroxyl) group is added through a nucleophile addition. In a condensation reaction, oxygen-metal-oxygen bond formation occurs and small molecules such as water or alcohol are eliminated. The main reaction parameters include metal reactivity, amount of water, solvent, temperature and the use of complexing agent or catalyst. The determining factor for the use of catalyst is the nature of the metal atom and the steric hindrance of the alkoxide group. Another important reaction parameter includes the electrophilic character of the metal atom and its ability to increase the coordination number. This method is advantageous for the formation of the nanoparticles because of the compatibility of the sol-gel method with polymers and polymerization process. The details of the sol-gel process are depicted in Figure 1 [37].

5.2. In-Situ Polymerization

In-situ polymerization was widely used for the preparation of nanocomposite coatings from organic matrices specifically which were conducting polymers. The nanofillers used in this

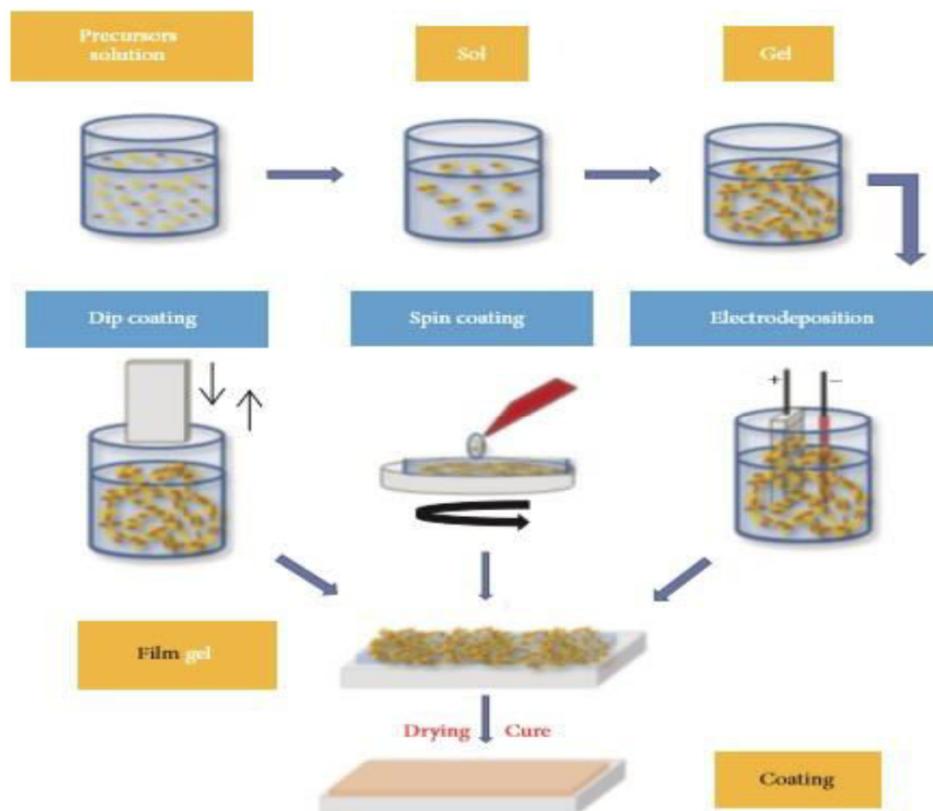


Figure 1: Methods of application of nanocomposite coatings [38].

technic are metal or metal oxides. Electric power, oxidizing agents or photon are used to carry out polymerization. Emulsion polymerization or latex emulsions are similar methods for the synthesis of nanocomposites from organic matrices [38].

5.3. Solution Dispersion Method

In this method instead of using traditional magnetic/mechanical stirring, ultrasound-assisted (sonication) stirring is used to enhance the dispersion of nanofillers and polymers. The method is specifically used for nanocomposite fabrication from polymers as the matrix and the reinforcing materials are metal oxides, nano clay and carbon nanotubes etc. [38].

5.4. Spray Coating and Spin Coating Methods

The method is widely used for polymer nanocomposite coatings. When the coating is done using the atomizer the coating shows better properties. The atomizer could also be used for thermal spray method, for example, atomized spray plasma deposition. The spin coating method gives uniform thin films to flat substrates. In this method, the coating is spread on the substrate by using centrifugal force by applying the high-speed rotation [38].

