

General Introduction

Highlights

This chapter delineates the fundamentals of waterborne polyurethane (WPU), encompassing suitable raw materials, preparation methods, standard scientific characterization techniques and tests involved, and evaluation of various inherent properties. Concerning environmental sustainability and performance of the material, special emphasis is given to the utilization of renewable feedstock as an alternative to petroleum-based starting materials, mechanical robustness, and smart attributes such as self-healing, shape memory, etc. A comprehensive explanation is also reported on various carbon-based nanomaterials, fabrication techniques, their impression on inborn properties of WPU, development of new smart advanced features, characterizations, and its potential applications from ground level to advanced level. Lastly, this chapter also reveals the scopes, objectives, and plan of the research for the present investigation.

1.1. Introduction

Smart-featured and nifty polymeric materials are indispensable for adorning a high-tech society [1]. People are searching for such futuristic and revolutionary polymers, inquisitively, which is a ceaseless practice and will continue till the sun goes down and rises. Nowadays, polymers are being considered as the primary choice over metal-based materials because of their lightweight, low cost for production and maintenance, tailorable properties, and myriad applications [2]. Polymers are extensively used in numerous commodities and have a wide assortment of industrial applications from common day-to-day appliances including coatings, foams, adhesives, textiles, etc. to advanced utility in wearable and flexible electronic devices, soft robotics, aircraft, spacecraft, biomimetic material, and so forth [3-4]. This widespread applicability of polymers can be accredited to the distinctive innate smart features which can be further amplified, or additional new features can be integrated via post modifications e.g., nanocomposite fabrication [5]. Interestingly, these smart attributes can be executed by mimicking some of the eye-catching natural phenomena that exist in living organisms. For example, spontaneous recovery of damaged or injured parts of the body (self-healing, SH), deformed shaped-animal hairs can revert to their initial shape stimulated by water (shape memory, SM), and the auto-cleaning nature of taro (*Colocasia esculneta*) (self-cleaning, SC) [6-8]. Notably, the development of these smart properties along with superior mechanical strength in a single elastomer is still a formidable challenge. This dilemma is because of some mutual contradictions that existed among themselves. A part of the scientific community has sketched and implemented enormous tactics to optimize these enigmatic properties. The most common and fruitful strategies such as 'introduction of dynamic hard domains', 'multiple hierarchical hydrogen bond', 'strain induced crystallization', and 'co-ordination complex formation' are applied in numerous polymers including polyurethane (PU), the secret superstar with ultimate versatility [9-12].

The versatile nature of the PU can be ascribed to the tunable micro-phase separated chemical structure i.e., hard phase or domain and soft phase or domain. Various types of PU viz. thermoplastic PU, flexible elastomeric PU, rigid/flexible PU foam, PU ionomers, and waterborne PU (WPU), can be prepared via judicious molecular engineering, precisely [13]. A recent statistic on plastic production reveals that PU has achieved the sixth position among the most popular and widely used polymers [14]. Nevertheless, most PU-based products are manufactured using petroleum-based raw materials and the production process involves excessive usage of volatile organic compounds (VOCs). These two primary factors stand against the environment sustainable development policy and insist that materials scientists positively develop eco-friendlier PU like WPU as compared to solvent-borne PU [15]. In the

past two decades, incredible efforts have been dedicated to discovering the usability of renewable feedstock [16-17]. State of art literature advocates that the prime paradigms of such raw materials include several vegetable oils (e.g., castor oil, palm oil, linseed oil, soya bean oil, coconut oil, sunflower oil, etc.), carbohydrates (e.g., sucrose, starch, chitin, isosorbide, etc.), and polyphenolic compounds (e.g., lignin, tannin, etc.), which can be used with or without further chemical modification [18-23]. Apart from environmental benignness, the use of these renewable resources is highly beneficial because of low cost, easy and abundant availability, reduced toxicity, biodegradability, and biocompatibility [18]. Again, most importantly, the replacement of organic solvent with a green solvent e.g., ionic liquid, supercritical CO₂, water, etc. would be more favorable for preparing PU dispersion. In this scenario, WPU would be one of the best candidates with the same versatility and performance as the solvent-borne PU. Henceforth, biobased WPU with smart attributes is just 'the icing on the cake' [24]. WPU is structurally similar to the conventional PU, but the polymeric backbone comprises a suitable emulsifier in addition to macroglycol, diisocyanate, and chain extender. The emulsifier assists in creating ionic groups on the WPU particle surfaces and stabilizes them in water [25].

Despite having marvelous congenital properties, the biobased smart WPU needs further modification to assure more durability and to introduce new fascinating features that are required for superior applications. Noticeably, pristine WPU cannot gratify all the demands of modern society. Many routes can be followed for the amendment with distinct levels of outputs from low to high. These are grafting or copolymerization (e.g., WPU/polyacrylic), interpenetrating polymer network formation (IPN), and most prevalently, fabrication of WPU nanocomposites (WPUNCs) with the appropriate nanomaterial (s) or nanohybrid (s) [26-28]. Initially, inorganic reinforcing agents, especially, metal nanoparticles, oxide nanoparticles of silicone (SiO₂), iron (Fe₃O₄), titanium (TiO₂), zinc (ZnO); nanowires of silver (AgNW); boron nitride, nano clay, etc. are extensively used to prepare the targeted nanocomposites [29-33]. Successively, carbon-based nanomaterials overtook them and became a game changer in various fields of science and nanotechnology. Commonly used carbonaceous nanomaterials include graphene and its modified versions e.g., graphene oxide (GO), reduced GO (rGO), carbon nanotubes (CNTs, e.g., single-walled (SWCNTs) or multiple-walled (MWCNTs), carbon quantum dots (CQDs/CDs), and graphitic carbon nitride (g-C₃N₄) [34-37]. Other two-dimensional (2D) nanomaterials also growing parallel and rapidly such as MXene, 2D metal-organic framework nanosheets(2D-MOFs), etc. and these are widely used in several advanced applications e.g., energy storage, electromagnetic interference (EMI) shielding, gas separation, and so forth [38-39]. Thus, the incorporation of reinforcing agents not only revamps the inherent properties but also

imparts new properties e.g., conductivity, fluorescence, flame-retardancy, motion sensing, EMI shielding, and so forth [40-43].

Thus, an extensive literature survey unveils the importance of smart WPU and WPUNCs in a highly developed society for running day-to-day life smoothly and comfortably. In this endeavor, exploring the biobased smart WPU, WPUNCs, and their possible advanced applications including, preparing self-healable coatings, artificial muscle, development of biomedical scaffolds via 3D-printing, bio-imaging, anti-counterfeiting, control release of antibacterial drugs, etc. may direct toward a well-defined research proposition and the subject of scientific investigation.

1.2. Background

PUs have been grabbing the attention of researchers and consumers since the 20th century till to date. In 1937, German scientist Prof. Otto Bayer synthesized the PU in IG Farben laboratory, Germany which was raised as a tough competitor of nylon [44]. This invention is considered one of the greatest triumphs in polymer chemistry because of the ultimate versatility of PU as mentioned earlier. Utilization of PUs as surface coatings, elastomers, and adhesives grown during the 1940s. Particularly, at the time of World War II (1945), PUs were employed broadly as an alternative to rubber. Flexible and rigid PU foams were introduced into the PU family in the early 1950s [45]. At the end of the 1950s, Lycra, a new Spandex fiber was launched into the polymer market by DuPont and created a revolution in the textile industry. Subsequent years have pioneered enormous developments of PU and earned global appreciation through its mesmerizing properties.

However, the ecofriendly WPU dispersion was introduced in the late 1960s [46]. Dieterich and his coworkers, in 1970, reported an aqueous dispersion of PU ionomers with particle size in the range of 20 to 5000 nm [47]. Another WPU dispersion was synthesized by Neumaier in 1974 and can be used for textile coating and lamination [48]. The most interesting technical advantage of WPU dispersion is the independence of its viscosity on the average molecular weight of the polymer. As a result, WPU dispersion with high solid content can be prepared and film with excellent performance can be obtained by simply evaporation of water even at ambient temperature. Over 1000 patents have been issued and published in the last five decades of their existence [49]. Presently, researchers are focusing on the modification and tailor-making of WPU for specific end uses. For example, Kim and his group investigated the effect of residual NCO groups and PU particle size on the degree of chain extension. They reported that decrement in the surface area of PU particles leads to less requirement of residual NCO and hence the amount of chain extender decreases for an

optimum chain extension [50]. Gong et al. developed oligo (carbonate ether) diol (a CO₂-polyol from telomerization of CO₂ and propylene oxide)-based cationic WPU (CWPU) by inducing terminal hydrophilicity which exhibits tremendous water- and oxidation-resistance [51]. Yin et al. prepared a series of two-component WPU (2K-WPU) using diethyl *N*, *N*-bis(2-hydroxyethyl) aminomethylphosphonate and halogen-free polyphosphate, which can be used as the reactive halogen-free flame retardants with the highest limit oxygen index (LOI) of 27.8% [52]. Importantly, in present years' environmental awareness, scarcity of fossil fuel, skyrocketing cost of crude oil, etc. have prompted a necessity of usage of biobased raw material for preparing WPU. A quick literature assessment can disclose that WPUs derived from renewable raw materials exhibited very much closer properties to that of petroleum-derived WPUs. For example, Larock and Lu synthesized a series of soybean-oil-based WPU using methoxylated soybean oil polyols (MSOLs) containing various hydroxyl functionalities and scrutinized the effect of polyol functionality and hard domain content on the resultant properties [53]. As per the report, the particle size, mechanical strength, and thermal stability were increased with the increase in the hydroxyl functionality from 2.4 to 4 because increment in the cross-linking density of the WPU matrix. Kessler and his co-workers developed castor oil-based WPU via homogenous solution polymerization in methyl ethyl ketone (MEK) followed by solvent exchange with water [54]. Also, they have investigated the rheological behavior of the prepared WPU using small-amplitude oscillatory shear flow experiments. Prof. Zhang and his group also used castor oil as the polyol to prepare a series of multi-functional WPUs that exhibit high mechanical strength (up to 38 MPa), excellent self-healing ability, extreme reprocessability, and double to quadrupole shape memory effect, simultaneously [18]. Moreover, WPU must undergo biodegradation to call it an environmentally benign material. Prior literature advocates that some WPUs with hydrolysable groups (e.g., esters) in polymeric backbone undergo partial degradation under the exposure of micro-organisms [55]. For example, Wang et al. synthesized biodegradable shape memory WPU and used it for developing fabricating bone scaffolds via post-modification with gelatin and superparamagnetic iron oxide nanoparticles (SPIO NPs) [56]. Another biodegradable and biocompatible SM WPU elastomer was synthesized by Hsu and his coworkers using poly(ϵ -caprolactone) (PCL) oligo-diol and poly(L-lactic acid) (PLLA) oligo-diol as the mixed soft segments [57]. They reported that a representative SM WPU elastomer comprising 38 wt% of PCL and 25 wt % PLLA segments can recover to its original shape (100%) in 37 °C water within 20 s.

Interestingly, a remarkable paradigm transformation in polymer science and technology was accompanied by nanotechnology, creating a new material so-called "polymer

nanocomposites". The development of clay/nylon-6 nanocomposite in Toyota's research laboratory in the late 1980s is considered the first report on polymer nanocomposites [58]. Again, the first-ever PUNC was prepared by Wang and Pinnavaia by employing montmorillonite (MMT) clay as the reinforcing agent in 1999 [59]. Another PUNC was developed by Zilg et al. using layered silicate which is composed of synthetic fluoromica in the following year [60]. Afterward, people started churning of nanomaterials' ocean for the discovery of the best of the best nano-reinforcements. For example, Lee and his group (2005) prepared a MWCNT/WPU nanocomposite with improved thermo-mechanical properties than the pristine WPU [61]. In 2006, Lee and Lin fabricated WPU/organophilic clay nanocomposites and studied the effect of the clay and its interlayer ion on surface morphology, and physical, and electrical properties [62]. Cao et al. (2007) reinforced the WPU by flax cellulose nanocrystals (CNC) and they observed the augmentation of tensile strength from 4.27 to 14.86 MPa with increasing filler content from 0 to 30 wt% [63]. Raghu et al. (2008) developed a conductive WPU/functionalized graphene sheets (FGSs) nanocomposite which showed conductivity of about 10^5 times that of pristine WPU [64]. Hsu et al. (2010) imparted antibacterial activity (*B. subtilis* and *E. coli*) into a polyester-type WPU by incorporating silver nanoparticles (nano-Ag, size 5 nm) [65]. Zhang and colleagues (2010) studied the synergistic effect of starch nanocrystals (SN) and cellulose whiskers (CW) on WPU [66]. The SN and CW were prepared from sulfuric acid hydrolysis of waxy maize starch granules and cotton linter pulp, respectively, and observed a strong hydrogen bonding network with the nanocomposites. Liu et al. (2012) introduced carboxylated cellulose nanocrystals (CCNs) and silver nanoparticles (AgNPs) as bifunctional nanofillers into WPU to improve the mechanical and antimicrobial properties of the same [67]. A series of lightweight and flexible rGO/WPU Composites was developed by Ma and his coworkers (2014), showing high electrical conductivity (approx. 16.8 S/m) and excellent EMI shielding effectiveness (approx. 34 dB) over the frequency range from 8.2 to 12.4 GHz [34]. Christopher et al. (2015) performed a comparative study of corrosion inhibition of mild steel coated by modified GO/ZnO/WPU nanocomposites and functionalized carbon black (CB)/ZnO/WPU nanocomposites [68]. Results revealed that the former nanocomposite performed better than the latter. A multifunctional lignin-modified graphene (LMG)/WPU nanocomposite was prepared by Shahabadi et al. (2017) via a green route and they reported that the resultant nanocomposite coating can resist UV light and healed within 150 s under exposure to infrared (IR) radiation [69]. Lee et al. (2019) developed a series of biodegradable graphene/WPU nanocomposite varying graphene loading weight percentages and evaluated its potential applicability as the neurovascular regenerator [70]. Smart TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) oxide CNF (TOCNF)/WPU hybrid films

were prepared by Jiang and his group (2022) which exhibited moisture-induced SH and SM abilities with unprecedented toughness [71]. Recently, Xue et al. (2023) prepared a flexible photonic and self-healable CNC/WPU nanocomposite which can be used for advanced applications including anti-counterfeiting [72].

