General Introduction

Highlight

This chapter chronicles a brief account of polyurethane and its nanocomposites with various kinds and nature of nano-dimensional materials, encompassing preparative methods, characterization methods, property evaluation and applications. Special emphasis is laid upon polyurethanes based on renewable resources and carbon based nanomaterials. A concise account on various spectroscopic, microscopic and analytical techniques engaged in the characterization of polyurethane, nanomaterials and polyurethane nanocomposites is presented. In view of the prominence of renewable resource based polyurethane nanocomposites, their fabrication methods, characterization, properties and prospective applications across the domains of polymer science and technology are comprehensively discussed. Ultimately, the chapter projects the scopes, objectives and plan of research for the current study.

1.1.   Introduction

Polymers have always been an integral part of the civilized society from the ancient times, transcending through history to the modern age as of now [1]. Since the last two centuries, extensive research has been devoted to develop polymers as a futuristic material. In the modern times, polymers are being regarded as the best alternative to the traditional-metal based materials, because of its inherent nature and myriad qualities. Presently, use of polymers dominates numerous applications ranging from common day-to-day appliances like coatings, foams, adhesives, sealant, packaging materials, etc. to advanced utility in automobiles, aerospace, electronics, optics, biomedical, etc [2, 3]. However, the alarmingly high level of polymer consumption, owing to its wide acceptability and rapidly expanding human population have cast serious concerns over safe use of polymeric materials [4]. This high level of polymer consumption has led to stockpile of polymeric materials not only on the earth surface but in the oceans as well, causing serious hazard to the delicate eco-system [5]. In similar lines, the production of polymers from petroleum based resources has further depleted the dwindling crude oil reserves [6-9]. These shortcomings make it imperative to find an alternative way to reduce or prevent polymer waste, in order to address the issue of ecological footprint.

The idea of synthetic biodegradable polymer was initially put forward to reduce the global ecological impact of polymer waste. These synthetic biodegradable polymers offered stable and durable service life, and undergo destruction after use by certain environmental factors [9-12]. Gradually, the concept of renewable resources as feedstock for polymer production began to garner support from the scientific community as a lucrative alternative to synthetic polymers, in a conscious bid to shift the dependency from petroleum based sources and minimize polymer waste accumulation [6-9]. In addition, waterborne polymers also started its foray as a bio-degradable sustainable material [13]. Thus, novel bio-based, bio-degradable, eco-friendly polymeric materials was eventually developed as an answer to the global polymer waste woes. In this milieu, polyurethanes (PUs) emerged as an important benefactor, owing to its acceptable biodegradability and adaptability to renewable resources [14, 15]. From the perspective of material chemistry, PU is a versatile class of polymer, consisting of three basic building blocks, namely, macroglycol, di/polyisocyanate and chain extender. The versatility of PUs stems from its wide range of physical and chemical properties, which can be customized to address the needs of modern-day applications like coatings, foams, paints, thermosets, fibres, elastomers, etc [16]. As mentioned earlier, synthesis of PU offers the scope for utilization of renewable resources as raw feedstocks [15-17]. This provides an environmentally benign and

economically viable approach towards PU synthesis, imparting high eco-friendly hallmarks to the finished product. By far most commonly, vegetation endows the largest source of renewable matter. State of art literature advocates the successful use of vegetable oils like castor oil, canola oil, linseed oil, olive oil, soybean oil, sunflower oil, nahar oil, etc.[18-30]; carbohydrates like starch, cellulose, chitin/chitosan, sugars, dextrin, isosorbide, etc.; polyphenolic compounds like lignin, tannins, etc., for sustainable production of PUs [31-43]. Apart from sustainability, these renewable resources based PUs show enhanced biodegradability and biocompatibility, making them suitable for manufacturing of eco-friendly appliances. Primarily, such PU systems reduce the operational and processing economics, paving way for affordable materials without compromising on quality.

Besides chemical structure, the architectural traits of polymers also account for numerous unique properties. In this perspective, hyperbranched polymers have attracted avid interest in the recent time for designing advanced polymeric materials with unique properties [44]. A hyperbranched polymer comprises of three elementary units, namely, linear, dendritic and terminal, arranged in an arbitrary way along the polymer backbone [44]. With many unique features like three-dimensional globular less-entangled structure, high solubility, large surface functionalities, low solution and melt viscosity, good compatibility with other, etc., hyperbranched polymers are almost comparable to dendrimers – the perfectly branched macromolecular structure of the dendritic polymer family [45]. Hyperbranched polymer also offers the added advantage of facile one-pot operation and processability, even in large scale which makes them resourceful commodity in industry and academia [45, 46]. In this context, the contribution of hyperbranched PUs (HPUs) towards the development of high-end polymeric materials with unique properties is also significant [47].

Despite, their versatility in terms of properties and applications, PUs require occasional modifications in order to meet the demands of modern-era applications. Regardless of many advantages of PUs, inadequacy in achieving the desired material properties is a shortcoming that has restricted their exploitation in advanced sectors. Conventionally, PU has been successfully modified by physical and chemical modifications like blending, cross-linking, interpenetrating network, etc., in a bid to improve these shortcomings [48-50]. However, operational complexities and processing difficulties hamper these conventional routes. Therefore, development of simple and inexpensive technique for improving the material properties of PUs is lucrative challenge before its utilization in advanced applications.

In recent times, nanotechnology based approaches have overhauled the conventional routes. Recent studies have established that material properties of virgin

polymers can be significantly improved by incorporation of even a minute amount of suitable nanomaterial (<5 wt%) [51-52]. Subsequently, polymer nanocomposites have been fabricated using different types of nanomaterials of organic and inorganic origin with pristine polymers [53]. Especially, carbon based nanomaterials have been in the forefront to build polymeric nanocomposites for advanced applications. These carbon based nanomaterials include carbon nanotubes (CNTs), graphene and its variants like graphene oxide (GO), reduced graphene oxide (rGO), carbon quantum dots (CQDs/CDs), and graphitic-carbon nitride (g-CN). At the same time, inorganic nanomaterials comprise the nanoclay, silicates, hydroxyapatite minerals, boron nitride, etc.; different metal and metal oxides like silver (Ag), copper (Cu), iron oxide (Fe_3O_4), copper oxide (CuO/Cu_2O), titanium dioxide (TiO_2), zinc oxide (ZnO), etc. have been used in polymer nanocomposites. State of art literature reveals the use of various nanomaterials employed as nano-reinforcing agents in PU nanocomposites (PUNCs) that led to enhancement of material properties [53-67]. Fabrication of PUNCs with these nanomaterials not only compensate for the material properties but also impart special properties to these materials, that is beneficial for demand-based applications like coatings, electrical, opto-electronics, catalytic, biomedical, etc [51-66]. In many occasions multiphase nanohybrid system, have also been employed to achieve the benefits of different nanomaterial-based properties in a single material [68].

Thus, the current scenario necessitates the importance of developing high performance, eco-friendly PUNCs to address the impending environmental status and modern day demands for advanced utility material. In this juncture, the designing of renewable resource derived biodegradable polymeric material in form of HPU nanocomposites (HPUNCs) may hold the key for solving the economic, ecological and environmental concerns related to conventional polymeric materials and present an appropriate research proposition.

1.2.   Background

PUs have enjoyed steady relevancy in the field of polymer chemistry from the 20th century till the contemporary times. PU was introduced for the first time by Otto Bayer in 1937 and since then development of PUs began its nascent stage [69]. The following decade saw rapid innovations in the development of PUs, eventually their commercialization as finished products. Applications of PUs in form of products such as coatings, elastomers and adhesive flourished during the 1940s. For example, extensive use of PUs was seen during the World War II, where PU was used as an alternative to the expensive and elusive rubber. By the 1950s, flexible and rigid foams of PUs were introduced, similar to those of today [70]. Subsequent decades have pioneered many further essential and remarkable

developments of PUs, culminating in their global recognition in several aspects of our day-to-day lives.

Fascinating advances in polymer chemistry emerged out in due course of time by the advent of highly branched polymers in the late 1980s [71]. DuPont researchers, Kim and Webster demonstrated the possibility of synthesizing a polymer with random "branch-on-branch" topology by a single pot process and subsequently coined the term "hyperbranched" polymer [72]. After a decade, HPU was successfully synthesized for first time by Spindler and Frechet in 1993 using AB_2 blocked isocyanate monomer, 3,5-bis((benzoxycarbonyl)imino)benzyl alcohol with one hydroxyl group (A) and two blocked isocyanate groups (B) [73]. In the same year, HPU was developed by Kumar and Ramakrishnan, using an *in situ* generated monomer, 3,5-dihydroxyphenyl isocyanate, derived from corresponding carbonyl azide precursor [74], followed by variations in oligoethyleneoxy-spacer segments between the branching points in 1996 [75]. Approaching the millennium saw the horizon of HPUs started to broaden with widespread production. Hong synthesized a pair of novel HPUs using AB_x macromonomers containing linear spacer units between branching points [76]. Raju and co-workers reported the synthesis of HPU from various commercial sources [77]. Park et al. reported the synthesis of waterborne HPUs using a hyperbranched (2,2-bis(hydroxymethyl)propionic acid (MPA) polyester-16-hydroxyl) polyol [78]. During this time, the focus of PU chemistry began to shift towards a more sustainable approach, in lieu of environmental and anthropological concerns. This saw a significant change in PU production, as use of petrochemical-based feedstocks gave way to bio-based resources. Use of bio-based precursors provided a much-welcome solution to tackle the problem of dwindling non-renewable sources and ecological safety. The potential of vegetable oils in polymer chemistry found momentum through the pioneering efforts of J. G. Kane [79]. In 1984, for the first time Petrović and Fajnik reported the synthesis of castor oil based PU [80]. Thereafter, vegetable oil-based PUs saw rapid development in the coming two decades. Javni et al. presented the synthesis of vegetable oil based PUs using polyols of soybean oil, castor oil, sunflower oil, etc [81]. In similar lines, Zlatanić et al. (2004) synthesized vegetable oil based PU using 4,4-diphenylmethane diisocyanate and polyols based on soybean, corn, sunflower, canola, and linseed oils [82]. Subsequently, HPU was prepared directly from vegetable oil-derivative by Karak and co-workers (2009) for the first time without any gel formation [83]. In recent times, Karak and his group members have been avidly pursuing the synthesis of HPU using different types of renewable sources [84-88].