Table 3 shows the details of different PU nanocomposites and its preparative methods which are reported in the literature.

Table 3: List of Reported PU Nanocomposites by Using Different Preparation Methods, Monomers and Nanofillers Use for its Synthesis

Preparation Methods	Matrix / Monomers use for polyurethane synthesis	Nanofillers used	Reference
Sol-gel process	Castor oil-based PU	Nano-silica	[39]
	Polyester Polyol based PU	Nano-silica	[40]
	Poly(caprolactone glycol), 3-dimethylamino-1,2-propanediol, isophorone diisocyanate (IPDI)	Tetraethoxysilane (TEOS)	[41]
	Poly(tetra methylene glycol) (PTMG), Dimethylol propionic acid (DMPA), Isophorone diisocyanate (IPDI)	Nano-size hydrophilic silica and nano-size hydrophobic silica	[42]
	Ester type TPU (Thermoplastic Polyurethane)	Tetraethoxysilane (TEOS)	[43]
	Poly-carbonate diol (Desmophen® C3200) and polyisocyanate (DesmodurN75)	Tetraethylorthosilicate (TEOS)	[44]
	Isophorone diisocyanate (IPDI), polyoxypropylene glycol (PPG)	Graphite powder	[45]
Sol-gel process	Novolac epoxy resin (EP), acrylic acid (AA), styrene (ST), butyl acrylate (BA), 2-hydroxyethyl methacrylate (HEMA), 1,6-hexamethylene diisocyanate homopolymer (HDI, Desmodur N3390)	3-methacryloxypropyltrimethoxysilane modified nano-SiO ₂ (MPS-SiO ₂)	[46]
	3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate (IPDI), Neopentylglycol (NPG), Polycaprolactone (PCL)	polysilicic acid nanoparticles (PSA)	[47]
In Situ method	polycaprolactone diol, poly(tetra methylene glycol), Isophorone diisocyanate (IPDI)	Natural graphite (HC-908)	[48]
	Phthalic anhydride Adipic acid, 1,4-butanediol, Neopentyl glycol and 4-methyl-2-pentanone, Isophorone diisocyanate (IPDI) trimer (Desmodur N-3300)	Nano silica (N-20)	[49]
	poly (caprolactone) diol, diisocyanatohexane (HDI)	TiO ₂	[50]
	Isophorone diisocyanate (IPDI), polycarbonate diol	dihydroxy polydimethylsiloxane(DHPDMS)	[51]
	butyl acrylate, styrene, methyl methacrylate 2-hydroxyethyl methacrylate, 1,6-hexamethylene diisocyanate homopolymer(HDI, Desmodur N 3300)	Nano-SiO ₂	[52]
	Phthalic anhydride, adipic acid, 1,4-butanediol, neopentyl glycol, and 4-methyl-2-pentanone, isophorone diisocyanate (IPDI) trimer	TEOS	[53]
In Situ method	Polycaprolactone (PCL), Dimethylol propionic acid (DMPA) and 4,4'-Diisocyanato-methylenecyclohexane (HMDI)	purified Na ⁺ -MMT clay	[54]
	Methylenediphenylenediisocyanate (MDI), castor oil polyol	organically modified montmorillonite (OMMT) clay	[55]
	Castor Oil, Methylene diisocyanate (MDI)	Nano zinc and organically modified montmorillonite clay (OMMT Clasite20A)	[56]
Emulsion Process	One-component liquid formula comprising 25% diphenylmethane-diisocyanate and 75% polyurethane pre-polymer (hexanedioic acid, polymer with 1,6-hexanediol and 1,1-methylene bis 4-isocyanatobenzene) which is moisture curable	fatty amine/amino-silane surface-modified montmorillonite clay (organoclay)	[57]
Spray Coating	Suspensions of polyurethane (PU)	Molybdenum disulfide(MoS ₂)	[58]
Spin Coating	Polytetramethylene ether glycol, 2, 4-diisocyanate-1- methyl-benzene (TDI)	Silica nanoparticle	[59]

6. NANOFILLERS USED IN PU COATING SYSTEMS

Nanofillers are widely used for the formation of PU Nano-composite coatings for the context of Nano-structuring [60,61]. Nano additives and functional nano-materials used in PU coating cause structural modification in a polyurethane coating. Because of the improved surface properties of polyurethane nanocomposites the resistivity of coatings towards corrosive chemicals, moisture, heat, and environmental repellency increases. Thus investigation in the field of nano/polyurethane composites plays an important role in the development of a high-performance coating with desirable properties [62].