This kind of incredible and exciting piece of literature motivates all enthusiastic researchers to work hard and play the key role as the driving force to explore the unfolded zones of WPU and its nanocomposites and to develop more smart materials for advanced applications.

1.3. Materials and methods

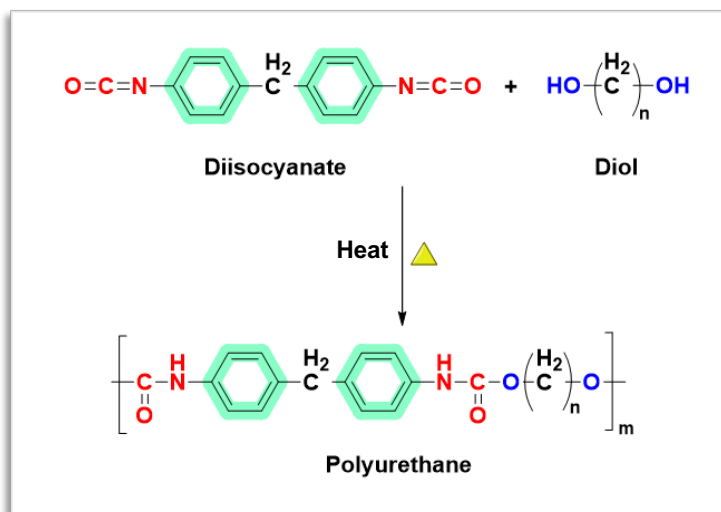
1.3.1. Materials

The tunable chemical structure of PU makes it a versatile polymer. Various forms of PU can be obtained by simply tuning the hard-to-soft segment ratio or altering the building materials, selectively [73]. This feasibility in the customization of polymeric backbone facilitates the wide spectrum of WPU applications in every arena of science and technology [74]. As aforementioned, both petroleum-based and renewable raw materials are extensively used to develop distinct PUs. Nowadays, everyone is focusing on the amplification of PU usability as a futuristic and revolutionary material via appropriate nanomaterial fabrication [75]. Precision in the selection of the building materials and compositional optimization are highly sensitive for controlling the resultant performance of WPUs and WPUNCs. So, this section illustrates overall information about raw materials, preparative methods, and plausible reaction mechanisms.

1.3.1.1. WPU

Urethane or carbamate (-NH-COO-) group is the repeating unit of WPU which can be generated from the rearrangement reaction between di/polyols and di/polyisocyanates, with or without the involvement of a catalyst, as shown in **Scheme 1.1** [76]. Depending on the starting materials, groups such as ester, urea, ether, etc. may also be present in the polymeric chain of WPU in addition to urethane linkages. Generally, the WPU preparation involves four basic components, namely, di/polyisocyanate, di/polyols as macroglycol, di/polyols/amines as the chain extender, and a suitable emulsifier (internal or external). Importantly, macroglycol with a flexible long hydrocarbon chain serves as the soft segment. On the other hand, the hard or rigid segment consists of di/polyisocyanate, chain extender, and internal emulsifier. Interestingly, the inherent properties of WPU can be maneuvered

easily by varying these two primary segments or domains [13]. A concise description of the starting materials is presented as follows.



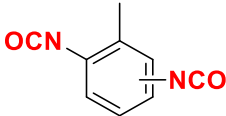
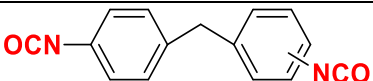
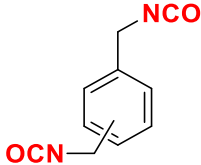
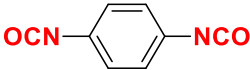

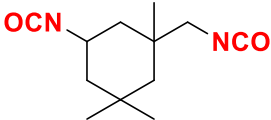
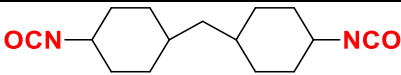
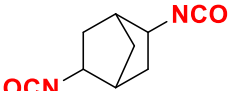
Scheme 1.1. Common route for synthesis of polyurethane.

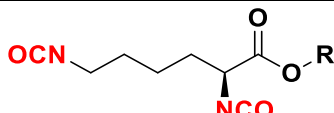
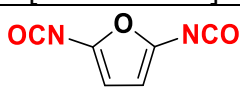
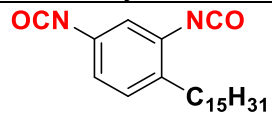
(a) Di/polyisocyanate

Isocyanates play a major key role in controlling the ultimate properties of PU. They are highly reactive and moisture-sensitive organic compounds containing the $-\text{N}=\text{C}=\text{O}$ groups which can easily react with any compounds possessing labile hydrogen-containing groups [74]. They can be divided into difunctional or polyfunctional and aromatic or aliphatic based on the structure. Aromatic diisocyanates with rigid benzene ring e.g., toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) and aliphatic diisocyanates e.g., isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI) are widely used in academia and commercial production of PU [77]. **Table 1.1** illustrates the structures of some commonly used isocyanates and applications in PU chemistry. Noticeably, TDI and MDI are inexpensive and more reactive as compared to other isocyanates and are used for producing PU foams (both rigid and flexible), insulators, elastomers, and so forth. These PU exhibit high mechanical strength and thermal properties but suffer from limitations such as opaque in nature and UV-light sensitivity. Contrariwise, aliphatic diisocyanates (more toxic and less reactive) based PU shows good transparency and color stability with low mechanical strength so broadly used as the coatings and other fields where transparency and color are exceedingly anticipated [13]. Therefore, precise selection of diisocyanates is highly recommendable. Literature advocates that there are two major difficulties raised during the use of diisocyanates. Firstly, the uncontrolled reactions of isocyanates with water, resulting poor control of the stoichiometry and hence the molar mass of the final product. Secondly, the coalescence of the initially stabilized PU particles affects the final film. Moreover, in the case of symmetric diisocyanates, both the isocyanate groups initially show the same

reactivity ($k_1=k_2$) but after some time, the reactivity of the second (unreacted) isocyanate group undergoes a substitution effect and its reactivity can be lowered by the electronic and steric effect of created urethane or urea group.

Table 1.1. Commonly used diisocyanates in PU synthesis.

Diisocyanate		Properties	Applications
Aromatic	 Toluene diisocyanate (TDI) 2,4- and 2,6-isomers	Liquid $T_m = 20-22\text{ }^\circ\text{C}$	Rigid PU foam for shoes, Elastomeric PU, Smart PU for electronics
	 Diphenylmethane diisocyanate (MDI) 4,4'- and 2,4'-isomers	Liquid $T_m = 19-21\text{ }^\circ\text{C}$	
	 Xylylene diisocyanate (XDI) para- and meta-isomers	Liquid $T_m = 10-12\text{ }^\circ\text{C}$	
	 para-phenylene diisocyanate (PPDI)	Solid $T_m = 94\text{ }^\circ\text{C}$	
Aliphatic	 Hexamethylene diisocyanate (HDI)	Liquid $T_m = -70\text{ }^\circ\text{C}$	UV-resistant coating, biomedical scaffold, adhesives
	 Isophorone diisocyanate (IPDI)	Liquid $T_m = -60\text{ }^\circ\text{C}$	
	 Bis(4-isocyanatocyclohexyl)methane (H_{12} MDI) ("Hydrogenated MDI")	Liquid $T_m = 10-15\text{ }^\circ\text{C}$	
	 Norbornene diisocyanate (NBDI)	Solid $T_m = 85-88\text{ }^\circ\text{C}$	

Renewable raw material-based	 <p>L-Lysine diisocyanate (LDI) ester [R = -Et or -Me]</p>	Liquid $T_b = 305 \pm 37 \text{ } ^\circ\text{C}$	Tissue engineering
	 <p>2,5-diisocyanatofuran</p>	-	
	 <p>2,4-diisocyanato-1-pentadecylbenzene</p>	-	

For example, the reactivity of the first isocyanate group of TDI with hydroxyl groups of poly(propylene glycol) at 60 °C is 5.8 times faster than the second one [78]. On the contrary, the reactivity of the two diisocyanate groups of an asymmetric diisocyanate is different ($k_1 \neq k_2$). The reactivity is again altered by the reaction of the first isocyanate group. Therefore, there will be four rate constants for a reaction between an asymmetric diisocyanate and diol. Burel et al. observed a decrement in selectivity between primary and secondary isocyanate groups of IPDI ($k_{\text{secondary}}/k_{\text{primary}}$) with temperature, from 31 at 25 °C to 15 at 90 °C [79].

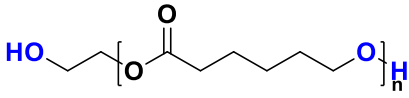
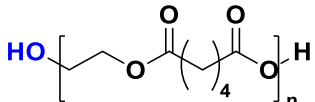
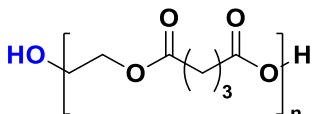
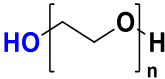
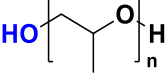
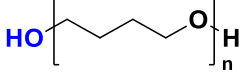
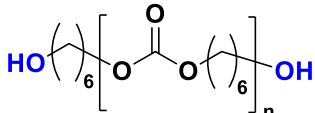
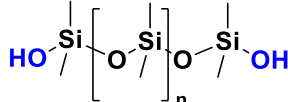
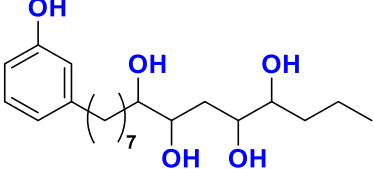
Furthermore, nowadays, biobased diisocyanates are also used for preparing PU. For example, Charlon et al. prepared a set of fully biobased thermoplastic PU using a dimer fatty acid-based diisocyanate along with other renewable raw materials [80]. Griffini and his coworkers developed a thermosetting biobased PU from an α, ω -diisocyanate monomer (1,4-bis(4-isocyanato-2-methoxyphenoxy) butane, VA-NCO) obtained from lignin-derived vanillic acid and other reactants [81].

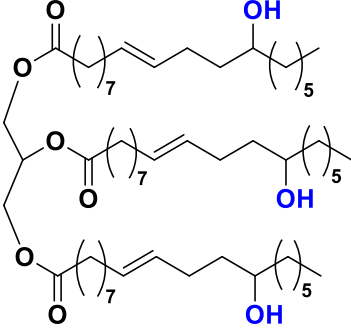
(b) Macroglycol

As mentioned earlier, macroglycol is the soft segment of the PU matrix with two or more hydroxyl groups and has a molecular weight from 400 g mol⁻¹ to 5000 g mol⁻¹. Most commonly used macroglycol are derived diol/polyol of polyether, polyester, polycarbonate, poly-siloxane, etc., as listed in **Table 1.2**. Notably, polyether and polyester-based macroglycol are widely used as compared to others. Polyether diol/polyols can be prepared from the reaction between epoxides and active hydrogen-containing reactants and ring-opening polymerization of epoxy monomers [82-83]. Polyester di/polyols can be prepared

from poly-condensation reactions of hydroxyl reactants and multifunctional carboxylic acids [84].

Table 1.2. Commonly used macroglycols in PU.