Another paradigm shift in the field of polymer chemistry was ushered by nanotechnology. This combination of polymer and nanotechnology led to the genesis of

"polymer nanocomposites". The advent of polymer nanocomposites began in the 1980s when Toyota Central Research Laboratories in Japan first developed clay/nylon-6 nanocomposites for designing timing belt covers [89]. In 1998, Wang and Pinnavaia reported the first ever PUNC using montmorillonite clay as nano-filler [90]. The following year saw Zilg et al. (1999) use layered silicates as nanofillers in PUNC [91]. Since then, a host of nano-dimensional materials, belonging to both organic and inorganic origin family have been employed in design of novel PUNCs. Kuan et al. (2005) reported multi-walled CNT (MWCNT)/waterborne PUNC with enhanced mechanical, thermal and rheological properties [92]. Guo et al. (2007) fabricated iron nanoparticle-reinforced PUNC by surface-initiated polymerization with magnetic and electromagnetic wave absorption properties [93]. Gunes et al. (2008) developed PUNCs having shape memory property with different nanofillers, viz. organoclay, carbon nanofiber, silicon carbide and carbon black [94]. Lee et al. (2009) prepared waterborne PUNC with functionalized nano-graphene sheets for the first time [95]. Kim et al. (2010) developed PUNCs with chemically and thermally exfoliated graphene sheets with improvement of electrical and gas barrier properties [96]. In similar lines, designing of HPUNCs also gathered momentum. Rana et al. (2008) reported the fabrication of HPUNC with enhanced dispersion of MWCNT [97]. Karak and co-workers (2010) fabricated vegetable oil based HPUNC with *in situ* formed Ag nanoparticles that showed biodegradability, biocompatibility and antimicrobial activity [98]. Thakur et al. (2014) reported bio-based HPU/graphene nanocomposites as stimuli responsive self-healing and shape memory materials [99]. Karak and co-workers (2016) demonstrated bio-based waterborne HPU/CD nanocomposite as a surface coating material [100].

However, the exploratory nature of science still offers plenty scope for further research and innovation in this field.

1.3. Materials and methods

1.3.1. Materials

Design and development of polymeric materials for meeting the demands of futuristic applications command thorough research and proper execution. In this regard, PU has served as a prime example, due to its wide array of properties that can be customized by varying the basic building materials and their compositions [16]. Again, owing to its ability to effortlessly combine with other materials of organic and inorganic origins, PU has served as an ideal material for forging advanced functional materials [53]. Introduction of nano-dimensional materials in PU has been seen as a noteworthy step in this direction. Evolution of PUNCs with nano-dimensional materials has been found to be most effective approach

for augmenting the inferior qualities of PU [51-53]. Thus, the rational selection of raw materials, variation and optimization of their compositions is crucial for governing the ultimate performance, and hence applications of PU and their nanocomposites. This section of the chapter presents an overview of different materials employed in the preparation of PU and their nanocomposites.

1.3.1.1.   PU

PU is a polymer obtained from the rearrangement reaction between di/polyols and di/polyisocyanates, with or without using a catalyst. The polymeric backbone of PU comprises essentially of carbamate or urethane (-NH-COO) linkages, as the repeating unit [16]. Although, additional linkages like ester, urea, ether, etc. can also be anchored to the polymer backbone. Synthesis of PU generally involves three basic functional components: (a) di/polyol as macrogylcol, (b) di/polyisocyanate and (c) di/polyol or amines as chain extender. The intimate amalgamation of these basic components gives rise to incompatible segments in the PU structure. The long chain macrogylcols constitutes the flexible soft segments, while the di/polyisocyanate and chain extender together forms the rigid hard segments. Numerous times, the properties of PU are maneuvered by controlling these hard and soft segments [16, 17]. These basic components are mostly derived from petroleum-based raw materials, however in recent times, the use of renewable resources based feedstocks have gained emphasis. In this regard, a brief description of these basic components is presented as follows,
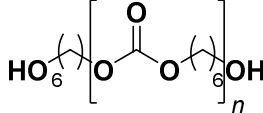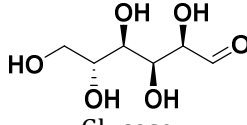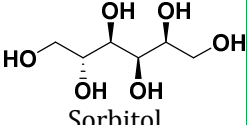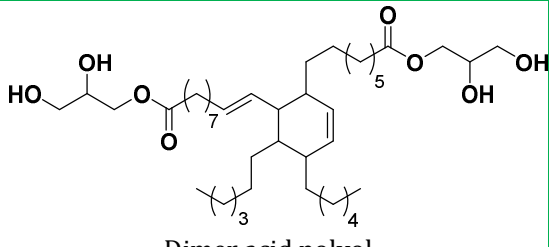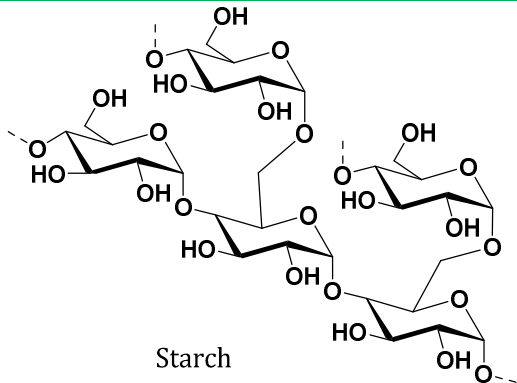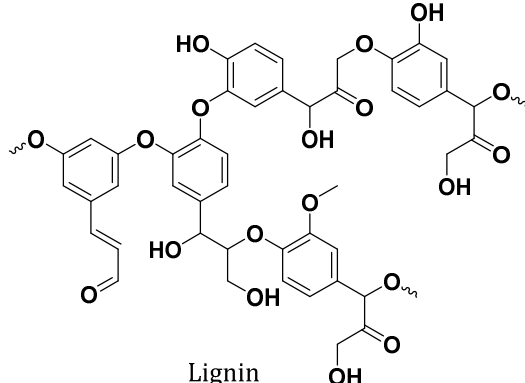
(a) Macroglycol

These are di or polyol compounds having molecular weight within the range of 400-5000 g mol^{-1} in general. These compounds contain two or more hydroxyl groups, which reacts with the diisocyanate during PU synthesis. The macroglycol component comprises the soft segments of PU and is responsible for influencing its inherent properties [16]. A variety of macrogylcols based on polyester, polyether, polycarbonate, siloxane, hydrocarbon, etc. has been employed for PU synthesis, as shown in **Table 1.1.** The choice and the nature of macrogylcols mostly determine the physico-chemical nature and the end-use of PU. Low molecular weight glycols (a few hundred mass units) are used to make rigid PUs; while high molecular weight glycols (around thousand mass units and above) are used to make flexible PUs. In most cases, polyether-based glycols and polyester-based glycols have been vehemently utilized. Polyether glycols dominate the market with the largest share of macrogylcols used in PU synthesis. However, in recent times the onus has shifted towards exploiting more sustainable options. The potential of renewable resources has been tapped to obtain green and bio-based macrogylcols for PU production. Polyols derived from

renewable resources such as vegetable oils, biopolymers, carbohydrates, natural polyphenolic compounds, etc. provide suitable precursors to develop eco-friendly and sustainable PU.

Table 1.1. Example and properties of macroglycols used in PU

Macrogylcol		Properties	Ref.

Polyether	Poly(ethylene oxide) glycol(PEG)
	
	  Poly(propylene oxide) glycol (PPG)
	
	  Poly(butylene oxide) glycol (PBG)
	
	  Poly(tetramethylene oxide) glycol (PTMEG)
	
	  Poly(hexamethylene oxide) glycol (PHMEG)
		Hydrolytic stability, low temperature, flexibility, viscosity, resistance to biodegradation	[101, 102]

Polyester	Poly(ethylene glutarate)
	
	  Poly(ethylene adipate)
	
	  Polycaprolactone diol (PCL)
		Oil/fuel/solvent resistance, thermo-oxidative stability, rigidity	[102]

Hydro carbon	Hydroxy terminated polybutadiene glycol (HTPB)	Low temperature, flexibility, solvent resistance	[101]
Siloxane	Poly(dimethylsiloxane) glycol (PDMS)	Hydrolytic stability, flexibility, biocompatibility	[50, 104]

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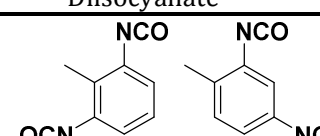
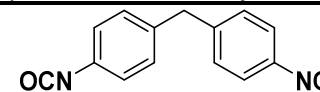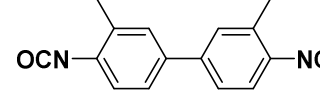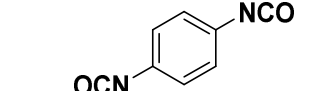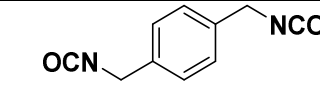|			
Poly carbonate	Polycarbonate diol	Hydrolytic stability, oxidative stability	[103]
Renewable resource based polyols	Glucose / Sorbitol	Rigidity, hydrophillicity, biocompatibility, biodegradability	[105]
	Dimer acid polyol		[88]
	Starch	Rigidity, hydrophillicity, biocompatibility, biodegradability	[32, 87]
	Lignin		[41, 42, 48]

(b) Di/polyisocyanate
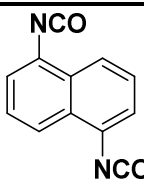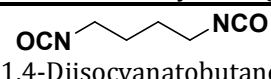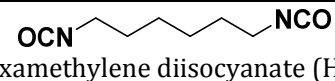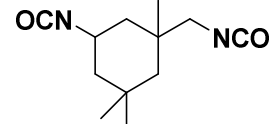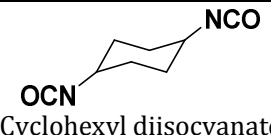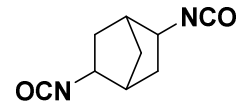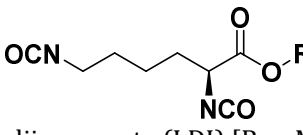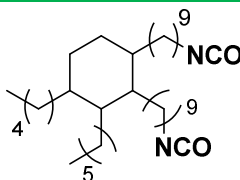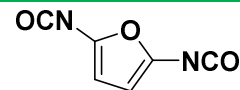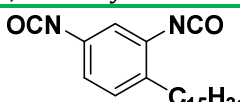
This is the key component of PU chemistry. Diisocyanates are highly reactive compounds, containing the –N=C=O functional group which is crucial for the formation of urethane linkage of PU. The diisocyanate component constitutes the hard segments of PU and is beneficial for influencing its inherent properties, together with the soft segments [16]. Generally, diisocyanates are divided into two types, based on their chemical constitution:

aromatic and aliphatic. A list of commonly employed diisocyanates in PU synthesis is shown in **Table 1.2**. Methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) are most widely used aromatic diisocyanates, while isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI) are two major aliphatic diisocyanates used in industry and academia [102]. Aromatic diisocyanates are usually more reactive than their aliphatic counterparts. The reactivity of the isocyanate group is mainly attributed to the structure, substituent, steric effect and stereochemistry of the isocyanates. For example, the *para*-NCO group is 25 times more reactive than *ortho*-NCO group [101]. PUs obtained from aromatic diisocyanates exhibit good mechanical properties and thermal stability, but suffers from drawbacks such as low oxidation and UV light sensitivity. Conversely, PUs obtained from aliphatic diisocyanate provides good color stability and transparency, but suffer from poor mechanical properties. But aliphatic diisocyanates poses more toxicity and less reactivity than aromatic ones [102]. Hence depending upon the application, both types of diisocyanates have been used to tailor PUs with desirable properties. Nevertheless, due to issues of toxicity and occupational hazard related to use of these commercial diisocyanates, there has been attempts to introduce renewable resource based diisocyanates in PU production, e.g., methyl or ethyl ester of L-lysine diisocyanate (L-LDI), sugar-based pentamethylene diisocyanate (PDI), dimer acid-based diisocyanate (DDI), cashew nut shell liquid-based diisocyanates, etc [106].