6.1. Polyurethane Coatings Containing Nano Inorganic Fillers

Use of inorganic fillers in a composite system is advantageous over the composites containing irregular shaped fillers because of its performance and reliability and for their effective environmental measures. Various spherical fillers that can be used include SiO_2 , TiO_2 , Al_2O_3 , ZnO , Antimony doped Tin Oxide, BaSO_4 and Fe_2O_3 [63]. PU nanocomposites loaded with various nanofillers and its effect on the various properties of the system is described in detail in the following section.

6.1.1. SiO_2 - Loaded Polyurethane Nanocomposites

The first produced inorganic particle and most commonly used is nano-silica, it is extensively studied in various polymer systems. The successful grafting of nano-silica with (2-hydroxy ethyl methacrylate) and poly(HEMA) is reported [64,65]. These nano-particles are successfully incorporated into poly(methyl methacrylate) [66]. Acrylic-based PU coating system containing nano-silica fillers shows improvement in mechanical properties such as hardness, abrasion resistance, scratch resistance and tensile but the elongation at break was decreased when compared with micro silica [52]. The moisture absorption properties of PU clear coats depends on the type and loading of nano- SiO_2 particle into the coating, the water uptake of hydrophilic nano-silica is rapid initially followed by the further slow increase in water uptake. On the other hand, when the hydrophobic silica is used the water uptake remained constant for a longer period of immersion [67]. PU/ SiO_2 coatings can be used for coating polyethylene (PE) films to improve UV weathering without affecting its transparency. It also reduces the photodegradation rate and there is no influence on the thermal degradation rate of PE film [68,69]. PU/ SiO_2 coatings also found to improve the coefficient of friction and wear rate of Polypropylene (PP) substrate, it is found that surface roughness has a considerable impact on wear properties. Higher roughness increases the asperities slope angle which in turn increases the friction coefficient [70,71]. The permanent antigraffiti coating can be prepared by loading nano SiO_2 particles without adversely affecting its transparency of PU clear coatings which indicates its good

dispersion degree [72]. Silica is modified to Si-CH_3 group it can be promisingly used in anti-abrasion coatings for flexible substrates such as fabrics, leather and paper [73]. Biomimetic Superhydrophobic PU composite coatings can be prepared by incorporation of SiO_2 nanoparticles [74].

6.1.2. TiO_2 Loaded Polyurethane Nanocomposite Coatings

Because of the stability, availability and applicability for applications such as painting, catalysis and photocatalysis, batteries, cosmetics etc. titanium oxide (TiO_2) has gained attention among different metal oxide nanoparticles. Rutile TiO_2 nanoparticles are opacifying and UV-stabilizing filler. Whereas anatase TiO_2 gives a photocatalytic effect. The appropriate percentage of each crystal structure when incorporated into the PU matrix, the composite can be used for outdoor applications, improving the service life of the products as well as impart self-cleaning properties to protect from outdoor contaminations [75]. PU/ TiO_2 nanohybrid membrane can be used to control water vapour permeation [76]. TiO_2 nanoparticles modified with amino silane are reported to control the photocatalytic activity of nanoparticle and improves the weathering performance of PU nanocomposite coatings [77]. Silver doped TiO_2 /PU composite shows excellent antimicrobial activity and can be used for coating textiles to give antimicrobial effect [78].

6.1.3. Al_2O_3 -Loaded Polyurethane Nanocomposites

Alumina is the most common inorganic filler which is mostly used for the preparation of ultrafiltration membranes. These are the inexpensive, accessible, non-toxic and highly resistant materials which make it commercially important. The filler is having spherical shape thus it enhances the packing density and it offers high thermal conductivity [79-81]. The incorporation of Al_2O_3 into 2K PU coatings enhances the scratch behaviour of the coating [82]. The scratch resistance of the coatings depends strongly on the concentration and surface treatment of nano- Al_2O_3 [83]. TDI- Al_2O_3 when dispersed in a coating it exhibits lower friction coefficient and higher wear life [84]. Incorporation of Al_2O_3 into WPU coatings for mild steel is reported for improvement in electrochemical performance [85].