	Macroglycol	Properties	Applications
Polyester	 <p>Polycaprolactone diol (PCL)</p>	White solid $T_m = 60\text{ }^\circ\text{C}$	SM materials, biomaterials
	 <p>Poly(ethylene adipate)</p>	Solid $T_m = 55\text{ }^\circ\text{C}$	
	 <p>Poly(ethylene glutarate)</p>	Solid $T_m = 55.2\text{ }^\circ\text{C}$	
Polyether	 <p>Poly(ethylene oxide) glycol (PEG)</p>	Solid or liquid $T_m = 33\text{-}40\text{ }^\circ\text{C}$	Flexible PU foam, abrasion resistant
	 <p>Poly(propylene oxide) glycol (PPG)</p>	Liquid $T_m = -40\text{ }^\circ\text{C}$	
	 <p>Poly(tetramethylene oxide) glycol (PTMEG)</p>	Solid $T_m = 23\text{-}28\text{ }^\circ\text{C}$	
Polycarbonate	 <p>Polycarbonate diol</p>	Solid $T_m = 50\text{-}60\text{ }^\circ\text{C}$	UV-curable coatings
Siloxane	 <p>Polydimethylsiloxane glycol</p>	Solid $T_m = -50\text{ }^\circ\text{C}$	Self-cleaning materials
Bio-based polyols	 <p>Cardanol-based polyol</p>	Liquid	PU foam

	 <p>Castor oil-based polyol</p>	Liquid	Flame-retardant PU, Self-cleaning materials
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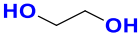
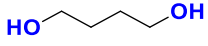
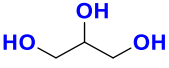
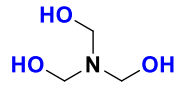

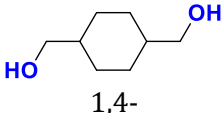
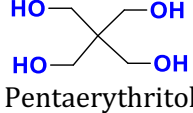
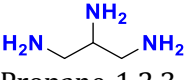
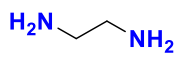
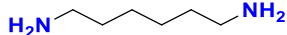
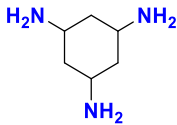
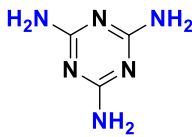
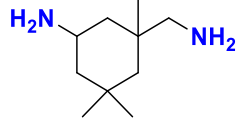
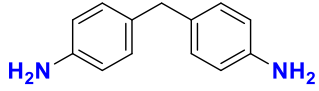
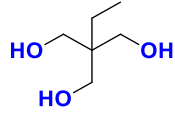
Generally, polyester-based macroglycol is of high viscosity and more expensive than polyether-based macroglycol. Nevertheless, these are popular because they can create PUs with good abrasion, solvent, and cut resistance along with excellent mechanical properties [85]. Remarkably, PU properties can be customized by altering the selection of the macroglycol. For example, flexible PU foams are obtained by using high molecular weighted (2000 to 10000 g mol⁻¹) and low functionality macroglycol (e.g., glycerine, f=3; dipropylene glycol, f=2, etc.) while rigid PU foams are developed from low molecular weighted and higher functionality macroglycol (e.g., sorbitol, f=6; Mannich base, f=4; etc.) [86-87]. Presently, polyols originating from renewable resources receive incredible attention due to environmental concerns. These renewable materials include lignin, vegetable oils, starch, and sorbitol [19, 88]. Lignin is a heterogeneous biomacromolecule having many phenolic groups. The aromatic hydroxyl group present in lignin is relatively low reactive than that of aliphatic polyols. Therefore, the hydroxyl group is modified prior to its reaction with diisocyanates, e.g., oxypropylated lignin-bearing aliphatic hydroxyl group. Again, common vegetable oils i.e., triglycerides of fatty acid from which polyols can be obtained are castor oil, soybean oil, linseed oil, palm oil, kernel oil, sunflower oil, and so forth. The functional groups viz. double bonds and ester groups can be modified easily in some reactions such as epoxidation, hydroformylation, metathesis, ozonolysis, transesterification, etc. [19].

(c) Chain extender

The chain extenders are another basic component of PU that often plays a vital role in controlling the polymeric morphology of PU adhesives, elastomers, fibers, and foams [89-90]. These are usually short-chain di/polyol/amine-terminated compounds having a low molecular weight (< 400 g mol⁻¹). The multifunctional chain extenders (f ≥ 3) are also known as cross-linkers. These chain extenders are responsible for the extension of each polymeric

chain present in the PU matrix and its molecular weight. Generally, chain extenders and diisocyanates react to form hard segments that are immobile and stiff. The covalent association of these hard segments with the soft segments results in plastic flow inhibition inside the polymeric chain and hence elastomeric resiliency. Additionally, hard segments are further coupled and realigned with multiple strong hydrogen bonds to accomplish high mechanical strength, fracture resistance, and good flexibility [91-92]. Most commonly used chain extenders include 1,4-butane diol (BDO), 1,6-hexane diol, ethylene glycol (EG), cyclohexane dimethanol, 1,6-hexamethylene diamine (HMDA), isophorone diamine (IPDA), and so forth [77]. **Table 1.3** demonstrate a list of chain extenders that are used for preparing various form of PU.

Table 1.3. Some common chain extenders used in PU synthesis.

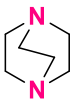
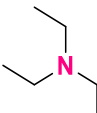
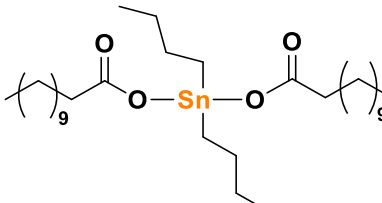
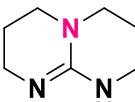
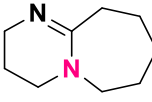
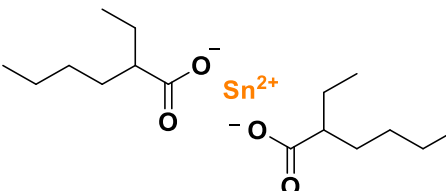
Di-functional chain extenders		Multi-functional chain extenders	
 Ethylene glycol (EG)	 1,4-butane diol (BD)	 Glycerol	 Triethanolamine
 Neopentyl glycol	 1,4-Cyclohexane dimethanol	 Pentaerythritol	 Propane-1,2,3-triamine
 Ethylene diamine (EDA)	 1,6-Hexamethylene diamine (HMDA)	 Cyclohexane-1,3,6-triamine	 Melamine
 Isophorone diamine	 4,4'-Oxydianiline	 Trimethylol propane	

(d) Emulsifier

It is well-known that WPU dispersion is a binary colloid in which PU particles are dispersed in water. Again, PU is completely incompatible with water so further special modification is required in the polymeric backbone. The inclusion of hydrophilic monomers with ionizable functional groups such as quaternary ammonium, carboxylate, or sulfonate groups, makes the PU dispersible and stabilizes in a continuous aqueous medium. These monomers are known as the emulsifier [47]. Broadly, emulsifiers can be categorized into two types: internal

and external. Internal emulsifiers may be non-ionic (e.g., polyethylene oxide) or ionic centred (e.g., anionic, cationic, and zwitterions) monomers. The most widely used internal emulsifiers are 2,2-bis(hydroxymethyl)propionic acid (DMPA), 2,2-bis(hydroxymethyl)butyric acid (DMBA), and external emulsifiers are sodium dodecyl sulfate (SDS), hexadecyl trimethyl ammonium bromide (CTAB), etc. Anionic WPU dispersion can be obtained by using diol with sulfonic groups [93], phosphonate [94], and carboxylic acid [95, 96] which are neutralized with a basic group (e.g., triethyl amine, TEA) before adding water. Conversely, cationic WPU dispersion can be prepared using nitrogen-containing alkyl diols or with sulphur-containing diols which are ionized by the quarterisation of nitrogen atoms or ternization of sulphur atoms [97]. The four major advantages of the usage of an internal emulsifier include (i) average shear force is sufficient to create the dispersion, (ii) high colloidal stability with fine particles can be developed, (iii) less water sensitivity of the developed WPU films after completely dried, and iv) high chemical resistance towards non-polar compounds [49].

Table 1.4. Common catalysts used in PU synthesis.

Amine compounds		Organometallic compounds
 <p>1,4-Diazabicyclo[2.2.2]octane (DABCO)</p>	 <p>Triethylamine</p>	 <p>Dibutyltindilaurate (DBTDL)</p>
 <p>Triazabicyclo[4.4.0]dec-5-ene (TBD)</p>	 <p>1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)</p>	 <p>Stannous octoate</p>

(e) Catalyst

The treatment of the catalyst in PU preparation is optional. However, the specific catalyst is used to perform PU preparation under mild conditions and to enhance the rate of polymerization. Two groups of catalysts are widely used viz. tertiary amines and organometallic complexes. Catalysts based on tertiary amines are dimethylcyclohexylamine (DMCHA), dimethylethanolamine (DMEA), 1,4-diazabicyclo[2.2.2]octane (DABCO) and triethylenediamine (TEDA), etc. Noticeably, the reactivity of these catalysts depends on their concentration and is deployed according to their aptitude to drive either the urea, urethane,

or isocyanate trimerization reactions [13]. Again, coordination complexes of metal such as bismuth (Bi), lead (Pb), zinc (Zn), tin (Sn), zirconium (Zr), iron (Fe), and mercury (Hg) are used effectively and they act as the Lewis acids [98-102]. Most commonly used catalysts and their chemical structures are summarized in **Table 1.4**. Remarkably, the tin-based complexes with general formula Bu_2SnX_2 (X is an anion) e.g., dibutyltin dilaurate (DBTDL), exhibit high catalytic performance. At present time, catalysts originate from N-heterocyclic carbenes (NHC) and organic acids (e.g., diphenyl phosphate (DPP), methane sulfonic acid (MSA), and triflic acid), have been observed in PU chemistry [103-105].

1.3.1.2. Nanomaterial

As mentioned earlier, nanomaterials have turned out to be a miraculous material with at least one dimension in the range of 1 to 100 nm. Interestingly, nanomaterials are significantly different from their bulk counterparts. For example, gold is a renowned shiny, yellowish noble metal and non-magnetic but gold nanoparticles (2-3 nm) can act as an excellent catalyst with considerable magnetism [106]. Unlike bulk materials, nanomaterials may retain mesmerizing properties including magnetism, electrical conductivity, optical activity, mechanical robustness, catalytic activity, etc. Moreover, these properties can be tuned as per the requirement via precisely governing size, shape, preparation settings, and suitable functionalization [107]. Nanomaterials can be categorized into three broad groups based on their origin viz. (a) organic (carbon-based), (b) inorganic (non-carbon-based), and (c) hybrid systems. Again, dimensionally, nanomaterials are divided into three types viz. (a) zero-dimension (0-D), (b) one-dimension (1-D), and (c) two-dimension (2-D), as shown in **Figure 1.1**. Most conspicuously, all these nanomaterials can be incorporated into WPU matrix. Importantly, the selection of the nanomaterial exclusively depends on the desired applications. A brief explanation of various nanomaterials used in WPUNC is provided in the following sub-sections.



Figure 1.1. Simple representations of (a) 0-D, (b) 1-D, and (c) 2-D nanomaterials.

(a) Inorganic nanomaterials

As the name suggests, inorganic nanomaterials are non-carbonaceous nano-sized materials [108]. These nanomaterials are available in different shapes such as spherical, cube, rod, wire, etc. Pure metals e.g., Fe, Cu, Ag, Au; metal oxides e.g. Fe_3O_4 , TiO_2 , ZnO, CuO/ CuO_2 ; metal sulfides are MoS_2 , WS_2 , ZrS_2 ; metal phosphides, metal ferrites (zinc ferrites, cobalt ferrites, nickel ferrites, etc.), nano clays e.g., halloysite, MMT, nano silica, and so forth, are used extensively as the inorganic nanomaterials in WPUNC [107]. Pure metallic nanomaterials are possibly the most studied class of nanoparticles with distinctive physical, catalytic, optical, and anti-bacterial activities. These nanomaterials can be prepared by reduction of their corresponding salts or coordination complexes. Due to their advanced physicochemical properties, metal nanoparticle finds applications in various fields of science. On the other hand, metal oxides, phosphates, and sulfides can be prepared by enormous methods including hydrolysis, solvolysis, wet chemical techniques, solvothermal methods, thermal decomposition, etc. [109].

(b) Organic or carbon-based nanomaterials

Organic or carbon-based nanomaterial family consist of numerous unique nanomaterials e.g., CNTs, fullerenes, graphene and its derivatives, carbon nanohorns or nanocones, CD/CQDs, and many others, as shown in **Figure 1.2**. These nanomaterials exhibited extraordinary tunable properties which attracted everyone and make them useful in new advanced technologies [110]. CNTs are cylindrical-shaped mono-layered or multi-layered nanomaterials with sp^2 hybridized C-atoms connected to each to form hexagonal wall architecture [111]. Based on the number of walls formed, CNTs are named SWCNT (single nano wall containing) or MWCNT (multiple nano wall containing). Individual defect-free CNTs manifest excellent thermo-mechanical and electrical properties, which has led to speculation on a wide spectrum of advanced applications such as supercapacitors, actuators, automobile parts, EMI shielding, etc. [112]. Like CNTs, graphene is also a brilliant nanomaterial with ultimate inherent properties. Graphene is a single-layer and aromatic-structured nanosheet, composed of sp^2 hybridized C-atoms. Graphite, the building block of graphene, has multiple numbers of graphene sheets assembled by π - π interaction with an interlayer spacing of 3.34 Å between the sheets, which are exfoliated via ultra-sonication to obtain the fine graphene nanosheets [113]. CQDs are a new class of fluorescent carbon-based nanomaterials that have found several applications in the areas of chemical sensing, biosensing, bioimaging, nanomedicine, photocatalysis, and electrocatalysis. In 2004, CQD was discovered accidentally by Xu et al during the separation and purification process of SWCNT [114]. Two years later, in 2006, Sun et al. proposed a novel synthetic path to develop via surface passivation and named the high-fluorescence active carbon nanomaterials the

“carbon quantum dots” [115]. Generally, CQDs are quasi-spherical nanoparticles consisting of amorphous to nanocrystalline cores with mostly graphitic or turbostratic carbon (sp^2 -C) or graphene and GO sheets fused by diamond-like sp^3 hybridized carbon insertions [116]. Moreover, $g\text{-C}_3\text{N}_4$ is one of the newest and unique 2-D layer-structured nanomaterials with exceptional chemical stability and tunable electronic structure (repeating heptazine rings) with a medium band gap (2.7 eV) which is extremely helpful in photo-catalysis and its associated applications [117]. Literature reveals that the $g\text{-C}_3\text{N}_4$ -based nanohybrids can be divided into six broad classes depending on the discrepancies in the photocatalytic mechanism and process, namely, (i) the $g\text{-C}_3\text{N}_4$ based metal-free heterojunction, (ii) the $g\text{-C}_3\text{N}_4$ /single metal oxide (metal sulfide) heterojunction, (iii) $g\text{-C}_3\text{N}_4$ /composite oxide, (iv) the $g\text{-C}_3\text{N}_4$ /halide heterojunction, (v) $g\text{-C}_3\text{N}_4$ /noble metal heterostructures, and (vi) the $g\text{-C}_3\text{N}_4$ based complex system [118]. Thus, pure metal-free $g\text{-C}_3\text{N}_4$ and its nanohybrids can be incorporated with WPU for various applications including, flame retardancy, anti-counterfeiting, etc.