Table 1.2. Commonly used diisocyanates in PU

Diisocyanate		Properties	Ref.
Aromatic	2,4/2,6-Toluene diisocyanate (TDI)	High reactivity, mechanical stability, thermal stability	[86]
	Methylene diphenyl diisocyanate (MDI)		
	Bitolylene diisocyanate (BTI)		
	p-Phenylene diisocyanate (PPDI)		
	m-Xylylene diisocyanate (XDI)		

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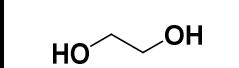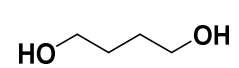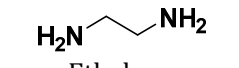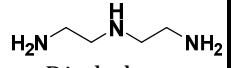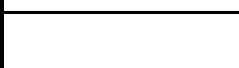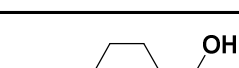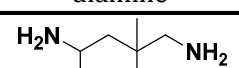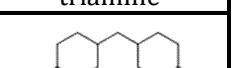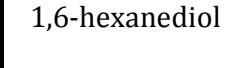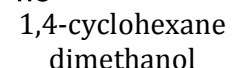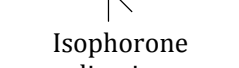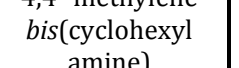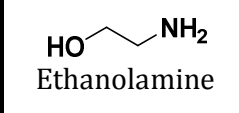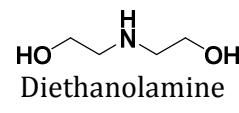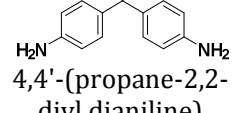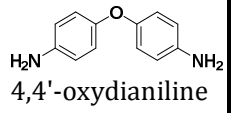
	Naphthalene diisocyanate (NDI)		
Aliphatic	1,4-Diisocyanatobutane Hexamethylene diisocyanate (HDI) Isophorone diisocyanate (IPDI) Cyclohexyl diisocyanate Norbornene diisocyanate (NBDI)	Transparency, oxidative stability, UV light stability	[86]
Renewable resource	Bio-pentamethylene diisocyanate (Bio-PDI) L-Lysine diisocyanate (LDI) [R = -Me or -Et] Dimer acid diisocyanate (DDI)	Less toxicity, Moderate reactivity	[106]
	2,5-diisocyanatofuran 2,4-diisocyanato-1-pentadecylbenzene	Less toxicity, moderate reactivity	[106]
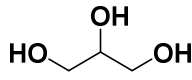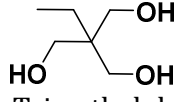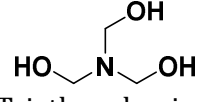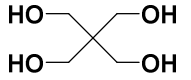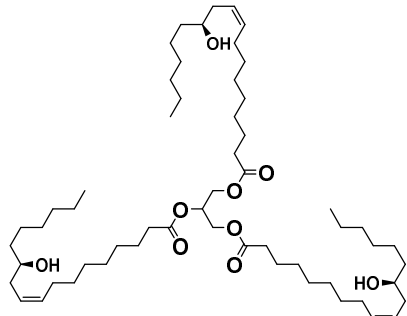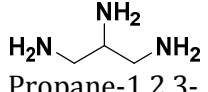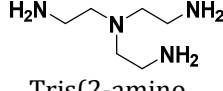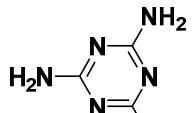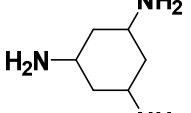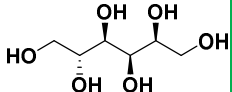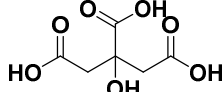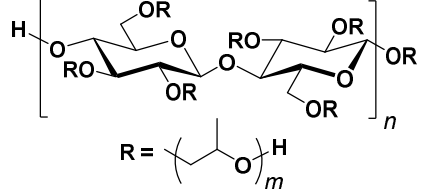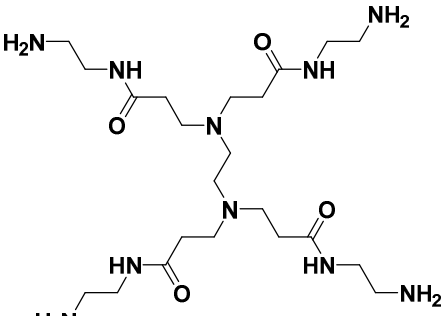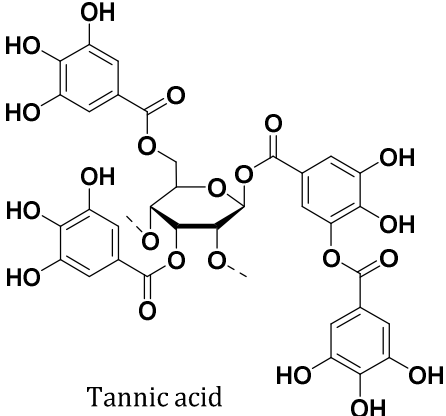
(c) Chain extender

These are di/polyol or di/polyamine compounds of low molecular weight (generally lesser

than 400 g mol^{-1}). Chain extenders react with the diisocyanate or the pre-polymer during synthesis of PU. These compounds increase the chain length and hence the molecular weight of PU. Chain extenders form an auxiliary part of the hard segment, alongside the diisocyanate moiety and helps in controlling the mechanical, thermal and hydrolytic stability of the PU [16]. Much like diisocyanates, chain extenders can be either aromatic or aliphatic. PU chain extenders are basically recognized into two classes: linear and branched. Some of the most commonly employed chain extenders are listed in **Table 1.3.** Most commonly, diol and diamine compounds are used as linear chain extenders in PU synthesis. Examples of linear chain extender includes ethylene glycol, 1,4-butanediol, 1,6-hexanediol, ethylene diamine, diethylene diamine, isophoronediamine, etc [102]. On the other hand, polyol and polyamine compounds containing more than two functional groups serve as branched chain extenders, which are useful in HPU synthesis. Examples of branched chain extenders include multi-functional compounds like glycerol, triethanolamine, pentaerythritol, propane-1,2,3-triamine, melamine, etc [16, 17]. In the last two decades, the feasibility of renewable resources as chain extenders has seen a considerable rise, due to economic and environmental factors. For example, vegetable oils and their derivatives [105, 107], natural sugars and carbohydrates [108, 109], natural polyphenols [86, 109], etc. have been innovated as chain extenders in PU and HPU synthesis.

Table 1.3. Commonly used chain extenders in PU synthesis

Linear diols/diamine	HO⌒OH Ethylene gylcol	HO⌒⌒OH 1,4-butanediol	H₂N⌒NH₂ Ethylene diamine	H₂N⌒N(H)⌒NH₂ Diethylene triamine
	HO⌒⌒⌒OH 1,6-hexanediol	HO-cyclohexane-OH 1,4-cyclohexane dimethanol	H₂N⌒NH₂ Isophorone diamine	H₂N-cyclohexyl-cyclohexyl-NH₂ 4,4'-methylene *bis*(cyclohexyl amine)
	HO⌒NH₂ Ethanolamine	HO⌒N(H)⌒OH Diethanolamine	H₂N-phenyl-C-phenyl-NH₂ 4,4'-(propane-2,2-diyl dianiline)	H₂N-phenyl-O-phenyl-NH₂ 4,4'-oxydianiline
	Monoglyceride of vegetable oil	Isosorbide	Isosorbide-based diamine	Vanillin-based diamine

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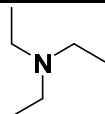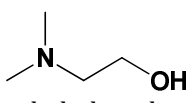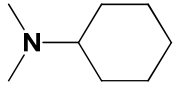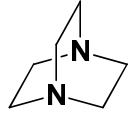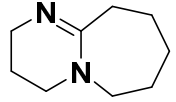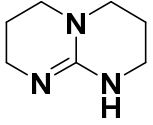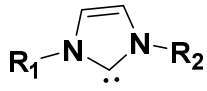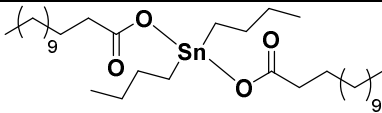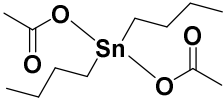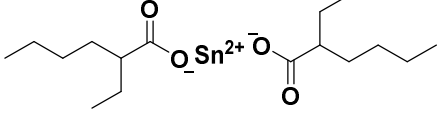
Branched polyols/polyamines	Glycerol	Trimethylol propane	Triethanolamine	Pentaerythritol
	Triricinolein (Castor oil polyol)		Propane-1,2,3-triamine	Tris(2-amino ethyl)amine
			Melamine	Cyclohexane-1,3,5-triamine
	Sorbitol	Citric acid	Hydroxypropyl cellulose	
	Poly(amido amine) G1		Tannic acid	

(d) Catalyst
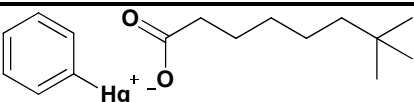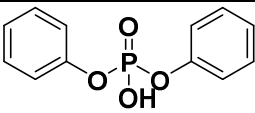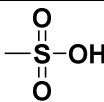
The role of catalyst in PU chemistry is sporadic. Usually, urethane formation reaction is achieved sans any catalyst. However, in order to conduct PU synthesis under mild conditions and rapid rate, catalyst is frequently employed [16]. Especially, in the case of PU reaction involving low reactive aliphatic diisocyanates and sterically hindered monomers, catalyst is required to expedite the reaction [102]. A list of commonly used catalyst for synthesis of PU, along with their unique properties is listed in **Table 1.4**. These catalysts comprises of mostly basic amine compounds and organometallic salts. Tertiary amine compounds such as triethylamine, dimethylcyclohexylamine, DABCO, etc; cyclic

guanidines/amidines such as DBU, TBD, etc. have been found to perform exceptionally well as catalyst. Organometallic compounds of Sn and Hg such as dibutyltindilaurate, stannous octoate, phenyl mercury neodecanoate, etc. have been used as catalyst in PU synthesis. However, these organometallic catalysts poses health and occupational hazard and hence, their use is restricted. Of lately, oxides and carboxylates of Zn and Bi have also been used as catalyst in commercial PU production. Most recently, *N*-heterocyclic carbenes (NHCs) and organic acids like diphenyl phosphate (DPP), methane sulfonic acid (MSA) and triflic acid have been found to catalyze PU formation.