6.1.4. ZnO -Loaded Polyurethane Nanocomposites

Large surface area to volume ratio, high ultraviolet absorption and long lifespan concerning its slow photodegradation are some of the important features of ZnO [86,87]. ZnO has a long history of colour protection [88]. ZnO particles treated with cyclic carbonate functional alkoxysilane are reported to improve scratch hardness and abrasion resistance along with the improvement in other performance properties when incorporated into PU/ ZnO nanocomposite coating [89].

6.1.5. Antimony-Doped Tin Oxide (ATO)-Loaded Polyurethane Nanocomposite

Antimony doped tin oxide (ATO) is an optically transparent, infrared light insulating and electrically conductive oxide, it

finds application in heat-insulating films, flat panel displays, solar cells and electromagnetic interference shielding [90-92]. Silane-treated nano-ATO is reported to be used as a mechanical property enhancer of UV-cured polyester acrylate films [93].

6.1.6. BaSO₄- Loaded Polyurethane Nanocomposites

Barium Sulfate (BaSO₄) is a chemically inert salt, biostable, insoluble, and possesses high thermal stability and are capable of retaining the transparency of the system. Biocompatibility and radio-opaque properties are the important features provided by composite systems consisting of a PU and Barium sulfate [94,95].

6.1.7. Fe₂O₃ Loaded Polyurethane Nanocomposites

3-amino propyltrimethoxysilane modified nano-Fe₂O₃ are reported, use of these nanoparticles in PU coating are reported to have significant improvement in mechanical properties [96,97].

6.2. Polyurethane/Nanocarbon Nanocomposite Coating

Apart from various inorganic fillers, PU nanocomposites are also made by using nanocarbon in various forms as a filler. Various PU nanocomposites loaded with nanocarbon in various forms and its effect on various properties are described in detail in the following section.

6.2.1. Polyurethane/Carbon Nanotube Nanocomposite Coating

The application of carbon nanoparticles in the organic coating is increasing day by day. The compatibility and chemical functionalization of carbon nanotube nanofiller organic resins is an important factor which is to be considered in this case [98]. Carbon nanotubes are also a widely used nanofiller in polyurethane composites it specifically affects thermal, mechanical and damping properties of the polyurethane composite systems [99]. When polymethyl methacrylate functionalized multi-walled carbon nanotubes are used for enhancement of modulus, strength and toughness of polymethyl methacrylate the rise in these properties occurs only up to certain filler content and on further increasing filler content it results in the deterioration of the properties [100]. Apart from carbon nanotubes carbon fibres can also be used as filler for polyurethane to form a composite having excellent mechanical and electrical properties [101]. Short carbon fibres and micro hollow beads improve the mechanical properties of the polyurethane(PU)/Epoxy resin (EP) graft interpenetrating polymer network composites [102].

6.2.2. Polyurethane/Graphene and Graphene Derived Nanofiller-Based Coating

Because of the inherent good anti-corrosive characteristics, high mechanical properties, high transparency, chemical and thermal stability graphene is widely used in coating formulations [103]. The functionalized graphene oxide can be incorporated into polyurethane acrylate to enhance thermal

stability and mechanical properties, the coating has UV curable properties [104]. Hexadecyl-functionalized graphene nanoribbon (HD-GNR) is used to improve gas barrier efficiency thermoplastic polyurethane (TPU) nano-composite coatings. The reason for improved gas barrier properties is the low defect structure of (HD-GNR) and uniform nanofiller dispersion in the system [105]. Along with PU matrix, these fillers are advantageous for epoxy systems graphene nanosheets have been used in epoxy coatings to develop a coating resistant to mechanical, thermal and corrosion environment. The graphene nanosheets which were used was reduced with polyvinylpyrrolidone and it is incorporated into the epoxy resin in the varying quantity. The results showed that as the number of graphene nanosheets increased it resulted in the reduced plasticity index of epoxy, this parameter has a significant effect of creep properties enhancement of this coating [106].