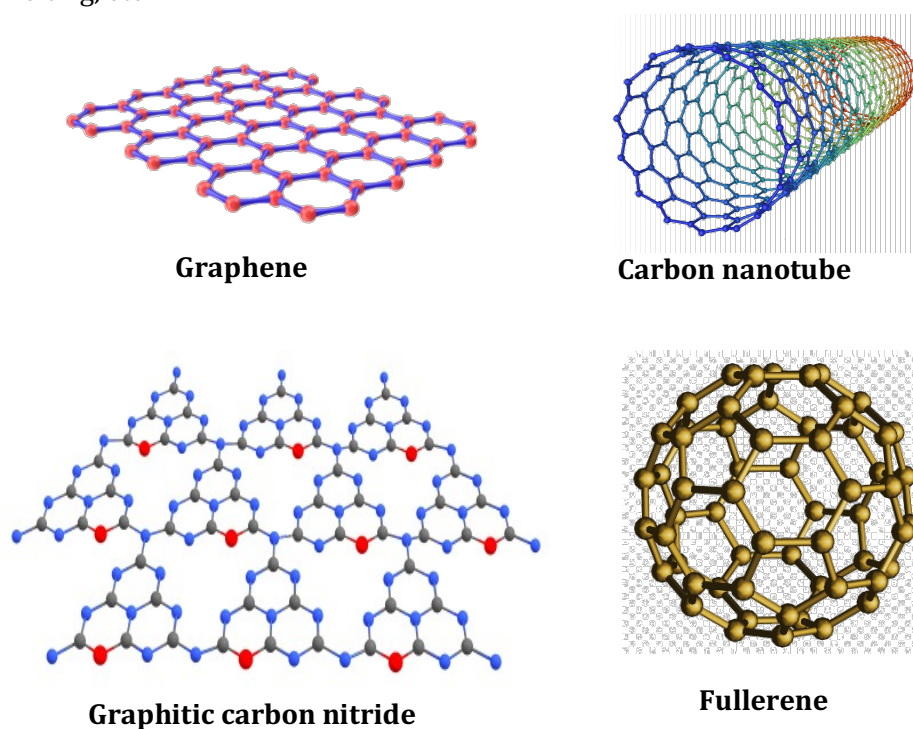


Figure 1.2. Structure of carbon-based nanomaterials.

(c) Hybrid nanomaterial

Nanohybrids are a special type of new-generation nanomaterials that have gained tremendous acceptance because of their outstanding intrinsic properties such as biodegradability, stretchability, re-processability, and high mechanical and optical properties. These nanomaterials comprise two or more distinct classes of nanomaterial (organic or inorganic or both) that are connected through either covalent bonds or non-

covalent interactions (e.g., ionic interaction or hydrogen bonds). Based on the starting materials, nanohybrids can be classified into three groups: (i) metal-metal, (ii) carbon-carbon, (iii) metal-carbon, and (iv) organic molecule end-capped, nanohybrids [119]. Again, depending on the individual interactions and morphologies, nanohybrids are also divided as supported, decorated, embedded, core-shell, etc. Fascinatingly, nanohybrids have superior properties than that of individual nanomaterials. For example, Yao and his coworkers reported that for reducing N_2 to NH_3 , the $TiO_2/Ti_3C_2T_x$ hybrid exhibited better catalytic performance, higher selectivity of NH_3 , and greater electrochemical stability than pristine TiO_2 and $Ti_3C_2T_x$ [120].

1.3.2. Methods

1.3.2.1. WPU synthesis

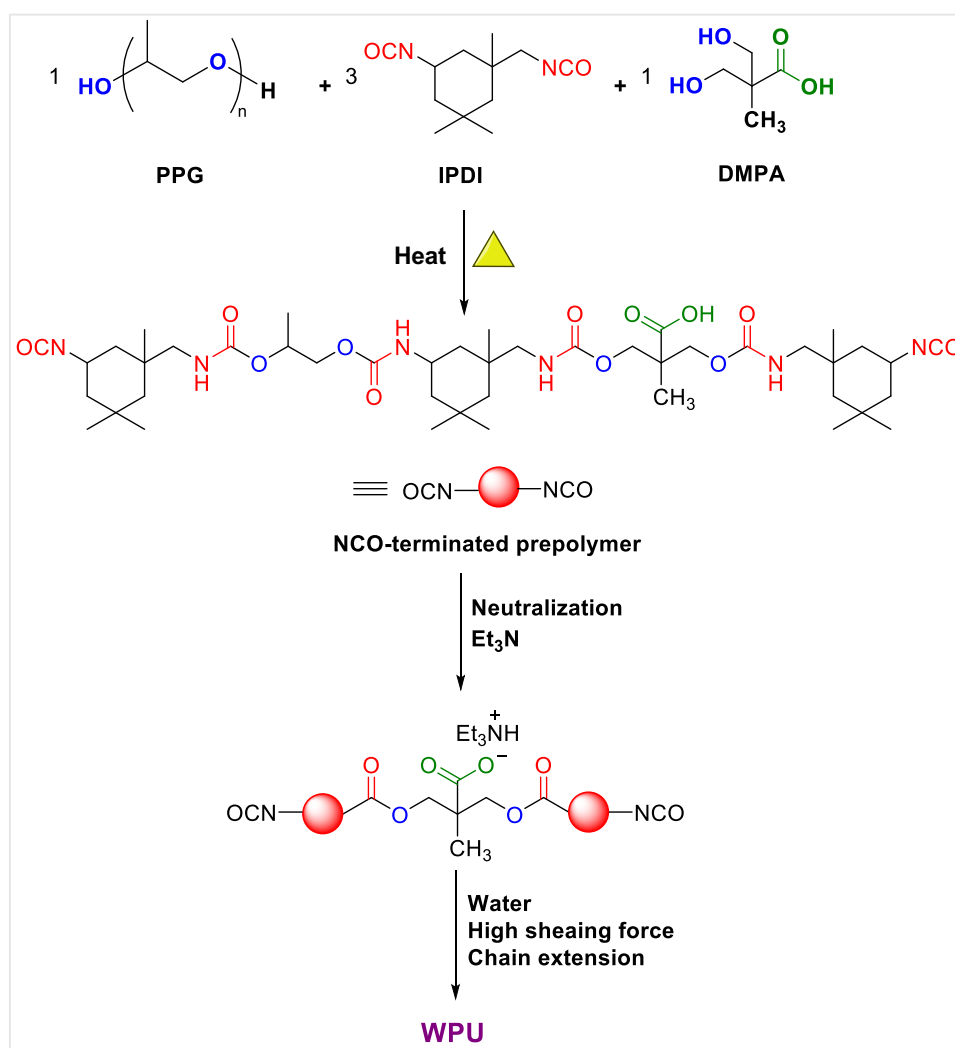
Usually, WPUs are synthesized using various reaction pathways viz. (a) emulsification or pre-polymerization technique, (b) acetone process, (c) hot-melt process, and (d) ketamine-ketazine [121]. A brief description of these methods is provided as follows.

(a) Emulsification or pre-polymerization technique

The pre-polymerization method is the most popular multi-stepped synthesis method in PU chemistry. In this method, an NCO or OH-terminated pre-polymer with low molecular weight is synthesized in the very first step from the reaction between macroglycol and diisocyanates (preferably, cycloaliphatic diisocyanates having low reactivity). Successively, neutralization or emulsification and chain extension steps are performed to obtain the final high molecular weight WPU dispersion using high shearing force and adding the desired amount of water. Notably, the dispersing step must be carried out within a short span of time below the critical point where free NCO groups begin to react with water molecules [13]. Moreover, in this method, approximately 12-15% or less amount of organic solvents (e.g. *N*-methyl-2-pyrrolidone (NMP)) are used during polymerization to reduce the viscosity of the reaction mixture. The typical steps involved in the pre-polymerization technique have been demonstrated in **Scheme 1.2**. Literature survey unveils that both industry and academia prefer to hire this technique to develop WPU, straightforwardly. For example, Ren et al. prepared a series of WPU using amino-terminated hyperbranched organosilicon (HPSi-NH₂) which can be used as adhesives for leather substrates [122]. A series of flame-retardant and self-healable WPU containing organic selenium was developed by Jin and co-workers that exhibited a maximum LOI of 28.5% with excellent UL-94 level (V-0) and self-healing efficiency (91.25%, at room temperature in a photoreactor) [123].

(b) Acetone process

In the acetone process, WPU is synthesized using acetone as the reaction medium or solvent which creates a homogenous environment for all reactants. In WPU synthesis, acetone is more favorable as compared to the other solvents because it does not disturb the PU-forming reaction, miscible with water, and has a low boiling point so that it can be easily removed. Moreover, acetone assists in reducing the viscosity of the reaction mixture and prevents gel formation by compressing the high reactivity rate of amine-based chain extenders via reversible ketamine formation [121].



Scheme 1.2. Steps involves in pre-polymerization technique for WPU synthesis.

However, the use of huge amounts of acetone is not suitable for the environment as it is associated with high energy consumption and direct release of VOCs into the open atmosphere. Notably, after the pre-polymerization technique, the acetone process is greatly used in industry to produce WPU dispersions. Literature advocates the popularity of the acetone process among many researchers across the globe. For example, Fang et al.

synthesized a series of recyclable and self-healable WPU from stimuli-responsive Diels-Alder (DA) diol via a modified acetone process [124]. Again, Unal and his groups developed a polydopamine (PDA)/WPU matrix that can convert light into heat. They reported that a representative PDA-WPU hybrid film can reach 105.8 °C when irradiated with solar light for 20 min [125].

(c) Hot-melt process

The hot-melt process is a solvent-free multi-stepped method used for synthesizing WPU. In the first step, biuret-capped oligomers are formed from the reaction between an NCO-terminated hydrophilic prepolymer and urea. Secondly, these low molecular weight capped oligomers are dispersed in water, and a chain extension reaction is carried out via methylation of biuret groups with formaldehyde. Lastly, polyurethane-urea dispersion is obtained via a condensation reaction at low pH [73]. Notably, it is very challenging to control the formaldehyde reaction, resulting in side reactions and forming WPU with low molecular weight.

(d) Ketamine-ketazine process

The ketamine-ketazine process is nothing but a modified version of the pre-polymerization technique. Initially, a hydrophilic NCO-terminated prepolymer is mixed with ketone-blocked amine (ketamine) or ketone-blocked hydrazine (ketazine) before it meets the aqueous medium. Then, the chain extension step is performed by hydrolysis of ketamine and ketazine into an amine and hydrazine, respectively [73]. However, this method is not as popular as the pre-polymerization method.

1.3.2.2. WPU modification

The literature survey discloses that the pristine WPU always integrated with some minute flaws such as low resistance towards water and alkaline substances, and low mechanical strength which can be vanquished via additional modifications. Apart from the ultimate nanocomposite fabrications, common and useful modification approaches are amendment in soft or hard domains, hybrid or IPN-formation, cross-linking, and so forth [126]. As trial-error exercises, material scientists adapt enormous strategies for modifying hard or soft segments of WPU to improve its performance and add novel properties. Yu et al. developed a β -cyclodextrin modified aliphatic WPU with an intumescent flame-retardancy attribute [127]. Zhang and his group incorporated octahydro-2,5-pentalenediol (OPD) into a castor oil-based WPU to enhance physical and thermo-mechanical properties [128]. Zhu et al. prepared a series of phosphorescent self-healing WPU by introducing Schiff bases containing

disulfide and acylhydrazone bonds [129]. Moreover, in IPN or hybrid system, two polymers are connected via chemical or physical cross-linking. Remarkably, WPU/acrylic hybrid dispersion is tremendously used as coatings and paints. For example, Meng et al. developed soybean oil-based WPU/acrylate hybrid dispersion which can be used as a self-matting coating [130]. Another WPU/acrylate dispersion was prepared by Du and co-workers via seed emulsion technique and utilized the same for designing fluoride-free water repellency cotton fabrics [131].