Table 1.4. Commonly used catalyst in PU synthesis

Catalyst		Ref.

Amine compounds	Triethylamine
	  Dimethylethanol amine
	
	  Dimethylcyclohexyl Amine
	  1,4-Diazabicyclo[2.2.2.] octane (DABCO)
	
	  1,8-Diazabicyclo[5.4.0] unde-7-ene (DBU)
	  1,5,7-Triazabicyclo[4.4.0] dec-5-ene (TBD)
	
	  N-heterocyclic carbenes (NHCs)
			[102, 111]

Organometallic compounds	Dibutyltindilaurate (DBTDL)
	
	  Dibutyltin diacetate (DBTDA)
	
	  Stannous octoate
			[102, 112]

<div align="right">Contd.</div>

Organic acids	Phenylmercury neodecanoate (Thorcat®)	[111]
	Diphenyl phosphate (DPP)	
	Methane sulfonic acid (MSA)	Triflic acid

(e) Additives

These are diverse set of materials, often serving as important or supplementary components during PU synthesis. On the basis of the function of the additives, they are classified into following sub-classes, *viz.* crosslinkers, plasticizers, fillers, curing agents, blowing agents, moisture scavengers, stabilizers, colorants, flame retardants, etc [70, 113]. These are often useful components used for achieving desired properties in PU. However, toxicity, leaching and migrating tendency from the matrix, and incompatibility with PU matrix are some issues that limit their usefulness. Nevertheless, sensing the utility of such additives, there has been profound efforts to develop bio-based bulky additives that can enhance the applicability as well as sustainability of the PUs.

1.3.1.2. Nanomaterial

These are materials of either organic or inorganic origin, possessing at least one of their dimensions in the nano-scale, ranging from 1 nm to 100 nm [114]. These nanomaterials having one-, two- or three-dimensions in the nano-scale region are either engineered, manufactured or incidental nanoparticles of various shapes and sizes, viz. rods, wires, fibers, sheets, ribbons, tubes, cubes, spheres, core-shell, etc. In order to understand the diversity of these nanomaterials, they are mostly classified on the basis of their origin and dimensions [115]. Depending upon their elemental origins, nanomaterials can be classified into three classes: (a) organic, (b) inorganic and (c) hybrid (containing both organic and inorganic constituents). Based on their dimensions, nanomaterials are classified into three classes: (a) zero dimension (0-D), (b) one dimension (1-D) and (c) two dimension (2-D), as illustrated in **Figure 1.1**. These naturally-occurring or anthropogenic and dimensionally diverse nanomaterials possess their own distinct set of properties that set them apart from one another. Most prominently, all of these nanomaterials are utilized for the fabrication of PUNCs.

Zero-dimensional   One-dimensional   Two-dimensional
(0-D)   (1-D)   (2-D)
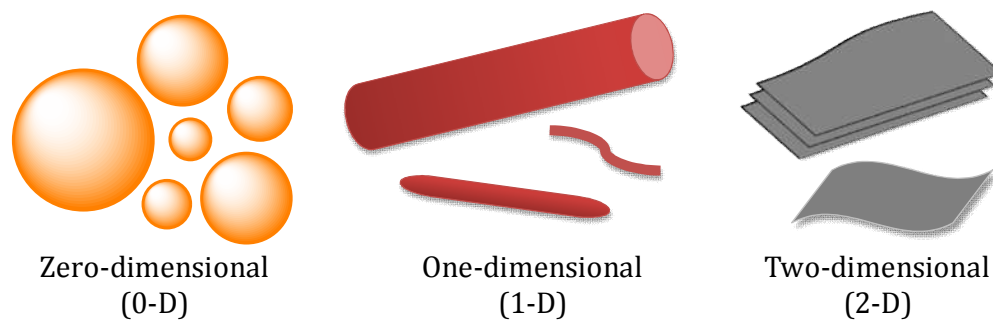
Figure 1.1. Different types of nanomaterials based on dimensions.

The morphology and distribution of these nanomaterials in the polymer matrix determine the ultimate properties of PUNCs. The choice of nanomaterial mostly depends upon the desired properties and targeted applications. A brief description of important nanomaterials is provided in the following sub-sections.

(a) Carbon based nanomaterials

Carbon based nanomaterials are organic nanomaterials origin-wise and are found in 0-D, 1-D and 2-D. These are a significant class of nanomaterials in modern times, owing to their diverse and tunable range of physical, chemical, electrical, thermal, optical and biological properties. Carbon based nanomaterials include graphitic nanostructures such as CNT, graphene and its variants viz. GO and rGO, CQDs or CDs, nanodiamond, fullerene C_{60}, g-CN, etc. as illustrated in **Figure 1.2**.

CNT is a hollow cylindrical (1-D) layer or layers of sp^2 hybridized carbon atoms, connected in a hexagonal lattice and possesses unique length-to-diameter ratio of 100,000,000:1 [116]. They occur either as single-walled CNT (SWCNT) or MWCNT. MWCNT or SWCNT exhibits extraordinary mechanical and electrical properties as well as thermal conductivity, due to which it is extensively used for PU fabrication. Graphene is a single-atom thick layer (2-D) of sp^2 hybridized carbon atoms, connected in a hexagonal lattice structure. Graphene possesses unique properties like high elastic modulus, large theoretical specific surface area, excellent strength, high thermal and electrical conductivity, etc [117]. These properties empower graphene as a suitable choice for fabrication of PUNCs. CQD is the newest member in the carbon nanomaterial family with a near-graphitic core spherical structure of dimension less than 10 nm (0-D). CQD exhibits outstanding nano-level aqueous dispersibility, exciting optical properties and profound biocompatibility [118]. In recent times, CQDs have been used for the development of PUNCs for optical, biological and photocatalytic applications. Other graphitic allotropes such as nanodiamond, fullerene C_{60}, have also been recently explored for manufacturing PUNCs.

g-CN is a polymeric material, that consists of layers (0-D or 2-D) of sp^2 hybridized carbon atom alternatively bonded to sp^2 hybridized nitrogen atom with C:N ratio of 3:4 and very small impurities of H. Since it exhibits a layered structure, g-CN is often considered as nitrogen-substituted variant of graphene. g-CN demonstrates special semiconductor photo-electronic and surface properties that make it an advantageous material for catalysis, energy storage, and other applications [119].
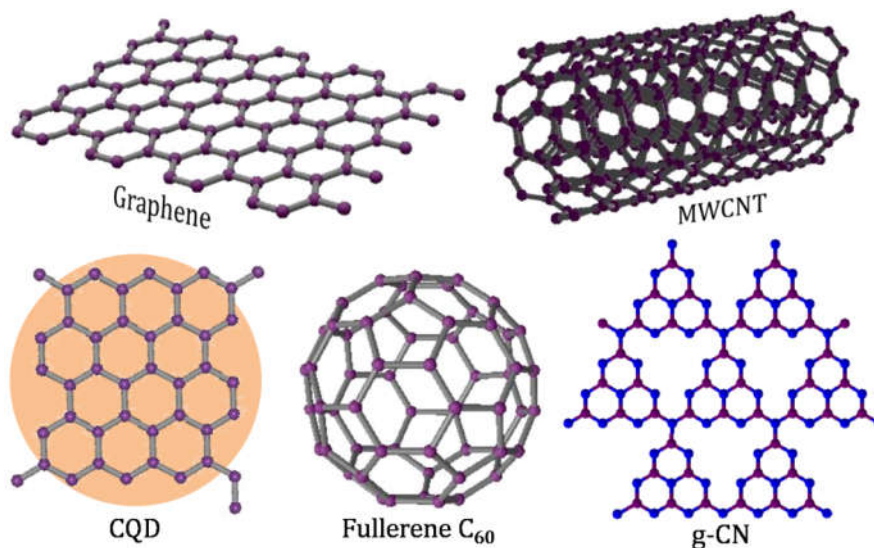
Figure 1.2. Carbon based nanomaterials.

(b) Inorganic nanomaterials

Inorganic nanomaterials are either naturally occurring or synthetically engineered nano-scale materials and come in 0-D, 1-D and 2-D with various sizes and morphologies. They include different metals, metal oxides, metal chalcogenides, inorganic minerals and nano clays. Metal nanomaterials are nano-sized materials of pure metal (e.g., Ag, Au, Pt, Pd, etc.) and their compounds (e.g., oxides, hydroxides, sulfides, phosphates, fluorides, and chlorides). Pure metal nanomaterials can be generated by reduction of their metal ions in the presence of suitable capping agents [67]. Nano metal oxides of titanium (TiO_2), iron (Fe_3O_4), copper (CuO/CuO_2), nickel (NiO), zinc (ZnO), etc. and metal ferrites (MFe_3O_4, M = Fe, Cu, Ni, Co, etc.) can be prepared by variety of techniques like solvolysis, wet chemical, sol-gel or hydrolysis method using organometallic precursors. Nanomaterials of metal chalcogenides (e.g. CdX, X = S, Se, Te) are prepared by reaction of metal salts with suitable sulfide or selenide agent under solvothermal condition [67]. These metal nanomaterials demonstrate excellent optical, electronic, magnetic and catalytic properties. Inorganic minerals like clays, silica (SiO_2) and hydroxyapatite (HAp) are some of the most abundant minerals on the earth surface. Nanoclays are hydrous aluminum phyllosilicate thin platelets

or sheets having layered structure (2-D). These layered nanoclays have good surface properties. Nanoclays like halloysite and montmorillonite are found to enhance mechanical and thermal properties of polymers [120]. On the other hand, nanosilica occurs in various polymorphic forms and dimensions (0-D, 1-D and 2-D) as nanoparticles, nanotubes, nanolayers, etc. Nanosilica has attracted copious interest in the past few years because of their interesting physical properties, active surface state, charactersitic photoluminescence and biocompatibility [121]. On similar lines, HAp is another naturally occurring mineral that possesses excellent biocompatibility and osteogenic activity. In recent times, nano-HAp is garnering copious interest as a biomaterial for use in prosthetic applications due to its similarity in chemical composition, size and crystallography with human hard tissue, like bone and teeth [122].