6.2.3. Polyurethane/Nano-Diamond Nanocomposite Coating

Polyurethane/nano-diamond nano-composite coatings with superior performance have also been prepared [107]. Tribological characteristics such as load-bearing ability, tear resistance, antifriction, and strength can be improved with nano-diamond reinforcement in polyurethane. Incorporation of modified nano-diamond led to significant improvement in the antifriction and wear resistance owing to the boundary friction of nano-diamond nano-composite coating on steel [108].

6.3. Surface Modified Fillers Used in Coating Systems

The surface modification of fillers is required to improve the interaction between the fillers and polymer matrix. The interaction ability of the clay with the polymer depends on the length of the modifier surface [109]. By using the technic of surface modification of fillers formulator can formulate the formulation according to the property requirement [110]. Many inorganic fillers do have compatibility with the organic polymer matrix, thus the inorganic fillers such as TiO₂ are modified with aminopropyl trimethoxysilane (APS) and are used in polyurethane composite to improve nanoparticles dispersion, mechanical properties and UV protection of urethane clear coatings [111]. The natural clay fillers such as MMT clays tend to agglomerate in polymer matrix because it has a hydrophilic character which makes it difficult to disperse. The difficulty of dispersion in such cases is the effect of the higher surface energy of such clays as compared to the polymer matrix [112-114]. Ion exchange of the inorganic cations present in the structure by cationic surfactants, such as quaternary ammonium salt is the most commonly used for the modification of MMT Clay surface to improve compatibility and dispersion of clay in the polymer matrix [115,116]. Organophilic character and interlamellar spaces can be produced in the clay with the help of surface modification, because of the presence of ammonium salt in the interaction of the interlamellar space between the layers