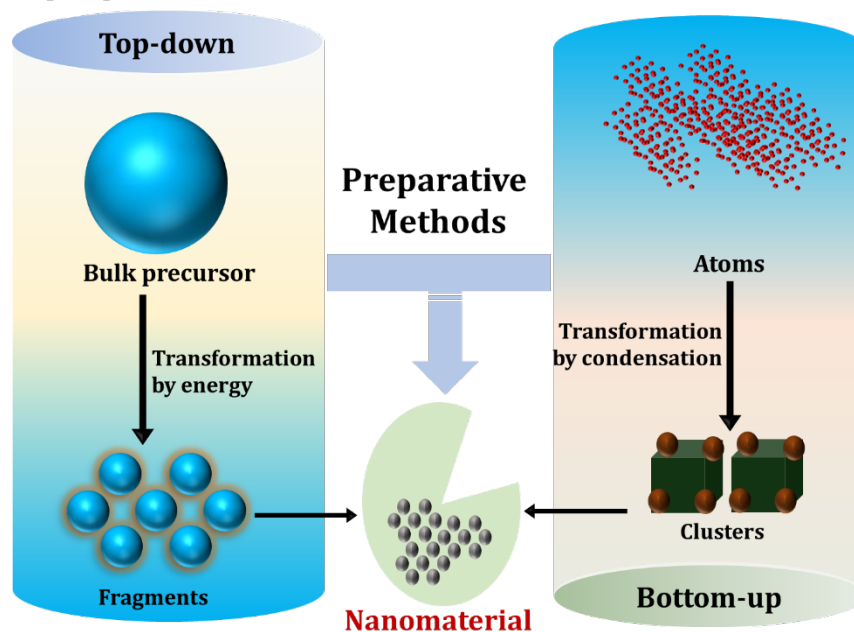


Figure 1.3. Preparative methods of nanomaterials.

1.3.2.3. Nanomaterial preparation

Nowadays several methods have been implemented to prepare nanomaterials and their hybrid which are broadly categorized into two groups: (i) top-down and (ii) bottom-up, as shown in **Figure 1.3**. As the name suggested, the top-down method involves reduction of the size of bulk precursors into the corresponding nano-dimensional materials via physical treatments including mechanical milling, laser ablation, etching, sputtering, and electro-explosion [107]. Conversely, in the bottom-up method, nanomaterials are synthesized by meticulous aggregation of molecular-level precursors viz. atoms or molecules. Examples of bottom-up methods are chemical vapor deposition (CVD), solvothermal and hydrothermal approaches, sol-gel method, reverse micelles formation, etc. Notably, the bottom-up approach is more expedient than the top-down approach because it is cheaper, requires less time, delivers high purity, and easy controllability in morphology and size distribution of the nanomaterials, and so forth [132].

1.3.2.4. WPUNC fabrication

To create a win-to-win situation, the specific nanomaterial is amalgamated with WPUs to obtain WPUNCs via physico-chemical interactions. Preferably, this synergistic effect always improves materials' quality and performance. The most used fabrication techniques are solution technique, *in situ* polymerization, and melt mixing, etc.

(a) Solution technique

This is an *ex situ* technique that is comprised of two basic steps viz. swelling and dispersion of the nominated nanomaterial in a suitable solvent or mixture of solvents (wherever it will disperse properly) assisted by mechanical force and ultrasonication. Subsequently, dispersed nanomaterials are mixed with a solution containing WPU using the same high shearing force and ultrasonication, resulting in WPUNC dispersion. Finally, used solvents are removed by reduced pressure or rotary evaporator. In this technique, solvent-nanomaterial interaction is dominant and WPU chains are confined within the solution which results in intercalated WPUNC, predominantly, and small portions of exfoliated version obtained. Moreover, the dispersion stability and interfacial adhesion can be amended using surfactant and functionalization. Varieties of WPUNCs can be fabricated using the solution technique, e.g., a series of WPU/ZnO nanocomposites prepared by Christopher et al. applicable for corrosion protection [133]. Recently, Jiang and his group designed a silver nanowire (AgNW)/WPU conductive nanocomposite film with self-healing ability which can be used in high-performance wearable electronics [134].

(b) *In situ* polymerization

In this highly effective fabrication technique, a particular nanomaterial is swollen and dispersed into one of the monomers or prepolymer which is polymerized successively to prepare the targeted WPUNC. Interestingly, the interaction that existed between polymer and nanomaterial is more dominating because of the low viscosity of the blend. As a result, a decent WPUNC dispersion is overserved, hence the formation of exfoliated WPUNC [135]. Therefore, *in situ* is more favorable than other fabrication techniques. Prior art literature divulges the availability of enormous articles related to WPUNC fabrication using this technique. For example, recently, Li et al. reported WPU/B-rGO@Ti₃C₂T_x nanocomposites with strain sensing, electrical conductivity, and EMI shielding ability; Nan et al. fabricated WPU/ND-NH₂ (amino-functionalized nanodiamond) nanocomposites to enhance thermos-mechanical properties, through *in situ* polymerization [136-137].

(c) Melt mixing

As the name suggested, in the melt mixing approach, the polymer matrix is amalgamated directly with a suitable nanomaterial in the molten state using appropriate machines such as twin-screw mixers, rollers, extrusion molding, injection molding, etc. [138]. In this technique, high temperature (above the melting temperature (T_m) but below the degradation temperature) and high shear forces were applied in an inert atmosphere (N_2 or Ar gas) to disperse the nanomaterials in the semi-crystalline thermoplastic WPU system. This technique is expedient for large-scale production of WPUNC because this technique avoids the volatile organic solvents in the fabrication process. Usually, partially exfoliated or only intercalated nanocomposites can be developed due to the high viscosity of the blend. Moreover, this technique offers a less toxic route to those polymers that cannot form nanocomposites via *in situ* polymerization or solution mixing techniques. For example, Sheng et al. prepared a series of 2-D Ti_3C_2 MXene/thermoplastic PUNCs with superior thermo-mechanical properties, and Pishvar and co-workers achieved thermoplastic PU/ PTFE (poly(tetrafluoroethylene)) fibril nanocomposites, using melt mixing technique [139-140].

Furthermore, other useful technique that can be employed for nanomaterials fabrications includes the pulverization process, latex stage fabrication, template synthesis, coagulation spinning, sol-gel process, plasma treatment, thermal decompositions, and so forth [107].

1.4. Characterization

WPU, WPUNC, and nanomaterials are characterized by various spectroscopic, microscopic, diffraction, TGA, DSC, and so forth techniques. For better understanding, a brief explanation is provided in the following subsections.

1.4.1. Spectroscopic techniques

1.4.1.1. Ultraviolet-visible (UV-Vis) spectroscopy

UV-Vis spectroscopy or absorption spectroscopy or reflectance spectroscopy is a common, powerful, cost-effective, and non-destructive analytical technique. It deals with the transition in molecule's electronic energy levels due to the absorption of electromagnetic radiation in the UV-visible region (UV: 200-400 nm and visible:400-800 nm). Simply, the optical and electrical properties of WPU, WPUNC, and nanomaterials can be evaluated by this technique. Each nanomaterial or nanocomposite possesses characteristic electronic transitions (e.g. $\pi \rightarrow \pi^*$, $n \rightarrow \pi$, etc.) which can be monitored and identified using this tool after successful nanomaterial formation and nanocomposite fabrication. For example, in a UV-Vis spectrum of oxygenated-g- C_3N_4 dots, an intense absorption maximum (λ_{max}) is overserved at 235 nm

which can be attributed to $\pi \rightarrow \pi^*$ electronic transition of the tri-s-triazine motif and a broad peak in between 280-490 nm corresponds to $n \rightarrow \pi^*$ electronic transitions within surface passivating functional groups [141]. In the case of GO, the characteristic λ_{\max} is observed at 232 nm ($\pi \rightarrow \pi^*$ transition) which is shifted to near 270 nm after reduction i.e., rGO formation [142]. Again, surface plasmon resonance (SPR) can be recognized by UV-vis spectroscopy which helps to investigate metallic nanomaterial embedded nanocomposites, specifically, shape, size, and distribution of the nanoparticles [143]. Besides, band gap (eV) and percentage of transmittance of nanomaterials and nanocomposites useful in electronic devices, can also be obtained using this technique.

1.4.1.2. Fourier transform infrared (FTIR) spectroscopy

Presently, FTIR or vibrational spectroscopy has become one of the ubiquitous analytical techniques in science due to its unique features e.g., sensitivity and specificity. This spectroscopic technique is concerned with the change in vibrational energies of polar groups or functional groups when it interacts with IR radiation (wavelength: 780 nm to 1 mm or wavenumber: 12,800 to 10 cm^{-1}). Basically, photo energies ($h\nu$) originating from the IR region cause vibrational excitation in covalently bonded atoms, and these bonds vibrate in different ways such as stretching, bending, rotating, and scissors. In PU chemistry, the presence of important functional groups such as carbamate or urethane group ($-\text{NH}-\text{C}(=\text{O})-\text{O}-$), carbonyl groups ($-\text{C}=\text{O}$) of amide, ester; amine ($-\text{N}-\text{H}$) group, etc., can be easily detected FTIR spectral analyses. Conspicuously, in an FTIR spectrum of WPU, N-H stretching frequency is observed near 3400-3500 cm^{-1} , while characteristic sharp peaks near 1620-1750 cm^{-1} correspond to $-\text{C}=\text{O}$ stretching vibration [25]. Importantly, this technique detects the completion of the isocyanate reaction by scrutinizing the disappearance of free $-\text{N}=\text{C}=\text{O}$ groups in the range of 2260-2270 cm^{-1} in an FTIR spectrum [16]. Moreover, the effective blending of nanomaterials with PU can also be verified by this technique. For example, the presence of a sharp characteristic peak of at 808 cm^{-1} (corresponding to triazine rings) in a PU nanocomposite reveals the successful amalgamation of g- C_3N_4 nanosheets [144].

1.4.1.3. Nuclear magnetic resonance (NMR) spectroscopy

It is familiar that NMR spectroscopy is one of the most sophisticated and inevitable structural elucidation analytical techniques. In other words, it is almost impossible to identify the chemical structure of an unknown compound. In this technique, a strong external magnetic field and particular radio frequency pulses are applied to an atomic nucleus having either an odd atomic number or mass (e.g., ^1H , ^{13}C , ^{15}N , etc.) to resonate with the nuclear spin frequency conferring to chemical environments. In addition to structural analysis, NMR

spectroscopy also offers exclusive information e.g., isomerism, stereo-selectivity, product yield, kinetics of polymerization, degree of branching, impurities, etc. For example, Raju et al. performed a complete structural investigation on a PU prepolymer derived from polypropylene glycol (PPG) and IPDI using 1D and 2D NMR spectroscopies [145]. Again, Karak and his groups have extensively studied the estimation of the degree of branching from the peak intensities of linear, terminal, and dendritic moieties of the hyperbranched PU [146, 147].

1.4.1.4. X-ray photoelectron spectroscopy (XPS)

XPS is a quantitative analytical technique widely used for determining the elemental compositions of the surface of the material, their binding energies (eV), binding states or oxidation states, film thickness, etc. In this technique, the highly energetic X-ray beam is produced by electron bombardment of a pure metal e.g., Al or Mg, resulting in the emission of radiation with specific energies, e.g., the k_{α} line for Al occurs at nearly 1486.6 eV. This X-ray beam is used as a photon to eject the surface electron of the considered material and characterize the same by quantification of kinetic energy and their corresponding binding energies [148]. Presently, XPS analyses are mandatory and utterly used for each nanomaterial, nanohybrid, and nanocomposite designed and executed for advanced applications. For example, Jian et al. established the development of heterogeneous $ZrN_{0.4}B_{0.6}/SiC$ nanohybrid with high-temperature oxidation-resistant and microwave absorption attributes and Zeng et al. confirmed the smooth modification of WPU/F-SiO₂ nanocomposite coating, using XPS analyses [149-150].

1.4.1.5. Photoluminescence (PL) spectroscopy

According to IUPAC, luminescence is defined as the spontaneous emission of radiation from an electronically excited species not in thermal equilibrium with its environment. This fascinating and colorful phenomenon can be evaluated and characterized by photoluminescence (PL) spectroscopy. The emission occurs in the UV, visible, or near IR range depending on the amplitude of the energy gap (E_g) existed between the valence band (VB) and the conduction band (CB). The state of literature advocates a huge number of luminescent materials that have been discovered in the past decades including MOF phosphors, carbonized polymer dots (CPDs), QDs, and so forth. Additionally, PL spectroscopy is widely used for determining quantum yield, band gaps of semiconductors, tracking solvation dynamics, monitoring biochemical reactions, etc.

1.4.1.6. Raman spectroscopy

Raman spectroscopy is another versatile and non-destructive analytical technique that provides useful information about chemical structure, phase separation, polymorphy, crystallinity, and molecular interactions. In this technique, scattered light is involved to determine the vibrational energy modes of the analyzed sample. Interestingly, Raman spectroscopy is extensively applied to characterize nanomaterials as it provides signature-like data. Most of the carbon-based nanomaterial shows characteristic Raman scattering bands in the range of 1000-3000 cm^{-1} [151]. For example, in a Raman spectrum of GO, the D-band appeared close to 1350 cm^{-1} and the G-band observed close to 1580 cm^{-1} can be accredited to graphitic structural defects and the breathing mode of sp^2 hybridized graphitic segments. Furthermore, the intensity ratio of these two bands viz. I_D/I_G assists in scrutinizing the structural defects. The greater the I_D/I_G value higher the defect within the matrix [152]. Julien et al. elucidated structure disorder present in $\gamma\text{-MnO}_2$, quantitatively, and Jian and coworkers established successful functionalization of GO with aminopropyltriethoxysilane (APTES) and 3-aminopropyltrimethoxysilane (APTMS), using Raman spectroscopy [153, 154].