(c) Hybrid nanomaterials

Hybrid nanomaterials are a fascinating class of nanomaterials that have received widespread attention in current times. Such nanostructures consist of two or more different types of nanomaterials interacting with each other through a definite mechanism within the same system [123]. Such hybrid systems may usually contain both organic and inorganic components, and hold unique advantages over the individual ones. Depending upon the interaction between the nanocomponents, different types of morphology can be achieved, e.g. supported-, decorated-, embedded-, core-shell-, etc. The benefit of such hybrid system is achieving different properties within a single nanostructure. Examples of such nanohybrids includes Fe_3O_4/CNT that shows excellent magnetic property, CQD/TiO_2 that shows outstanding photocatalytic activity, HAp/graphene that shows osteogenetic activity, Pd/Fe_3O_4/graphene that shows catalytic activity and many more [124].

1.3.2. Methods

1.3.2.1. PU synthesis

PU synthesis involves the polymerization of the three basic components, *viz.* macroglycol, chain extender and diisocyanate. Generally, PU can be synthesized by two techniques, a) one-shot polymerization process, and b) pre-polymerization process [16, 125]. The one-shot polymerization technique entails the addition of all the basic monomers, namely macrogylcol, diisocyanate and chain extender simultaneously in a one-step reaction at definite conditions (**Scheme 1.1**). On the other hand, the pre-polymerization technique is a two-step process, conducted under definite or separate step-wise conditions. The first step usually results in the formation of an isocyanate or hydroxyl-terminated pre-polymer by reaction between macroglycol and diisocyanate. The second step involves chain extension

of the pre-polymer by reaction with diol or polyol chain extender to form linear PU or hyperbranched PU polymer of considerably high molecular weight (**Scheme 1.2**).
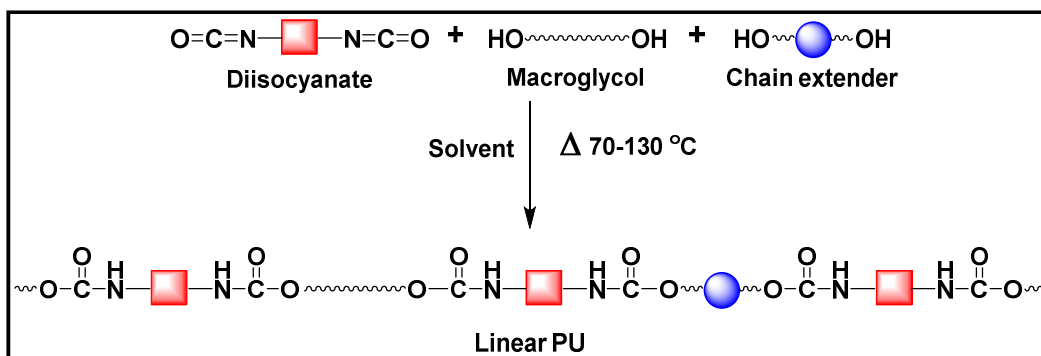
Scheme 1.1. Schematic representation of one-shot polymerization technique of PU.
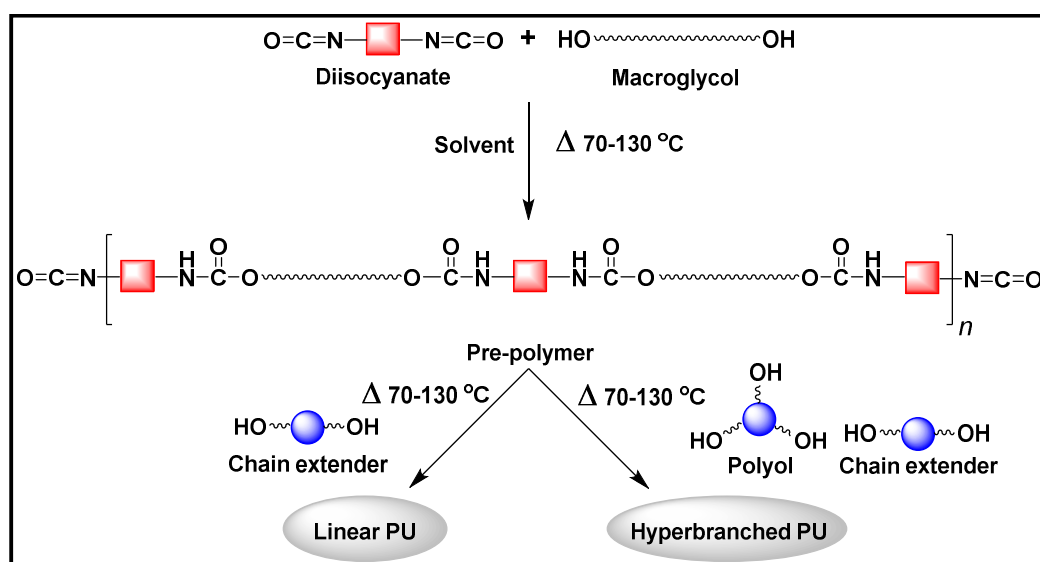
Scheme 1.2. Schematic representation of pre-polymerization technique of PU and HPU.

Common organic solvents like xylene, tetrahydrofuran (THF), dimethylformamide (DMF), etc. are often used to achieve better homogeneity of the reactants during polymerization. In general, one-shot polymerization process is rapid and poses difficulty in reaction control, especially in the case of a multi-functional polyol chain extender. In stark contrast, pre-polymerization process is more consistent, gradual and permits better control over the reaction. This process is most favored for the synthesis of HPU, allowing attainment of high degree of branching without any risk of gel formation [16]. Monomeric systems of $A_x + B_y$ (x,y ≥ 2) types are best suited to this process for HPU synthesis. In this milieu, there is an abundance of recent literature on synthesis of HPU using commercial as well as bio-based resources. Duarah et al. presented the synthesis of HPU by pre-polymerization process using a starch-based polyol as the branching moiety [87]. Zou et al.

reported the synthesis of HPU by one-shot polymerization process using PTMEG as the macrogylcol and used the polymer as toughener in fashioning diglycidyl ether of bisphenol A (DGEBA) based epoxy thermosets [126]. Du and co-workers demonstrated the synthesis of HPU by pre-polymerization process, using a hyperbranched polyol composed of PEG and *bis*-MPA [127]. Again, HPU synthesis using a dimer acid-based macroglycol and PDMS by pre-polymerization process was highlighted by Ghosh and Karak in two separate reports, indicating the relevance and utility of HPU and their synthetic processes [88, 128].

1.3.2.2.   Nanomaterial synthesis

Preparative methods of nanomaterials are broadly classified into two major approaches: (i) top-down and (ii) bottom-up (**Scheme 1.3**). Top-down approach entails synthesis of nanomaterials by size reduction of bulk materials, using mostly physical methods. This approach generally requires harsh and extreme conditions. Various physical methods like ball-milling, mechano-chemical, laser ablation, electrochemical, etc. come under the purview of top-down approach. Alternatively, bottom-up approach entails synthesis of nanomaterials from atomic or molecular-level self assembly of precursors through physico-chemical processes like polymerization, condensation or pyrolysis. Different methods employed under this approach include hydro/solvo-thermal, sol-gel, sono-chemical, microwave-assisted pyrolysis, co-precipitation method, etc. Bottom-up approaches are more widely used for preparation of nanomaterials due to advantages like expeditious process, reproducibility, large scale production and better control over morphology and size [129].

Various state-of-art literatures report the use of these approaches for nanomaterial synthesis. Recently, Stelter and co-workers demonstrated dry ball-milling route to produce GO from pristine graphite flakes with 86-97% yield [130]. Liu and co-workers achieved controlled synthesis of various crystalline Mn nanostructures including α-MnO$_2$, γ-MnOOH and Mn$_3$O$_4$ with different morphologies by hydrothermal method [131]. Deeney et al. described the preparation of luminescent cylindrical carbon nanofibers by template-assisted microwave pyrolysis with an average diameter of *ca.* 200 nm [132]. Of lately, eco-friendly and green methodologies have been given more importance for nanomaterial synthesis. Varma and co-workers summarized the utility of microwave chemistry as a green methodology in synthesis of Ag nanoparticles [133]. Hydrothermal method was highlighted as a green technique for synthesis of CDs from plant resources in two separate reports by Jing et al. [134], and Arul and Sethuraman [135]. Meanwhile, Das and Marsili acclaimed natural biosynthesis using microorganisms as a green approach for biosynthesis of Au nanoparticles [136].

- Physical Methods
  - ✓ Ball-milling
  - ✓ Mechano-chemical
- Gas condensation
- Laser ablation
- Lithography

Top-down approach

Bulk

Powder

Nanomaterial

Clusters

Atoms

Bottom-up approach

- Chemical Methods
  - ✓ Sol-gel
  - ✓ Precipitation
  - ✓ Hydro/Solvo-thermal
- Gas phase synthesis
- Microwave assisted synthesis
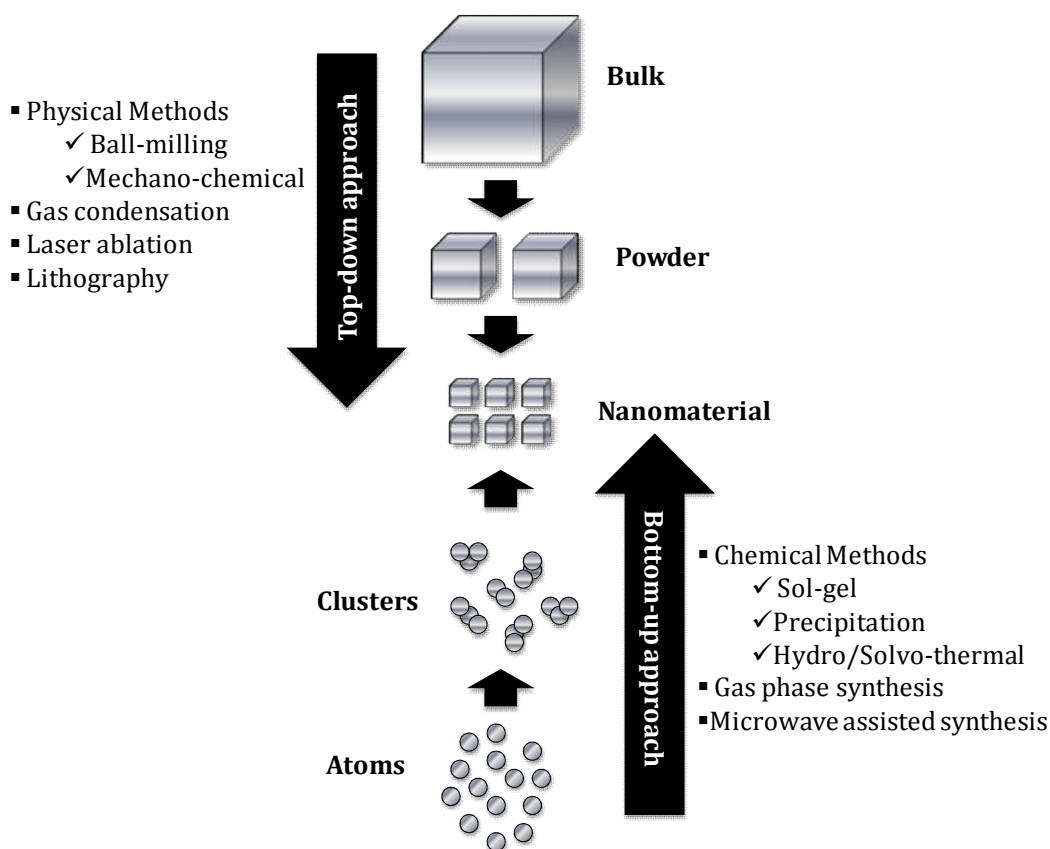
Scheme 1.3. Preparative methods of nanomaterials.