Table 4: Applications of Different Polyurethane Nanocomposite Coating Systems

Application Area	Coating systems used	Effect of nanoparticles on Coating properties
Corrosion protection	functionalized graphene oxide (FGO) nanofillers are incorporated in polyurethane [120]	Addition of nanofillers in PU coatings significantly increase the number of microscopically dispersed areas and improves the barrier protection properties if the coating [121].
Corrosion protection	Acidic pyrophosphate ($Rb_2Co(H_2P_2O_7)_2 \cdot 2H_2O$) (DP) incorporated in waterborne polyurethane (WBPU) coatings [122].	When DP nano-particles are incorporated into WBPU coating it creates a tortuous path for O_2 gas molecules. This causes an increase in the total path of the gas. Which results in corrosion protection of the steel [123].
	Na ⁺ -MMT (montmorillonite) clay platelets loaded into Waterborne Polyurethane matrix [54].	Effective dispersion of Na ⁺ -MMT clay increases tortuosity of the water diffusion pathway making material corrosion-resistant [54].
	Organically modified montmorillonite (OMMT) clay loaded into the castor oil-based polyurethane [55].	Increases the length of diffusion pathways for oxygen and water [55].
	Multi-walled carbon nanotubes (MWCNTs) loaded into conductive polyurethane nanocomposite coatings [124].	The loading of (MWCNTs) provides a physical barrier to the attack of corrosive ions in a solution on stainless steel and provide a channel for conductivity [124].
	Graphene oxide (GO) modified with polyisocyanate (PI) loaded into the polyurethane matrix [121].	The improved resistance to corrosion in this system is because of the barrier performance and ionic resistance [121].
Corrosion protection	OMMT clay with quaternary ammonium salts i.e. dilauryldimethylammonium bromide (LD) and 4,4-diaminodiphenylmethane (AP), are loaded into the Polypropylene glycol (PPG), Toluene diisocyanate(TDI) and 1, 4 butanediol based polyurethane [125].	Enhancement of corrosion resistance is because of the increased tortuosity of the diffusion pathways for oxygen [125].
	Nano zinc and organically modified montmorillonite nano clay loaded into the polyurethane matrix [56].	The better corrosion properties in this system are attributed to the presence of nano clay i.e. nano montmorillonite clays since it has less water permeability and it also helps to fill voids, crevices and pinholes in the system thereby enhancing the adhesion to the substrate which ultimately results in better corrosion resistance properties [56].
	12-Aminolauric acid-modified montmorillonite clay (ALAMMT) loaded into the polyurethane matrix [126].	Because of the presence of the silicate nanolayers tortuosity of the pathways for the diffusion of oxygen molecule increases which ultimately results in enhanced corrosion protection [126].
	Functionalized graphene (FG) loaded into the polyurethane (PU) matrix [127].	The anticorrosive properties of the coating systems are attributed to the hydrophobicity and barrier effects of the system which reduces the contact between water and the surface [127].
Textile Application	Polyurethane/graphene coatings [128]	Electrical conductivity, antibacterial activity, thermal conductivity, and features of far-infrared radiation can be attained [129].
	Polyurethane/clay and Polyurethane/POSS [130]	Fire retardant coating for polyester or cotton fabrics [130].
	Cloisite 30B loaded into the polyurethane matrix [62].	Improves thermal behaviour and reaction to fire [62].
	Polyhedral oligomeric silsesquioxanes (POSS) loaded into the polyurethane matrix [130].	Shows fire retardancy on polyester and cotton fabric [130].
	Nanosilver doped titania ($nAg-TiO_2$) loaded into polyurethane coated on polyester fabric [131].	The presence of nanosilver inhibits the growth of bacteria by oligodynamic ability under black light illumination [131].
	Multi-walled carbon nanotubes (MWNTs) dispersed into the hydrophilic polyurethane (HPU) [132].	When the nanocomposite coating is coated on cotton fabrics it fills the gaps and enhances the UV resistance along with excellent vapour permeation for the comfort of the wearer [132].
Biomedical Relevance	Graphene Oxide (GO) loaded electrospun polyurethane coatings used for stent coatings [133].	Because of the increased hydrophilicity, the biocompatibility of the material enhances. The coating also shows better mechanical properties [133].
	Mg-particles/PU thin layer coatings [134]	Alkaline treated Titania to develop bioactivity of orthopaedic devices [134].
	Waterborne polyurethane loaded with nanosilver used for catheter coating [135].	Shows good antibacterial properties and biocompatible. It also has good thermal and chemical properties [135].
Antimicrobial Activity	Fe_3O_4 -Ag hybrid nanoparticles/acrylic polyurethane coatings [136]	The high bactericidal activity of Fe_3O_4 -Ag nanoparticles is because (i) Ag nanoparticles have high catalytic activity. And Fe_3O_4 has good dispersion and aggregation stability. (ii) The physical surface area between the bacterial cell membrane and the hybrid nanoparticles is large [137, 138].
	Copper acetate (CuAc) loaded in linseed oil-based polyol polyurethane [139].	Because of the presence of positive charge on polyurethane chain and negative charge present on bacterial cell there is electrostatic attraction between the polymer and bacterial cell, the flexible and long chains of polymer engulfs the cell within the polymer which makes bacterial cells to gain essential nutrients and the food-deprived bacterial cells become weak apart from this the lethal action of copper oxide kills the bacterial cells [139].
	Nanosilver (nAg) loaded in 2K waterborne polyurethane nanocomposite [140].	Restricts the bacterial cell growth [140].
	Flower-like zinc oxide (ZnO) nanowhiskers loaded into waterborne polyurethane [141].	In absence of light hydrogen peroxide (H_2O_2) is generated on the surface of ZnO, This H_2O_2 damages bacterial cell membrane or causes Some kind of injury which inhibits the cell growth or even sometimes kills the bacterial cell [141].
	ZnO nanoparticles dispersed in polyurethane varnish [142].	ZnO effectively inhibits the growth of the Staphylococcus aureus colonies [142].

(Table 4). Continued.

Application Area	Coating systems used	Effect of nanoparticles on Coating properties
Wood Coating	Nano silica loaded into UV- waterborne polyurethane acrylate nanocomposite coatings [143].	Provide good scratch resistance and adhesion on the wooden surface [143].
	Tempo oxidized cellulose nanofibers loaded in waterborne polyurethane [144].	Improved hardness and shows good mechanical properties [144].
Defence application	Carbon nanoparticles loaded into 2K polyurethane resin based on polyester polyol and hexamethylene diisocyanate [145].	This coated fabric can provide EMI(Electromagnetic interference) shielding of 18 dB in 8–18 GHz frequency. Protection from the hazardous nature of microwave and can be used as material for defence application is possible [145].
	Iron-nickel nano graphite (FeNiNG) loaded in thermoplastic polyurethane coating for fabrics [146].	Suitable for coatings used in aerial surveillance because of the ability to absorb microwaves [146].
Aerospace applications	Functionalized MWNTs doped in thermoplastic polyurethane nanocomposite [147].	Shows excellent mechanical and electrical properties suitable for aerospace applications [147].