1.4.2. Microscopic techniques

1.4.2.1. Optical microscopy

Optical microscopy, also known as light microscopy, is comprehensively used to study the morphology of nanomaterials and other particles, crystal growth behavior, and kinetics of polymeric materials. In this technique, visible light is employed in order to illuminate the sample and a group of lenses to create magnified images of small objects. For example, Stanciu et al. determined complex permittivity mapping along with other important properties using special optical microscopy i.e., scattering-type scanning near-field optical microscopy (s-SNOM) [155]. Again, Gao et al. evaluated the dispersion state of graphene, GO, hexagonal boron nitride (h-BN) nanosheets in PPG by an optical microscope at 400X magnification [156].

1.4.2.2. Scanning electron microscopy (SEM) and field emission SEM (FESEM)

SEM is an advanced microscopic technique that uses highly energetic and focused electron beams rather than light and electromagnetic lenses instead of normal glass, to produce high-resolution and 3D images. Typically, two types of electron beams are used in SEM, namely, the backscattered electrons (BSE) and the secondary electrons (SE). Recently, SEM has been widely used in nanoscience and biology as it provides precise information about surface morphology i.e., texture, shape, size, etc. For example, Tan and co-workers developed non-canonical self-assembly of multifunctional DNA nanostructures or nanoflowers (NFs) from

long DNA building blocks generated via rolling circle replication (RCR) and they observed the beautiful images of NFs in SEM [157]. Again, Hejazi et al. verified the hierarchical packed morphology of silica nanoparticles using SEM that was embedded in self-cleanable PU/silica nanocomposites [158].

Furthermore, FESEM is another advanced and powerful microscopic technique that produces higher magnification and resolution images than SEM. Noticeably, this technique offers topographical and elemental data at magnifications of 10x to 300,000x, with virtually unlimited depth of field. In SEM, the focused electron originates from a thermal emission source such as a heated tungsten filament while a field emission gun discharges that highly energetic focused electron beam in FESEM. Recently, Chang et al. prepared a ferrocene/ZnO/nitrogen-incorporated nanodiamond/Si heterojunction nanostructure for measuring glucose in saliva and confirmed its typical acicular-shaped structure using FESEM [159].

Moreover, SEM or FESEM merged with the electron dispersive X-ray (EDX) technique is widely employed to gain information regarding the elemental composition of an unknown material, nanomaterial, or WPUNC.

1.4.2.3. Transmission electron microscopy (TEM)

TEM is the most sophisticated and indispensable microscopic analytical technique deployed to visualize the tiniest structures in matters. It can divulge magnificent detail at the atomic scale by magnifying nano-sized structures up to 50 million times. The extremely high energetic electron beam is accelerated through a strong electromagnetic field and then transmitted through the sample to be analyzed, resulting in microscope images of several orders of magnitude. Nowadays, the most commonly used TEM instruments are (i) conventional TEM (CTEM) and (ii) scanning TEM (STEM). Remarkably, in addition to topographical information, other vital nano-scaled properties such as structural defects, crystallinity, interplanar distance, particle size distribution, etc. can be obtained accurately from high-resolution (HR-TEM) micrographs and selected area electron diffraction (SAED) pattern [109]. Because of its accuracy and great array of information, TEM is incredibly useful in life science and nanotechnology. Recently, Yu et al. confirmed the 3D hollow colloidosomes and multilayer sheet-like structure of polymer-tethered gold nanoparticles using TEM [160].

1.4.3. Diffraction technique

1.4.3.1. X-ray diffraction (XRD)

XRD is a versatile analytical technique that provides decisive information about the chemical composition, crystal structure, crystallite size, lattice strain, preferred orientation, layer thickness, and inter-layer distance, accurately and non-destructively. Materials consist of either single phase or multiple phases and they may be crystalline semi-crystalline or amorphous. In an X-ray diffractometer, distinct crystalline phases result in distinct diffraction patterns. Specifically, the X-ray diffraction pattern originates from the constructive interference between a crystalline material and X-rays. Again, the resultant diffraction pattern carries vital information related to crystallinity which can be analyzed in various ways including the most famous Bragg's law.

$$n\lambda = 2d \sin\theta \quad \text{Eq. 1.1}$$

Here, n , λ , d , and θ refer to the order of diffraction, the wavelength of X-ray employed, interplanar distance, and diffraction angle, respectively.

Notably, the outcome diffraction pattern of an unknown sample is compared with existing reference databases for phase identification. Nowadays, the ICDD (International Center of Diffraction Data) maintains and stores all exclusive XRD data that can be used as a reference. Therefore, XRD can be prominently employed to characterize nano-structures and WPUNCs. For example, graphite shows a strong diffraction peak at $2\theta = 26.4^\circ$ for plane 002 which shifts to $2\theta = 7.80^\circ$ after oxidizing into GO [161]. Again, for a pure bulk g-C₃N₄, a characteristic peak observed near $2\theta = 27.6^\circ$ corresponding to the interlayer stacking of aromatic segments (002) with an inter-planar distance $d = 0.32$ nm and another peak near $2\theta = 13.3^\circ$ can be accredited to the in-plane repeated tri-s-triazine units (100) with a separation of $d = 0.66$ nm [162]. Moreover, the crystallite size of a sample is evaluated by the Scherrer equation as written below.

$$L = \frac{K\lambda}{\beta \cos\theta} \quad \text{Eq. 1.2}$$

Here, L , K , λ , β , and θ , denote nano crystallite size, shape factor or Scherrer constant, the wavelength of X-ray, the full width at half maximum (FWHM), and Bragg's angle, respectively. Zhao et al. synthesized hydrotalcite-like layered double hydroxides (LDHs)-based nanomaterials with crystallite size in the range of 60-80 nm [163].

1.4.4. Other techniques

1.4.4.1. Thermogravimetric analysis (TGA)

TGA is a popular analytical tool used to evaluate a material's thermal stability and its fraction of volatile parts by supervising the weight change with temperature in a specified

environment and at a constant heating rate. As per the requirement, TGA is performed in oxygen (O₂) or inert (e.g., N₂) atmosphere. In addition to thermal stability, this technique also offers different information associated with a sample e.g., transitions in phases, adsorption-desorption, thermal oxidation-reduction reactions, thermal degradation kinetics, and so forth. The first order derivative curve i.e., the DTG curve helps to find out the precise degradation pattern, maximum weight loss temperature, etc. Notable, the thermal degradation temperature of pure urethane linkages falls in the range of 220-350 °C which can be enhanced by nanomaterial fabrications. For example, Lio et al. prepared a series of jatropa curcas oil-based WPU/clay nanocomposites and Kale et al. developed WPU/GO-silica nanocomposites, exhibiting better thermal stability than that of pristine WPU [164-165].

1.4.4.2. Differential scanning calorimetry (DSC)

DSC is another powerful thermal analytical tool used extensively to understand the thermal transition behavior of a sample. This involves the determination of the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature, in an inert atmosphere (e.g., N₂). The DSC thermogram is obtained as the plot of deviations in heat flow (mV) versus temperature. From a comprehensive DSC curve of a particular material, several vital information can be acquired such as glass transition temperature (T_g), melting temperature (T_m), melting enthalpy, crystallization enthalpy, specific heat, and so forth [166]. Recently, Sun et al. developed a series of flame retardant WPU and they reported that T_g obtained from DSC is consistent with that value overserved in dynamic mechanical analyzer (DMA) [167]. Furthermore, Gogoi et al. studied the cross-linking kinetics to optimize the curing parameters of a hyperbranched PU/epoxy thermoset, using a DSC machine [168].

1.4.4.3. Gel permeation chromatography (GPC)

GPC, also called size-exclusion chromatography is a highly effective separating method in which molecular separation occurs according to their molecular weight or size. In polymer science, GPC is used to determine various average molecular weights e.g., number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity indices (PDI). A standard polymer comprises several segments and short to long polymeric chains so the separation can be accomplished based on the hydrodynamic volumes or molecular weight. In GPC, samples are passed through a chromatographic column packed with a material (reference polymer) with known pore size, e.g., semi-rigid polystyrene bead cross-linked with divinylbenzene and organic solvent (e.g., THF, DMF, NMP, etc.) used as the eluent.

Interestingly, high molecular weighted chains possess lower retention time as they cannot penetrate through the reference so elute faster than low molecular weighted chains. The GPC chromatograms correlate the refractive index or UV-absorption intensity as the function of elution volume with distinct average molecular weight. Recently, Rwei and co-workers determined the molecular weights of WPU/urea using GPC with 270 and 3580 RI detectors and a Shodex GPCKF-805L column [169].

1.4.4.4. Dynamic light scattering (DLS)

DLS also known as quasi-elastic light scattering (QELS) or photon correlation spectroscopy, is a non-invasive analytical technique used for assessing the hydrodynamic size and distribution of particles or molecules that have been dispersed or dissolved in a liquid. Laser lights incident on dispersion or solution started scattering at various intensities because of the Brownian motion of dispersed particles or molecules. Brownian motion of particles associated with their hydrodynamic size i.e., diameter. Remarkably, analysis of the intensity fluctuations yields the velocity of the Brownian motion and hence the particle size using the Stokes-Einstein equation mentioned below.

$$D = \frac{kT}{6\pi\eta R_h} \quad \text{Eq. 1.3}$$

Here, D , k , T , η , and R_h refer to diffusion coefficient, Boltzmann's constant, temperature, solvent viscosity, and hydrodynamic radius of particle solution, respectively. Moreover, DLS commonly regulates and measures the agglomeration state of nanoparticles in terms of zeta potential (ζ). Recently, Chen et al. measured the size and distribution of dye-incorporated WPU-urea using DLS [170].

1.4.5. Testing method

Different testing methods are used to evaluate the performance of WPU, modified WPU, and WPUNC. The following sub-section entails these tests.

1.4.5.1. Mechanical test

Mechanical properties such as tensile strength, strain (%), mechanical toughness, and fracture toughness of WPU and WPUNCs are investigated using a universal testing machine (UTM). The tensile test is performed on thin WPU and WPUNC films by following the ASTM D882 method. The standard ASTM D1037 method is adopted for calculating impact resistance. Fracture toughness was measured using Greensmith's method as per the ASTM E1820 method [171]. Furthermore, scratch resistance ability was studied using the standard

ASTM D7027 method. Additionally, a stress-relaxation experiment was carried out to understand rheological behaviors using a DMA.

1.4.5.2. Self-healing (SH) test

For the SH test, a standard-size polymeric film is cut by a new and sharp razor blade into a transverse direction. Then, cut pieces are joined carefully and healed using various stimuli e.g., microwave radiation, heat, sunlight, etc. The SH efficiency was calculated by measuring the tensile strength of the considered specimen before and after healing according to the following equation.

$$\text{Self – healing efficiency (\%)} = \frac{\text{Tensile strength}_{\text{after healing}}}{\text{Tensile strength}_{\text{before healing}}} \times 100 \quad \text{Eq. 1.4}$$

1.4.5.3. Shape memory (SM) test

Shape memory aptitude of WPU and WPUNCs is scrutinized via two standard tests namely, spiral bending and envelope-like square bending test as discussed below.

(a) Spiral bending test

As the name suggested, in this test, the polymeric films are deformed into a temporary spiral shape by heating above their T_g and immersed in an ice bath immediately to fix that shape. Finally, the original shape is recovered by inducing external stimuli e.g., heating, warm water, and microwave radiation. The test is based on two special parameters viz. shape fixity (%) and shape recovery (%) which can be determined by the following equation.

$$\text{Shape fixity (\%)} = \frac{90 - \theta_f}{90} \times 100 \quad \text{Eq.1.5}$$

$$\text{Shape recovery (\%)} = \frac{180 - \theta_r}{180} \times 100 \quad \text{Eq. 1.6}$$

Here, θ_f and θ_r refer to the angle after the shape fixation step and the unrecovered angle after the shape recovery test, respectively.

(b) Square bending test

This test involves the measurement of the same parameters as in the case of spiral bending tests. However, the polymeric films are temporarily fixed into a rectangular shape instead of a spiral shape. The percentage of shape recovery is calculated using equation 1.6. But shape fixity is measured by the following equation.

$$\text{Shape fixity (\%)} = \frac{180 - \theta_f}{180} \times 100 \quad \text{Eq.1.7}$$

1.4.5.4. Reprocessability test

A reprocessability test is carried out using a compression molding machine under the desired pressure (say, 60-80 kg cm⁻²) at different temperatures. In this test, used films are cut into small pieces (approx. 1 cm²) and then placed inside the two heating plates of the compression molding machine for reprocessing under ambient conditions.

1.4.5.5. Surface hydrophobicity/hydrophilicity test

This test is performed to investigate the hydrophobic or hydrophilic nature of the developed film using an automatic contact angle meter DropMaster. Digital photos of water droplets (approx. 5 μL) dropped on the film surface are captured using a camera equipped with the DropMaster.

1.4.5.6. Biocompatibility test

To establish the biocompatibility nature of the developed WPU and WPUNC films a series of tests are carried out including platelet adhesion study and lactate dehydrogenase (LDH) activity, erythrocyte lysis study, *in vitro* degradability assessment, *in vitro* cytocompatibility and cell proliferation assessment, MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay, etc. For the *in vitro* hemocompatibility study goat blood is used, while for the cell compatibility study, different types of cells are employed (say, human dermal fibroblasts (HDF), mouse fibroblast cell lines (L929), etc.).