1.3.2.3.   PUNC fabrication

In a polymeric nanocomposite, the nanomaterial is dispersed in the polymer matrix and a synergistic relationship exists between the macro and nano structures by various physico-chemical interactions. Different preparative techniques have been employed for fabrication of polymer nanocomposites so far. In this context, solution mixing (*ex situ*), *in situ* polymerization and melt mixing are the most frequently utilized techniques for fabrication of PUNCs. These techniques are briefly summarized below.

(a) Solution mixing (*ex situ*) technique

In solution mixing technique, the nanomaterial is swollen and properly dispersed in a suitable solvent or mixture of solvents by shear mechanical force and ultrasonication. The solvent-dispersed nanomaterial is then mixed with a solution of PU by shear mechanical force and ultrasonication. Ultimately, the nanocomposite is obtained by evaporating the solvent under reduced pressure. In this technique, the interactions among the polymer, nanomaterial and solvent govern the nanomaterial dispersion in the polymer matrix. [137, 138] When nanomaterial-solvent interactions dominate, the nanomaterial disintegrates in

the solvent itself. This results in non-formation of polymer nanocomposite. In contrast, when polymer-nanomaterial interactions dominate, the polymer chains penetrate into the nanomaterial, leading to the formation of an intercalated or exfoliated nanocomposite. This intercalated or exfoliated nanocomposite remains intact even after solvent removal. However, in some cases, the polymer-nanomaterial interactions are very poor, leading to agglomeration of nanomaterial on contact with solvent molecules. After solvent removal, the polymer chains stack in between the nanomaterial aggregates, resulting in formation of agglomerated nanocomposite. Gogoi et al. reported successful fabrication of tannic acid based waterborne HPU with CQD by solution mixing (*ex situ)* technique [139]. The results displayed effective interactions between CQDs and waterborne HPU that lead to enhancement of mechanical performance.

(b) *In situ* polymerization technique

During the *in situ* polymerization technique, the nanomaterial is directly swollen and dispersed onto the monomer or pre-polymer, which are then subjected to polymerization reaction to obtain the polymeric nanocomposite. In this technique, the polymer-nanomaterial interaction dominates, due to lesser viscosity of the monomer or pre-polymer, in comparison to the polymer. As a result, the level of dispersion of the nanomaterial in the polymer matrix is better compared to the solution mixing technique. Since the nanomaterial is added before the initiation of the polymerization reaction, hence it can participate in the reaction or cross-linking process, thereby reinforcing the polymer matrix. *In situ* polymerization technique often leads to the formation of exfoliated nanocomposite [137, 138]. This technique is mostly followed in case of PUNCs and HPUNCs. Eventually, the nanomaterial is swollen and dispersed either before or after the pre-polymerization step. In this way, the being-formed polymer chains can easily penetrate and adhere to the surface of nanomaterial, resulting in strong polymer-nanomaterial interactions. Mahapatra et al. reported the *in situ* polymerization of HPU/functionalized-GO nanocomposites [140]. The results demonstrated effective exfoliation of GO in HPU matrix and enhancement of nanocomposite properties.

(c) Melt mixing technique

The melt mixing technique involves the direct mixing of nanomaterial and polymer in the molten state. Suitable mixing and processing equipments like twin screw mixers, injection moulding, extrusion moulding, compression moulding, etc. are used to obtain the fabricated nanocomposites [137, 138]. In this technique, amorphous polymers are generally processed above their glass transition temperatures, while semi-crystalline polymers are processed above their melting temperatures. Compared to *in situ* polymerization technique,

the penetration or intercalation of the polymer in the nanomaterial is poor, due to high melt viscosity of the polymer. Thus, mostly partially exfoliated nanocomposites are obtained from this technique. This technique also permits the use of polymers which are not conducive for *in situ* polymerization or solution mixing technique and is compatible with current industrial processes. Weder and co-workers reported a scalable melt-mixing process to produce nanocomposites of cellulose nanocrystals (CNCs) with thermoplastic PU (TPU) elastomers [141]. The melt-processed nanocomposites achieved by compression moulding, displayed transparent and homogeneous appearance without any visible aggregation effects.

In addition to these, other techniques such as sol-gel process, coagulation spinning, latex fabrication, template synthesis, thermal decomposition, plasma treatment, laser ablation, gas condensation, template synthesis, thermal decomposition, plasma treatment, etc. are also employed for the fabrication of PUNCs [138, 142].

1.4. Characterization

A cluster of spectroscopic, microscopic, analytical and visual techniques are considered for the characterization of HPU, nanomaterial and HPUNC. These techniques are summarized in the following sub-sections.

1.4.1. Spectroscopic techniques

1.4.1.1. Ultraviolet-Visible (UV-Vis) spectroscopy

UV-Vis spectroscopy is one of the most general spectroscopic tools. This technique is used for detection of functional moieties capable of absorbing electromagnetic radiation in the UV-Visible region (200-800 nm). Especially, functional moieties that exhibit electronic transition such as $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, charge-transfer, etc. can be easily identified by this technique. UV-Visible technique is very resourceful, particularly in the characterization of nanomaterials and their corresponding HPUNCs. Carbon nanomaterials like graphene, CD exhibit characteristics bands in the UV-Vis region that can be comprehensively identified in the HPU matrix. The UV-Vis spectrum of CD shows a maximum absorption band near 280 nm, which can be attributed to $\pi \rightarrow \pi^*$ transition of conjugated C=C group and $n \rightarrow \pi^*$ of C=O group [143]. However, in HPUNCs, the position, intensity and nature of the UV-Vis bands may emerge differently with different amount of nanomaterials. Ghosh et al. reported a gradual increase in intensity of CD absorption band with increasing dose of CD in a bio-based waterborne HPUNC [100]. Also, metallic nanomaterials with their characteristic surface plasmon resonance (SPR) can also be identified by this technique. The SPR bands

appearing in the UV-Vis spectrum can provide details about the shape, size and distribution of the metallic nanoparticles [144]. Therefore, this technique is quite useful in characterizing PUNCs loaded with metallic nanoparticles. UV-Visible analysis was used as a vital tool by Münstedt and co-workers to illustrate differences in size and distribution of Ag nanoparticles in PU matrix, during *ex situ* and *in situ* fabrication of Ag/TPUNC [145]. Further, this technique is quite helpful in determining the band-gap of nanomaterials, specially the likes of semi-conductor quantum dots. Additionally, UV-Vis can also be employed to quantify transparency of PU and PUNC films, in terms of percentage transmittance.

1.4.1.2.   Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectroscopy is the most common and fundamental technique used for characterization of HPUs, nanomaterials and HPUNCs. Generally, this technique gives vital information regarding the presence of different chemical linkages and functional moieties in PUs and PUNCs. FT-IR helps in identifying the key functional groups like carbonyl (C=O) group of amide-I, amine (-N-H) group, alkoxyl (-C-O) group, which provides evidence for presence of urethane (-NH-C(=O)-O-) linkage in PU. In HPU, FT-IR bands of N-H stretching appear around 3400-3500 cm^{-1}, while C=O stretching and C-O stretching appears near 1620-1750 cm^{-1} and 1020-1060 cm^{-1}, respectively [47, 84]. Additionally, this technique can also provide key information about H-bonding within macromolecular structure of PU. The extent of H-bonding can be acknowledged from the blue-shift of amide-I and N-H bands [146]. Further, FT-IR serves as an important tool for monitoring the completion of PU reaction by observing the disappearance of free isocyanate (–N=C=O) group band within 2260-2270 cm^{-1} [84]. In the same vein, different nanomaterials and their effects on PUNCs can be recognized by this technique. Sahoo et al. comprehensively demonstrated the successful acid-functionalization of MWCNT and its effect on the functionalized-MWCNT dispersed PUNCs by using FT-IR technique [147].

1.4.1.3.   Nuclear magnetic resonance (NMR) spectroscopy

NMR is an important and resourceful technique for structural elucidation of HPU. This technique reveals important information related to chemical environment around different kinds of atomic nuclei. In general, ^{1}H and ^{13}C NMR are recorded to determine the presence and orientation of ^{1}H nuclei and ^{13}C nuclei in the HPU, even though other nuclei like ^{19}F, [29]Si and ^{31}P can also be detected, if present. Duarah and Karak extensively illustrated the structure of starch polyol-based HPU using ^{1}H and ^{13}C NMR spectral analyses [87]. Besides structural analysis, other parameters like physical state, isomerism, stereochemistry, yield, polymerization reaction kinetics, degree of branching, etc. can be determined by NMR.

Notably, NMR is a helpful tool for studying the branched architecture of HPU. Detailed analysis of NMR spectrum permits the estimation of degree of branching (DB) of the hyperbranched structure. DB can be estimated from the peak intensities of linear, terminal and dendritic units of the hyperbranched structure, as reported by Duarah et al., along with Ghosh and Karak [87, 128].

1.4.1.4.   Photoluminescence (PL) spectroscopy

PL spectroscopy is a special optical characterization technique that explores the luminescent properties of materials. This technique is particularly useful for studying photoluminescent nanomaterials like semi-conductor quantum dots, CQDs, polymeric quantum dots, etc. and their corresponding polymeric nanocomposites. PL is generally obtained in form of an emission band spectrum, often observed in form of fluorescence or phosphorescence by the naked eye. De and Karak reported the synthesis of CDs from banana juice that demonstrated green fluorescence under UV light (365 nm). PL emission spectrum of CDs showed excitation wavelength-dependent PL behavior with strong band near 460 nm (excitation wavelength of 360 nm) [143]. Again, Karak and co-workers demonstrated concentration dependent-PL behavior of bio-based waterborne HPU/CD nanocomposites [100]. In addition, quantum yield and unusual PL behavior such as up-conversion can also be studied with the help of PL spectroscopy.