of clay reduce and facilitates the intercalation or exfoliation in the polymer matrix [117]. Silica is modified with renewable castor oil to form alkoxysilane castor oil and it is used for the synthesis of NCO terminated prepolymer, the prepolymer was then allowed to get cured with the moisture to form polyurethane/urea-silica modified hybrid coating films and its effect on mechanical and viscoelastic properties were studied. It is found that the coating which was having alkoxysilane castor oil had better properties as compared to unmodified castor oil-based coatings [118]. NIR (Near-infrared reflectance) reflective and HRI(High refractive index) anticorrosive multifunctional nanocomposites are reported, in this investigation, titania nanoparticles are modified with sulfur-rich hyperbranched polyols, these modified titania nanoparticles are further used to produce TiO_2 /poly(thiourethane-urethane)-urea nanocomposites. The NIR reflectivity of the composite matrix is found to be increased because of the use of titania nanoparticles since these nanoparticles are having a high refractive index and provides numerous scattering centres. The reason for the enhancement of corrosion resistance is explained as the effect of the very dense and homogeneous matrix because of the cross-linked structures mediated by modified nanoparticles. The adhesion between metal-coating interface enhances because of the presence of polar thio-ether linkages, resistant to oxidation and water absorption of these thio-ether linkages is excellent which results in excellent anticorrosive properties [119]. The chemical modification of graphene and graphene oxides effectively enhance the tribological and anticorrosion properties of PU composite coatings by improving its dispersion and compatibility [120].

7. APPLICATIONS OF PU NANOCOMPOSITE COATING

Polyurethane nanocomposites have potential application in various fields like corrosion protection, textile applications, biomedical application, antimicrobial application, wood coating, defence as well as aerospace applications. Various coating systems and the reason for the enhancement of properties of coatings are tabulated in Table 4.

CHALLENGES ASSOCIATED WITH POLYURETHANE COATINGS AND FUTURE TRENDS

The most commonly used coating material for aerospace and transportation industry is polyurethane but the problem associated with the pristine PU coating systems is that it does not possess good weathering properties, so to enhance the weathering properties of PU coating systems nanofillers can be used [148]. Design and development of new weathering resistant nanocomposite coating have great scope for the research. Final properties of the coating depend on the procedure which is selected for the coating thus proper coating procedure selection such as solution method, solvent-free method, spraying, and sophisticated techniques such as spin coating and inkjet printing may improve the final coating characteristics [149]. Polyurethane/carbon nanotube, polyurethane/graphene, and polyurethane/nanodiamond coating technology may become increasingly successful materials in the industrial coating market owing to high performance in the aggressive conditions but the problem associated with these materials is that they are having a very high cost. Nowadays, waterborne polyurethane coatings have gained considerable interest due to non-toxicity, eco-friendly nature, versatility, UV resistance, chemical resistance, and excellent mechanical properties. However, solvent resistance, thermal stability, and tensile strength of waterborne polyurethane coatings need to be enhanced using various type of nanoparticle. Several unaddressed areas of research for polyurethane nanocomposite coatings have been identified such as employment in aerospace, automobiles, energy devices, electronics, sports industries, etc. [150].

CONCLUSION

One of the most common, versatile and researched materials in the world is polyurethane (PU). This material is useful in many applications including coating because of its extraordinary properties and the facility to tailor-made various formulations according to property requirement using a wide variety of available raw materials. Though the material is having fascinating properties it also has problems such as

yellowing, low adhesion, low thermal resistance, low anticorrosive properties and low mechanical properties. Properties of polyurethane coatings can be improved by the addition of nanofillers into the system. There are various factors such as fillers morphology, size and filler loading etc. which affect the final properties of coatings. Various classes of inorganic nanofillers such as SiO₂, TiO₂, Al₂O₃, ZnO, BaSO₄, Fe₂O₃ etc. have been used to improve the mechanical and optical properties of the PU coatings. Apart from these various nanofillers such as carbon nanotubes and fibres, graphene and nanodiamond are also reported to be effective for improvement of the properties in various fields such as defence, medical textiles etc. but with use of these nanofillers the problem is associated with its high cost, therefore, it cannot be used for general purpose applications or where the cost is a concern.

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