1.4.5.7. Antimicrobial test

The antimicrobial activity of drug-loaded WPUNC films is evaluated by the agar diffusion method [172]. All bacterial strains (Gram-positive and Gram-negative) are grown overnight in Luria Broth (LB) inside an incubator. The optical density (OD) or absorption at 600 nm of the fresh cultures is set at 0.4 and then spread on Luria-Bertani agar (LBA) plates. These plates are incubated again for 24 h at 37 °C. Finally, the plates were assessed for antimicrobial activity and the zone of inhibition (ZOI) was measured.

1.4.5.8. UV-aging test

The standard ASTM G53-96 protocol is employed to study the effect of UV light on the mechanical properties of WPU by irradiating them with a UV light of the wavelength of 256 nm for a certain period [173]. To determine the retention (%) of mechanical properties, a tensile test is carried out on WPU and WPUNC films before and after the UV-aging test.

1.4.5.9. Chemical resistance test

The chemical resistance ability of WPU films is scrutinized by dipping them in different media such as acid, base, alcohol, and tap water for a long period of time as per the standard ASTM D543 method. The weight loss percentage is considered for the quantitative evaluation of chemical resistance.

1.4.5.10. Biodegradation test

The standard ASTM D6691 method is implemented to establish the biodegradability nature of the WPU and WPUNC films. Like antimicrobial test, two bacterial strains viz. *B. subtilis* and *P. aeruginosa* are cultured in an incubator under a suitable environment. Then, sterilized polymeric films are submerged in the bacterial solution and allowed for bacterial growth for a certain period. The biodegradation is monitored and calculated by measuring weight loss percentage and OD or absorbance at a fixed wavelength of 600 nm. Additionally, soil burial tests are also performed in an open environment to ensure real-life practices.

1.5. Properties

The marketability of a material entirely depends on its performance and hence its innate properties. Interestingly, WPU has various eye-catching properties that make it a versatile polymer, undoubtedly. These properties can be further tuned, or new advanced features can be introduced into the pristine WPU matrix by incorporating a specific nanomaterial. The following sub-sections explain the indispensable properties of WPUs and WPUNCs.

1.5.1. Physical properties

The numerous physical properties of WPU and PUNC in the form of film and dispersion are color, the particle size of WPU and WPUNC in the dispersion, colloidal stability, molecular weight, specific gravity, viscosity, transparency, water contact angle, etc. Mostly, the color of bare WPU dispersion is milky white but may be available in others depending on the reactants and nanomaterial used. Similarly, the color of the WPU and WPUNC films varies with the color of the raw materials. For example, WPU films prepared from castor oil and 2-APDS are found to be brown in color [18]. Notably, WPU and WPUNC particle size widely rely upon the degree of neutralization, amount of emulsifier, and cross-linking density. Small particles can be obtained by optimizing these three primary factors. Generally, small particle size results in good colloidal stability with a zeta potential (ζ) value lower than -30 mV for anionic dispersion and greater than +30 mV for cationic dispersions [174]. The molecular weight of WPU is directly associated with other properties. For example, WPU elastomers with high molecular weight exhibit better mechanical strength than that of lower molecular weight counterpart [74]. Solubility test reveals that WPU films are soluble in polar solvents

such as THF, DMF, DMSO, etc. An increment in specific gravity is observed with an increase in crystallinity, content of metal-nanohybrids, and polar groups [16]. WPU films are found to be sufficiently transparent which gradually decreases with an increase in crystallinity and number of cross-linkers. Furthermore, the contact angle of WPU films is always lower than 90° due to the presence of high number of polar groups on their surfaces.

1.5.2. Mechanical properties

WPU and WPUNC must possess optimum mechanical properties as the polymeric materials otherwise no one will prefer to use them. Fortunately, they have incredible mechanical properties such as tensile strength, stretchability, toughness, scratch, impact, and puncture resistance, and fracture toughness under static and dynamic conditions. Interestingly, these properties can be revamped by altering the soft segment to hard segment ratio and nanocomposite fabrications as stated in the introductory section. The interactions that exist between the WPU matrix and nanomaterial play a key role in controlling the performance of the nanocomposites and a minute amount of appropriate nanomaterial can greatly enhance inborn properties [118]. A literature study discloses that the tensile strength of WPU elastomers can be increased exponentially using various nanomaterials. For example, Kuan et al. reported that the tensile strength of WPU increased up to 370% of the original value after incorporating MNCNT into it [61]. Similarly, Li and co-workers observed an increment in the tensile strength of WPU/CNC nanocomposites from 4.27 to 14.86 MPa with increasing CNC content from 0 to 30 weight (wt)% [63]. Prior literature also reveals the decrement of stretchability concurrent with the increment in the tensile strength. For example, Gurunathan and Chung found that strain (%) at break decreases from 392.11% to 140.16% with an increase in 3-aminopropyl trimethoxysilane (APTMS) from 0 to 2% in WPU/silica nanocomposites [175]. Moreover, Lee and Lin reported that tensile strength and strain percentage can be increased, simultaneously via WPU/clay nanocomposite formation [62]. Therefore, it is noteworthy to mention that tensile strength is dose-dependent, and the extent of its improvement exclusively depends on the dispersability of the selected nanomaterial in the WPU matrix.

1.5.3. Thermal properties

Like mechanical properties, the thermal properties of WPU and WPUNCs also play an important key role in designing a high-performance material. The thermal properties entail a thermal degradation profile and various thermal transition temperatures such as T_g , T_m , crystallization temperature (T_c), etc. Prior literature advocates that the thermal stability of WPU is greatly influenced by cross-linking density, segmental rigidity, and availability of

thermostable nanomaterials. Generally, metal-based and carbon-based nanomaterials enhance the thermal stability of WPU by creating a physico-chemical barrier that inhibits the escaping affinity of volatile moieties and delays the thermal degradation process. For example, Liao et al. reported that thermal stability and T_g of jatropha curcas oil-based WPU/clay nanocomposite films increased with an increase in clay content which raises high cross-linking density [164]. Jean and co-workers observed two types of T_g viz. lower $T_g \sim 220$ K (soft segment) and higher $T_g \sim 380$ K (hard segment) for WPU/ZnO nanocomposites which were increased with increasing ZnO content from 0% to 5% [31]. Recently, Ye et al. also observed a significant increment in the thermal stability of WPU/tetraphenylethylene (TPE)-CNC nanocomposite films increase in the content of TPE-CNCs [176].

1.5.4. Shape memory (SM) property

SM is a smart property that originates from the shape memory effect (SME). WPU and WPUNCs with SM ability are extensively used in medical and biomimetic devices (e.g., soft artificial muscle), self-healable materials, actuators, biosensors, and so forth. The SME is associated with two main attributes viz. (i) “memory” of a stress-free permanent shape i.e., original shape and (ii) “programming or fixing” of an impermanent shape by external stimuli such as heat, sunlight, etc. through the three stepped heating–deformation–cooling cycle [177]. Conspicuously, memory is governed at the molecular level by a reversible phase (covalent or non-covalent crosslinks), while programming is accomplished by kinetic trapping of the fixation phase through distinct processes such as crystallization, vitrification, crosslinking, or plastic deformation [178]. Finally, these molecular-level dynamic and changeable transformations transfer polymeric chain that causes macroscopic shape deformations. Over the past few years, there has been a significant focus on SM and other smart properties, as evidenced by literature studies. For example, Ma et al. developed a series of robust room temperature self-healable WPU with a shape fixation rate of 99% and recovery rate of 98% using 5-(2-hydroxyethyl)-6-methyl-2-aminuracil (HMA), 4-aminopyridine (4-APD) and PCL moieties [179]. Jian and co-workers prepared TOCNF)-WPU hybrid films which exhibited excellent self-healing and shape memory ability [71]. Recently, Liu et al. reported a series of nonionic WPU/iron-gallate (GA-Fe) composites that showed outstanding near-infrared (NIR) light-induced shape memory behavior [28].

1.5.5. Self-healing (SH) property

SH is another vital smart property of smart WPU and WPUNCs that has created a great deal of fame within a short span of time. Generally, self-healing mechanisms can be divided into two broad groups: extrinsic and intrinsic [6]. In extrinsic self-healing mechanisms, external

healing agents such as reparable monomers, catalysts, and initiators are amalgamated with the polymer that assists in repairing damaged surfaces. However, this route is not the first choice for healing as it occurs in a single event. Conversely, intrinsic self-healing is induced by dynamic covalent bonds or non-covalent bonds, and the repairing process is repeatable. Nowadays, researchers have developed enormous strategies based on reversible covalent bonds such as disulfides bonds, diselenide bonds, B–O bonds, hindered urea bonds, etc., and non-covalent interactions e.g., hydrogen bonds, metal-ligand interactions, π - π stacking interactions, ionic interactions, host-guest interactions, and so forth [2,6]. Regardless of the nature of the dynamic interactions, the self-healing process consists of five major stages, (i) segmental surface rearrangement, (ii) surface approach, (iii) wetting, (iv) diffusion, and (v) randomization. External stimuli such as solvent, sunlight, microwave radiation, heat, electricity, etc. are used to help the polymeric chains undergo wetting, diffusion, and randomization. Moreover, the introduction of a suitable nanomaterial into a WPU can amplify the healing ability by reducing healing time and the amount of energy required for healing. Presently, a huge number of articles are available that explain various tactics adopted for achieving high-healing efficiency and mechanical robustness. For example, Zhu et al. prepared a series of WPU with excellent self-healing (up to 93.7%) based on Schiff bases containing disulfide and acylhydrazone bonds (PD) [129]. They have used PD not only as a physical cross-linking center which encourages the microphase separation of WPU to enhance the thermal stability and toughness, but also as serves as a “clip” to integrate various dynamic bonds to increase chain mobility with faster fluidity. Luo and coworkers developed a self-healable WPU by introducing silver–thiol coordination interactions and reported that a maximum self-healing efficiency of 98.69% was obtained for the representative WPU–Ag@S-0.50 film at room temperature within 30 min [180]. Recently, Liu et al. also prepared self-healable WPU containing dynamic quadrupolar hydrogen (UPy) and aromatic disulfide bonds and observed self-healing efficiency of 95.1% within 8 h at room temperature and 98.6% within 30 min at 80 °C [181].

1.5.6. Chemical and weather resistance properties

The chemical-resistant nature of WPU deals with the change in their inherent properties after being in contact with other chemicals, such as acid, base, salt solution, alcohol, etc. For real-life applications, WPU should be chemically inert to these chemicals. Notably, the resistance ability absolutely depends on the chemical structure, availability of free form, and their polarity. Generally, WPU shows low resistance towards water and alkaline media due to the presence of numerous polar groups in the polymeric backbone (e.g., ester linkages) which easily undergo hydrolysis in the presence of a base. However, this issue can be

resolved by precise molecular engineering such as hybrid formation and nanocomposite fabrications. For example, Zhu et al. improved the chemical resistance and abrasion durability of WPU by incorporating highly dispersed PAA-nGO (poly(acrylic acid) modified GO) along with an increment in mechanical strength of 56.1% of the pure WPU film [182]. Again, Liang et al. carried out chemical grafting of GO within the WPU matrix in order to improve mechanical properties and solvent resistance power and they observed satisfactory results [183].

Again, the aging of polymeric material in a harsh environment is an inevitable process that shortens their service life. Remarkably, WPU with chemical moieties (e.g., aromatic rings, and double bonds) that are sensitive to UV light or other light, will easily undergo photo-degradation in an outdoor environment. Nevertheless, the weather resistance capacity of WPU can be amplified via chemical modifications. For example, Dall Agnol et al. prepared a series of WPU/AgNPs that exhibited extreme weather resistance capability along with antibacterial activity against *E. coli* and *S. aureus* even after three months of use [184].

1.5.7. Biological properties

In real-life practices, WPU's biological properties are highly significant which include biodegradability, hemocompatibility, cytocompatibility, anti-bacterial activity, etc. Biodegradation of a polymeric material involves four major steps: (i) swelling or permeation of water molecule, (ii) cleavage of ester linkages via hydrolysis, (iii) solubilization of hydrolyzed products, and (iv) transformation into water, carbon dioxide, and humus by enzyme catalysis and bacteria. Notably, biobased WPU is more biodegradable than other synthetic polymers e.g., polyethylene due to the presence of large numbers of hydrolyzable moieties (e.g., ester and amides) in their polymeric backbone. Literature reveals that some nanomaterial assists in the biodegradation of pristine polymer rather than its suppression which commonly occurs. For example, Sheen et al. developed regenerated cellulose nanoparticles (RCNs)/WPU nanocomposites that exhibited better biodegradability than the bare WPU via enzymatic hydrolysis using cellulase [185]. Chang et al. also observed improvement in the biodegradability of WPU after incorporating starch nanocrystal-graft-PCL into it [186]. Moreover, biocompatible WPU and WPNCs are widely used in many areas of medical sciences e.g., bone scaffold. Luo and co-workers prepared a hybrid cobalt-doped alginate/WPU 3D porous scaffold with nano-topology of a "coral reef-like" rough surface via two-step freeze-drying and this scaffold can be used in nerve tissue engineering [187]. Yoo and Kim developed WPU/poly(N-vinylpyrrolidone) composite films usable for wound-healing dressings [188]. Literature advocates that some WPUNCs are extensively used in

anti-bacterial applications. For example, recently, Borse et al. prepared MOF (Ni-ZIF-67) decorated Ni-ZIF-67@WPU films that exhibited optimum water vapor permeability performance at 5 wt% filler with the potential antibacterial application [39].