1.4.2. Scattering techniques

1.4.2.1.   X-ray diffraction (XRD)

XRD is a highly sophisticated diffraction technique useful for characterization of nanomaterials and polymeric materials including PUNCs. This technique supplies information pertaining to the degree of crystallinity or amorphousness of such materials, in terms of diffraction patterns, intensity and angles [138]. XRD is particularly useful for study of nanomaterials, relaying information regarding their crystallinity and crystal structure. XRD patterns of CD shows a broad diffraction pattern near $2\theta = 20°$, which indicates its amorphous nature [143]. This technique also provides vital information to investigate the interlayer distance in a nanostructure, calculated using Bragg's equation,

$$n\lambda = 2d \sin\theta$$ (**Eq. 1.1**)

where, n is order of diffraction, λ is wavelength of X-ray, d is interlayer distance, and θ is diffraction angle. Formation of GO from graphite powder can be confirmed by analysis of crystallographic data obtained from XRD. Graphite exhibits a strong (002) peak at $2\theta = 26.4°$, which shifts to lower angle $2\theta = 7.80°$, upon its oxidation to GO. This shift is accompanied by increase in the interlayer distance from 0.34 nm to 0.78 nm

due to introduction of oxygen-containing functional groups in GO [148]. XRD is also helpful in exemplifying PUNCs. XRD patterns can help to establish the effect of nanomaterials in PU matrix. Sahoo et al. demonstrated that incorporation of upto 10 wt% MW-CNTs effectively enhanced the PU crystallinity and crystallite size in MWCNT/PUNCs [147].

1.4.2.2. Raman scattering

Raman scattering is a useful technique for detecting vibrational and other low-frequency modes in nanomaterials. This technique is particularly helpful in characterization of carbon based nanomaterials. Raman scattering provides signature data on carbon nanomaterials, which directly assist in their characterization. All carbon nanomaterials and their allotropes exhibit signature Raman scattering bands, *viz*. D band, near 1350 cm^{-1} due to graphitic structural defects; and G band, near 1580 cm^{-1} due to breathing mode of sp^2 hybridized graphitic domains. An additional 2G band around 2800 cm^{-1} is also often detected due to the presence of multi-layered graphitic domains [149]. Additionally, the relative intensities of D and G bands (ratio of I_D/I_G) reveal information about the extent of defects in the graphitic structure, with high values pointing towards large number of structure defects. Ye and co-workers reported increase in the ratio of I_D/I_G attributed to higher level of disorder and defects in graphitic domains of GO, compared to virgin graphite [148]. Raman scattering is also adept in characterization of metallic and hybrid nanomaterials. Magnetic Fe_3O_4 nanoparticles can be confirmed by the presence of a narrow Raman mode (A_{1g}) near 660 cm^{-1} [150]. Further, this technique can be used to exemplify the effect of nanomaterials in polymeric nanocomposites. Gogoi and Karak demonstrated increase in the intensity of D band of CD in CD/thermosetting waterborne HPUNC, due to defects and disorder encountered during the fabrication process [139].

1.4.3. Microscopic techniques

1.4.3.1. Optical microscopy

Optical microscopy is one of the most common microscopic techniques that use polarized visible light and a system of lenses to magnify images of small objects. Images generated by optical microscopy can be captured by normal, photosensitive cameras to generate a micrograph. Optical microscopy is considered to be an elementary technique to study the surface of nanomaterials, polymers and polymeric nanocomposites. Especially, this technique is used to study the topology of polymeric nanocomposites. Cheng and co-workers observed beautiful cross-extinction patterns indicating crystalline morphology of HPU-based phase changing material at room temperature using optical microscopic images [127]. Elsewhere, Ghosh and Karak investigated the self healing behavior of thermoplastic

silicone-containing bio-based HPUNCs by monitoring the optical microscope images during the healing process [128].

1.4.3.2. Scanning electron microscopy (SEM)

SEM is a vital microscopic technique for in-depth studying the surface topology of polymers, nanomaterials and polymeric nanocomposites. This technique involves scanning the surface of material with a beam of focused high energy electrons and generating images from the back scattered electrons in form of micrographs. SEM provides valuable information about the surface morphology of nanomaterials, including size and shape. Sayed and Polshettiwar reportedly identified six different morphologies of iron oxide nanoparticles by SEM images, which were prepared by a single synthetic protocol using different iron salts as precursor [151]. This technique can be also used to study the presence of inhomogeneity and crystallinity within the polymer matrix [138]. Most importantly, SEM is employed to study the distribution and orientation of nanomaterial in polymer matrix, as well as the overall morphology of the nanocomposite matrix. Ansari et al. reportedly synthesized PU/montmorillonite clay nanocomposites with well dispersed, approximately 3-5 nm thick nanolayers of clay on the PU surface, as inferred from SEM. The SEM images further demonstrated the homogeneous dispersion of the clay particles in the PU matrix [152]. Thomas and co-workers reported rough surface morphology of GO/HPU from SEM images, attributed to fine interfacial interaction between GO and HPU matrix [153]. Additionally, SEM, in combination with Electron Dispersive X-ray (EDX) technique is useful for the elemental composition analysis of nanomaterials and PUNCs.

1.4.3.3. Transmission electron microscopy (TEM)

TEM is a highly sophisticated and important microscopic tool for analyzing the bulk morphology of nanomaterials and polymeric nanocomposites. This technique involves scanning of the bulk matrix of the nanocomposite with the help of focused beam of electrons and generating micrographic images from the transmitted electrons. TEM helps in acquiring valuable information about dispersion, morphology, crystalline structure and elemental composition of materials. TEM images reveal information about the shape, size and distribution of nanomaterials. High Resolution TEM (HRTEM) images provide information about the interplanar distance within a nanostructure. Selected Area Electron Diffraction (SAED) pattern obtained from TEM furnishes evidence of crystallinity, crystal structure and help to identify the crystal planes. Convergent Beam Electron Diffraction (CBED) acquired from TEM aids in determination of structure, symmetry details and atom positions in a crystalline nanomaterial [154]. Because of its wide range of information, TEM is fairly utilized for studying the dispersion of nanomaterials in polymeric matrix [138].

Gogoi et al. skillfully demonstrated the potency of TEM in characterization of CD decorated HAp nanohybrid and its nanocomposite with tannic acid based waterborne HPU [155]. TEM and HRTEM images furnished decoration of CD over HAp surface with needle shaped morphology of length 50–80 nm and diameter 20–30 nm. Other information such as interlayer distance and crystallinity obtained from TEM were comprehensively described. Moreover, uniform distribution of CD decorated HAp over the HPU matrix was confirmed by the TEM study.

1.4.4. Other techniques

1.4.4.1. Elemental analysis

Elemental analysis is a classical characterization technique for determining the elemental composition of polymers, nanomaterials and polymer nanocomposites. Several techniques including CHN (carbon, hydrogen, and nitrogen), heteroatom (halogens, sulfur, phosphorus, etc.), atomic absorption spectrometry (metals, metalloids, halogen, sulfur, phosphorus, etc.), Energy dispersive X-ray (EDX) spectroscopy, X-ray photoelctron spectroscopy (XPS), etc. are used for elemental identification of nanomaterials and PUNCs [138]. EDX, often used in conjunction with TEM or SEM microscopic technique is quite useful in determining the elemental composition of PUNCs. Luo et al. reported the use of SEM/EDX to confirm the presence of the elements Ag, C, N, and O in *in situ* synthesized Ag nanoparticles/tannic acid-based waterborne HPUNCs [156].

1.4.4.2. Gel permeation chromatography (GPC)

GPC is the most popular technique to determine the molecular weight and distribution, i.e. number average molecular weight, weight average molecular weight, etc. and dispersity index of polymers. Since polymers can be mixture of different sizes of segments and chain lengths, their separation can be achieved on difference in hydrodynamic volumes of the polymer molecules having varying molecular weights. In this technique, the chromatographic column is packed with semi-rigid polystyrene bead crosslinked together with divinylbenzene as the standard. The polymer sample solution is eluted through the column and collected in terms of their chain lengths. The large sized polymer chains will elute out initially, followed by small sized polymer chains. The chromatogram depicts the refractive index or UV absorption intensity as function of elution volume, from which molecular weights can be determined compared to the standard polymer of known molecular weight [16]. Recently, Ghosh and Karak reported the synthesis of high molecular weight dimer acid macrogylcol-based thermoplastic HPU [88]. GPC results showed the

number average molecular weight and weight average molecular weight in the order of 10^5 and a polydispersity index within 1.32–1.57.

1.4.4.3.   Thermogravimetric analysis (TGA)

TGA is a very important analytical technique for determining the thermal stability of polymers and polymer nanocomposites. TGA determines the weight loss of polymeric material under air or under inert atmosphere and records the change of weight (weight loss or weight residue percentage) of the polymeric sample as a function of temperature or time in form of a thermogram (TG). First derivative of the thermogram (dTG) gives rate of weight loss at a particular temperature. TGA provides useful information regarding thermal degradation temperatures, thermal degradation patterns, thermal degradation kinetics, etc. that not only help in determining the thermal stability of polymeric materials but also identify the thermally labile chemical linkages or bonds in these materials. In addition, the amount of moisture plasticizers, fillers or any other volatiles, etc. present in the material can be obtained from TGA. TGA is a very helpful analytical technique, in case of PU and HPUNCs. Duarah et al. reported superior thermal stability of rCD/starch-modified HPUNC, in comparison to pristine HPU using TGA analysis. Using dTG analysis, they further identified a two-step thermal degradation pattern of the nanocomposites, attributed to their hard-soft segmental composition [61].

1.4.4.4.   Differential scanning calorimetry (DSC)

DSC is a sophisticated thermal analytical technique employed to study the thermal transition behavior of polymers and polymer nanocomposites. DSC determines the heat changes in a polymeric sample with respect to a reference sample, under an inert atmosphere as a function of temperature. These heat changes occur as the sample is heated or cooled and obtained as a plot of changes in heat flow versus temperature. DSC provides vital information pertaining to polymeric materials such as glass transition temperature (T_g), melting temperature (T_m), melting enthalpy, crystallization enthalpy, specific heat, etc. This technique is frequently utilized in characterization of HPUNCs. Duarah et al. noted changes in melting temperature, melting enthalpy and crystallization behavior of rCD/starch-modified HPUNC compared to pristine HPU from DSC analysis [61]. Additionally, DSC can be used to study the cross-linking kinetics of polymeric blends or thermosets. Gogoi et al. reported a DSC study on cross-linking kinetics and optimization of various curing parameters of hyperbranched epoxy-cured HPU thermosets using poly(amido amine) as the cross-linker [157].

1.5.   Testing methods

Various testing methods are employed to estimate the overall performance of HPU and its nanocomposites. These methods are summarized in the following sub-sections.

1.5.1. Mechanical

Mechanical performance of the HPU and its nanocomposites is defined on basis of various parameters like tensile strength, tensile modulus, elongation at break, scratch hardness, impact resistance, etc. Parameters like tensile strength, tensile modulus and elongation at break are evaluated by Universal Testing Machine (UTM). Standard testing protocol ASTM D882-12 is adopted to measure the aforementioned parameters using polymeric thin film samples of HPU and their nanocomposites [158]. Impact resistance of the polymeric films is estimated by using impact tester equipment with a standard falling weight, following the standard testing protocol ASTM D1037-16a [159]. Measurement of scratch hardness of the polymeric thin films samples involves following the standard ASTM D7027-13 testing protocol [160].