1.6. Applications

WPU and WPUNCs have a diverse range of applications that extend across all areas of science and technology. A brief description of some of the major applications is provided in the following subsection based on previously published pieces of literature. Also, **Figure 1.4** summarizes these applications.

1.6.1. Coatings and paints

WPU and their modified versions are extremely useful for coatings and paint applications which increase the service life of materials by protecting them from corrosion, and abrasion, physical and chemical damage. WPU-based coatings are employed for the beautification and protection of building materials, furniture, floors, analytical equipment, various parts of automobiles, aircraft, and so forth. Interestingly, an appropriate nanomaterial or hybrid triggers the protecting power of WPU to another level by introducing advanced attributes such as anti-bacterial activity, anti-fungal, anti-fouling, anti-corrosive, SH, SC, UV-resistance, etc. [189-190]. For example, Fu et al. synthesized a series of castor oil-based WPU/Ag-HNT (silver-halloysite nanotubes) via *in situ* polymerization that exhibited excellent antibacterial activity against *S. aureus* and *E. coli* [191]. Wu et al. prepared WPU films with a fluorinated side group via a thiol-ene “click” reaction using dihydroxy-terminated 1,1,2,2-tetrahydroperfluorodecyl methacrylate (FDMA(OH)₂) and other desire reactants and they acclaimed that those films can be used as the waterproof and antifouling coatings [192]. A polydopamine -functionalized GO/WPU nanocomposite was prepared by Xiang and co-workers via solution blending which has excellent corrosion protection ability [193]. Furthermore, Zhao and coworker prepared CTAB modified-TiO₂/rGO-WPU-acrylate composites that exhibited good self-cleaning ability in photocatalysis [194].

1.6.2. Shape memory (SM) material

WPU and WPUNCs with SME are a unique emerging class of polymers because they can respond to temperature, microwave radiation, light, pH, solvent, moisture, etc. Presently, as an SM material, WPU and WPUNCs are found in numerous areas such as smart textiles, self-deployable sun sails in spaceships, self-expandable stents, self-tightening sutures, implants for minimally invasive surgery, and so forth [195-196]. To date, people searching for more WPU and WPUNCs with SMEs for more advancement in this field. For example, inspired by

skin, Hu and her coworkers prepared a skin collagen fiber (SCF)/WPU composite with water-responsive shape memory ability through a facile “paper-making” procedure, successfully.

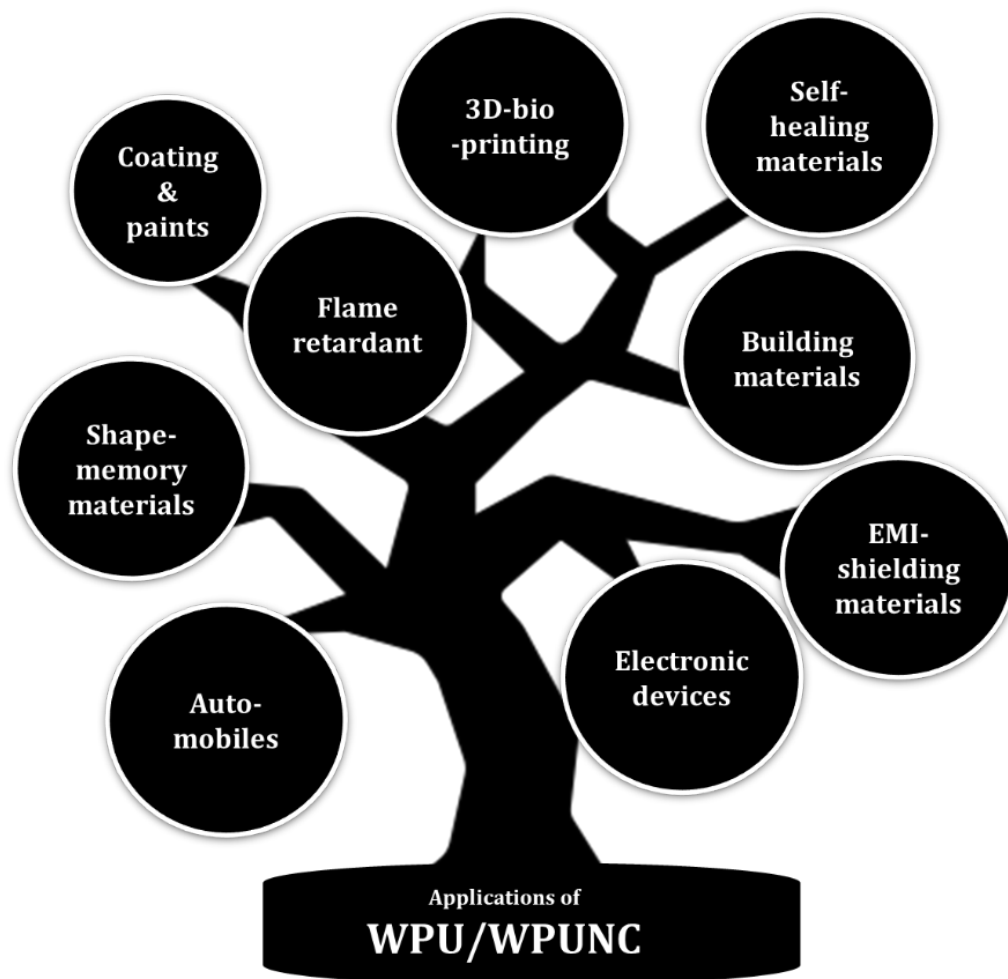


Figure 1.4. Applications of WPU and WPUNCs.

The composite showed water-responsive shape memory with high shape fixation (99%) and shape recovery (>90%) [197]. Lu et al. synthesized a series of a series of flexible and self-healable EMI shielding WPU/MXene films with SM attribute via mechanical blending of castor oil-based WPU with $Ti_3C_2T_x$ [198]. Again, Du et al. fabricated WPU/f-GO composites containing diselenide bonds via *in situ* polymerization in which NCO-terminated prepolymers were covalently bonded with GO surface. These composites showed both SME and repeatable SH activity upon exposure to NIR irradiation [199].

1.6.3. Self-healing (SH) material

SH is a smart feature that was introduced to WPU chemistry a long time ago, inspired by natural phenomena. Nowadays, the applications of self-healable WPU and WPUNCs are proliferated in diverse fields including smart coatings, wearable electronic skins, 3D/4D printing, biomaterials, soft conductor or supercapacitors, automobiles, spacecraft, and so on

[200]. According to recent literature, people are examining the potential uses of SH WPU and simultaneously seeking more SH materials. For example, Qian et al. reported a series of SH reprocessable waterborne poly(thiourethane-urethane)s based on terpene and polysiloxane and having thiourethane as a dynamic covalent bond [201]. Shi and co-workers developed bionic WPU-Fc (ferrocene)/CD hybrid films with different loading molar ratios of ferrocenediol (Fc-diol) to methylated β -cyclodextrin (Me- β -CD) (act as host-guest) that showed an almost 100% restoration effect for scratches and an excellent SH efficiency of 98.54% for totally damaged wounds [202]. A fluorescent SH WPU was synthesized by Li and co-workers using a naphthalimide derivative i.e., 4-N-acetylenehydrazide-N-(2-hydroxy-1-hydroxymethylethyl)-1,8-naphthimide (BHHNA-AM) as the chain extender which can be used as anti-counterfeiting agent [203]. Wang et al. prepared a series of thermo-driven SH WPU/organic/inorganic nanohybrid films by introducing furfuryl (furan@SiO₂)-modified silica nanoparticles into a maleimide-terminated WPU matrix and the hybrid film exhibited SH efficiency greater than 88% [204]. Moreover, recently, Jin and co-workers synthesized a series of room temperature SH fluorescent WPU containing irregular 6-fold and diamide hydrogen bonds which originated from carbohydrazide (CHZ) and N, N-bis(2-hydroxyethyl)-3-amino propionyl glycinamide (HO-NAGA-OH) groups. Interestingly, the developed robust films are useful in information encryption, anti-counterfeiting, and strain sensor [205].

1.6.4. Miscellaneous

It is well-known that WPUs and WPUNCs can be used in diverse fields encompassing common day-to-day applications to advanced applications. For example, through molecular contact at their surfaces, adhesives are routinely used to adhere or join two substrates e.g., wood-wood, metal-metal, paper-paper, etc. Lopez et al. developed a series of WPU-acrylic hybrid nanoparticles via miniemulsion polymerization that can be used as pressure-sensitive adhesives [206]. Shi and co-workers recently developed a fluorescent and degradable castor oil-based WPU matrix that has the adhesive capacity and strain-sensing ability to detect human activity [207].

Currently, 3D printing is one of the most demanding fields that growing exponentially in biomedical sciences and other branches of sciences because it can produce complex organs or any other structures via a layer-by-layer method using a computer-created design. People are searching for WPUs and WPUNCs-based 3D printable ink and their potential applications, inquisitively. For example, Eceiza and co-workers designed and executed a 3D-printable alginate-WPU reinforced by CaCl₂ which can work as a suitable implant for hernia repair [208]. Choi et al. have developed four types of 3D-printed auxetic lattice structures using thermoplastic PU which were coated further by castor oil-based

WPU/graphene composites to make those structures useful in strain sensors [209]. Presently, WPUs and WPUNCs are used in superior applications such as artificial muscle [210-211], EMI shielding [212], anti-counterfeiting [213], drug delivery [214], sensors and actuators [215], and so forth.

1. 7. Scopes and objectives

Biobased WPU has established renowned fame and gained marvelous attention among consumers and researchers within a short span of time because of its eco-friendly nature and favorable other attributes. However, it lacks some smart properties which are highly recommended for advanced applications such as 3D bio-printing, bioimaging, artificial muscle, etc. Therefore, there is an urgent need to explore the potential of the WPU and its NC for such superior applications. In this regard, it is necessary to ripen new visionary tactics, molecular engineering, and incorporation of suitable carbon-based nanomaterials (e.g., graphitic carbon nitride, $g\text{-C}_3\text{N}_4$) using chemical modifications. The fabrication of NCs not only enhances the inborn material properties but also assists in supplementing new interesting characteristics up to a high benchmark. Therefore, smart WPU and its NCs may construct a useful research proposition and open a new avenue toward the development of high-performing multidimensional advanced materials.

Based on the aforementioned perspectives and the pioneering concepts derived from the previous literature, the following objectives are targeted for the present study:

- i) To synthesize reactive free hydroxyl groups containing biobased internal emulsifiers like glycerol ester of citric acid (GECA) with comparable reactivity to commercially available 2,2-bis(hydroxymethyl)propionic acid (DMPA) towards isophorone diisocyanate.
- ii) To synthesize smart WPU dispersions and their films using GECA, biobased chain extender monoglyceride of castor oil (MG_{CO}) along with other desired reactants including di/poly-ols, diamines, and diisocyanates.
- iii) To modify WPU and to impart advanced features (e.g., smart attributes, 3D printability, fluorescent activity, etc.) by introducing dynamic hard domain (2-aminophenyl disulfide, 2-APDS), asymmetric architectural hard domains like isophorone diisocyanate (IPDI)-isophorone diamine (IPDA) gelatin and GelMA (gelatin methacryloyl), nanomaterials like $g\text{-C}_3\text{N}_4$ and the formation of the self-healable-WPU/acrylic (SWPUA) hybrid dispersions with various acrylate monomers.

- iv) To characterize the synthesized smart WPU, modified WPU and their NCs using different instrumental techniques viz. spectroscopic techniques (e.g., FTIR, and NMR), DLS, GPC, diffraction techniques (e.g., P-XRD), etc.
- v) To evaluate different film properties like physical, mechanical, thermal, UV resistance, chemical resistance, and biodegradation along with smart properties like SH, SM, etc. of the synthesized WPU, self-healable WPU (SHWPU), and their NCs.
- vi) To explore the applicability of the WPU and their NCs in the field of artificial muscle, 3D-printable bone scaffolds, bioimaging, anti-counterfeiting, etc.

1.8. Plan of Research

To fulfill the above objectives of the present investigation, the following plans have been adopted.

- i) An extensive literature survey on smart WPU and their NCs derived from renewable raw materials and their advanced applications has been conducted.
- ii) With precise molecular engineering, WPU has been synthesized from renewable resourced-based reactants and other desired reactants.
- iii) The characterization has been done by using different analytical and testing methods.
- iv) Further, the pristine WPU has been modified by various acrylate monomers, dynamic hard domains, asymmetric architectural hard domains, gelatin with GelMA, and nanomaterials like g-C₃N₄.
- v) The resultant modified NCs have been characterized by various standard instrumental techniques and testing methods.
- vi) Various properties like physical, mechanical, thermal, UV, and chemical resistance, biocompatibility, and biodegradation along with different smart properties of the synthesized WPU and their NCs have been evaluated for WPU, modified WPU, and NCs.
- vii) The possible potential applications in the field of artificial muscle, 3D-printable bone scaffolds, bioimaging, anti-counterfeiting, etc. have been explored.

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