1.5.2. Thermal

Thermal properties of HPU and their nanocomposites are described on basis of various parameters such as thermal degradation temperatures, thermal degradation patterns, transition temperatures like glass transition, melting transition, etc., and many more. These thermal parameters are evaluated with the help of thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC), as described previously in Section 1.4.4 (Sub-section 1.4.4.3 &1.4.4.4)

1.5.3. Chemical

Chemical resistance of HPU and their nanocomposites is performed by exposure to diverse chemical environments (acidic, alkaline, saline, etc.), in order to determine their stability in different chemical media. ASTM D543-14 is the standard testing protocol adopted to determine the chemical resistance of polymeric materials [161].

1.5.4. Optical

1.5.4.1.   Transparency

Transparency is a key optical property for any polymeric materials. It is quantitatively determined with the help of a UV-Vis spectrophotometer by directly measuring the percentage of light transmitted through a polymeric film in the visible region (400-800 nm).

1.5.4.2.   Photoluminescence (PL)

PL is a special optical property, displayed by some carbon based nanomaterials like carbon quantum dots and their corresponding PU and HPUNCs. Apart from its quantitative measurement as described in Section 1.4.1 (Sub-section 1.4.1.4), PL is qualitatively detected by observing the luminescence under UV light at irradiation of wavelength 254 nm and 365 nm.

1.5.4.3.   UV-resistance

UV-resistance of the HPU and their nanocomposites is studied by following the standard ASTM D 5208-14 testing protocol [162]. The polymeric thin films of HPU and their nanocomposites are subjected to UV-aging by exposure to UV irradiation under ambient condition. Subsequently, the mechanical properties (like tensile strength and elongation at break) of the films before and after UV-aging are evaluated, in order to determine the retention (%) of properties. The retention (%) of properties indicates the UV-light resistance of the polymeric samples.

1.5.5. Miscellaneous

1.5.5.1.   Biodegradation

The biodegradation test of HPU and their nanocomposites is performed as per the standard ASTM D6691-09 protocol [163]. The polymeric samples are stored in a bacterial medium for a definite amount of time. The extent or rate of biodegradation is estimated by determining the change in weight of the polymeric samples and calorimetric estimation of bacterial growth at regular intervals of time.

1.5.5.2.   Shape memory

Shape memory behavior of HPU and their nanocomposites are studied by certain techniques, as described below:

(i)   Stretching technique

In this technique, the polymer thin film is heated just beyond its melting temperature T_m and lengthened to twice its original length (L_0). Subsequently, the stretched film is cooled instantly to low temperature (usually below T_m) using an ice bath, which fixes the temporary stretched shape for a specific amount of time. The length of this temporary fixed shape (L_1) is calculated. On release of the stretching force, the length of this temporary fixed shape (L_2) is once again calculated. Ultimately, the original length of the film is recovered by activating the temporary fixed shape with various external stimuli like heat, MW, light, electricity, magnetic field, etc. and the recovered length (L_3) is measured. The

shape fixity and shape recovery of the polymeric film are calculated using the following equations [164].

$$\text{Shape fixity (\%)} = \frac{L_2 - L_0}{L_0} \times 100 \qquad \textbf{(Eq. 1.2)}$$

$$\text{Shape recovery (\%)} = \frac{L_1 - L_3}{L_0} \times 100 \qquad \textbf{(Eq. 1.3)}$$

(ii)   Bending technique

In this technique, the polymeric thin film is heated just beyond its melting temperature T_m for a specific time and deformed from its original shape to a spiral or ring shape. The deformed spiral or ring shape is temporarily fixed by instantly cooling the sample in an ice bath for a specific time. After releasing the deforming force, the angle of deformation of temporary fixed shape is measured (θ). Ultimately, the original shape of the film is recovered by activating the temporary fixed shape with various external stimuli as stated earlier. The shape fixity and the shape recovery of the polymeric film are then calculated using the following equations [165].

$$\text{Shape fixity (\%)} = \frac{\theta}{90°} \times 100 \qquad \textbf{(Eq. 1.4)}$$

$$\text{Shape recovery (\%)} = \frac{90° - \theta}{90°} \times 100 \qquad \textbf{(Eq. 1.5)}$$

where, θ (degree) is calculated as the angle formed between the tangential line at the centre of the sample and the line connecting the centre and the terminal end of the deformed sample.

1.5.5.3.   Self healing

Self healing behavior of PU and their nanocomposites was studied by fracture test of the polymer film. In this testing method, the polymeric film is fractured or cut in a transverse direction and then the fractured area is healed by using various external stimuli as stated previously. The minimum time required for healing is considered as the optimal healing time. The self healing efficiency is calculated by measuring the percentage ratio of tensile strength of the films before fracture and after healing of fracture using the following equation [166].

$$\text{Healing efficiency (\%)} = \frac{\text{Tensile strength}_{\text{after healing}}}{\text{Tensile strength}_{\text{before healing}}} \times 100 \qquad \textbf{(Eq. 1.6)}$$

1.5.5.4.   Self cleaning

Self cleaning ability of PU and their nanocomposites are determined by dirt cleaning capacity of the surface by adequate surface hydrophobicity or hydrophillicity. In this testing method, the surface of the polymeric film is covered with dirt and mire. Cleaning of the polymeric thins films is indicated by sliding or rolling motions of water droplets on the hydrophobic or hydrophilic surface, carrying the dirt particles.

1.6. Property

Property is the central aspect of polymeric materials that delineates their ultimate utility. The primary instinct behind the formation of PUNC is the improvement of the inferior properties of PU and HPU without affecting their existing ones. The nature and extent of improvement is governed by the individual properties of the nanomaterials employed and their interactions with the PU matrix. This section discusses the general properties of PUs and the effects of nanocomposite formation on them.

1.6.1. Physical

The important physical properties that define PU include molecular weight, solubility, viscosity, specific gravity, etc. Molecular weight plays an important role in consolidating the structure-property relationship of PU and remains largely unaffected on formation of PUNC [101]. Solubility of PU depends upon the solvent polarity and molecular weight. Conventional solvent borne PU are soluble in polar organic solvents like xylene, THF, DMSO, DMF, etc. and insoluble in aqueous medium and alcohols. However, PU dispersion in aqueous medium can be obtained by using an emulsifier [16]. Solubility of pristine PU remains largely unaffected by formation of PUNC, though it is only swelled. Physical properties of PU can be considerably influenced by its architectural features. HPU has a quite narrow molecular weight distribution, which tends to approach unity with increase in degree of branching [167]. Specific gravity of HPU tends to be greater than unity, rising with increase in degree of branching. Further, HPU is more easily soluble and possess considerably low solution viscosity in contrast to its linear counterparts with the similar molecular weight. Solution viscosity tends to decrease with increase in degree of branching [138]. Thakur and Karak reported a castor oil modified HPU that is highly soluble in DMSO, DMAc, THF, etc. and possess higher specific gravity as well as low solution viscosity than its linear analog [85]. However, viscosity increases upon formation of nanocomposite, depending on the nature of nanomaterial used.

1.6.2. Mechanical

Mechanical properties are important features that define the performance of PU. These properties include tensile strength, tensile modulus, elongation at break, toughness, scratch hardness, impact strength, etc [16]. As mentioned in the introductory section, advancement of mechanical properties of PU is the benchmark achieved by the fabrication of PUNC. The extent of advancement depends upon the nature and distribution of the nanomaterial, along with the interactions between the polymer matrix and nanomaterial [137, 138].

Properties like tensile strength and tensile modulus are greatly improved upon formation of nanocomposite. Uniform dispersion of nanomaterial augments tensile strength while agglomeration diminishes the same. However, this improvement is mostly nanomaterial loading-dependent [142]. Conversely, elongation at break deteriorates after formation of nanocomposites. At the same time, toughness, which is a combined measure of tensile strength and elongation at break, significantly improves on fabrication of PUNC [142]. Similarly, mechanical properties like scratch hardness and impact strength exhibit enhancements upon formation of PUNC [138]. In the recent years, fabrication of PUNC has demonstrated major enhancement of overall mechanical properties in comparison to their pristine counterparts. These PUNCs includes different types and architectures of PU as well as nanomaterials of various origins. Most of these reported PUNCs involve PU and HPU with carbon based nanomaterials like MWCNT, GO, rGO, CQD, etc. Jomaa et al. [56] reported the mechanical stiffening of PU matrix by dispersion of grafted CNTs. This stiffening resulted in a 10-fold increase in tensile modulus by addition of 2 vol% CNT. Patel and Purohit [57] reported improvement in various mechanical properties of thermoplastic PU/graphene nanocomposites. Especially, improvement in tensile strength reached 20% with only 2 phr of graphene nanoplatelets. Duarah and Karak [61] reported improvement in various mechanical properties such as tensile strength, elongation at break, toughness, etc. in HPU/reduced CD nanocomposite. Further, different nanohybrids of carbon nanomaterials also efficiently enhance the mechanical properties of PUNCs. Han and Cho [55] demonstrated the synergistic effect of GO/CNT hybrids on mechanical properties of PUNCs. Mahapatra et al. [168] showed profound enhancement in mechanical properties of HPU/nanodiamond nanocomposites, especially tensile stress and modulus by integration of MWCNTs. Besides carbon based nanomaterials and their nanohybrids, other nanomaterials have also been employed to augment the mechanical properties of PUNC. Xu et al. [169] reported enhancement in mechanical properties like tensile strength, tensile modulus and elongation at break, due to highly exfoliated montmorillonite clay in HPUNC.

1.6.3. Thermal

Thermal properties usually communicate the thermal stability through various parameters like thermal degradation temperatures and degradation patterns, thermal transition behavior, glass transition temperature, etc. that governs the thermal performance of the PU [16]. Fabrication of PUNC is usually accompanied by improvement in thermal properties of PU. Thermal degradation temperatures and patterns of PU depend upon the composition of the PU matrix [142]. Employment of metallic nanomaterials in PUNC augments the thermal degradation stability of the PU matrix by hindering the escape of volatile decomposed

compounds [170]. Al-Mohammadi and co-workers [171] reported enhanced thermal stability of vegetable oil-derived PUNC due to dispersion of nano TiO$_2$. In similar vein, carbon nanomaterials such as graphene and CNT, along with inorganic nanomaterials like nanoclay, SiO$_2$ also contributes towards efficient improvement in thermal stability of PUNC. They hinder the rate of decomposition by forming char residues that serve as thermal insulators [54, 170]. Strankowski et al. [59] reported enhanced thermal properties of PUNCs reinforced by commercial graphene and rGO. Notable enhancement in thermal degradation temperature like T_{onset} (6 °C increment), $T_{50\%}$ (6 °C increment) and char residue (~4% mass increment) were recorded for PU/rGO nanocomposites. Wang et al. [64] demonstrated that better thermal stability of PUNCs with the incorporation of nano-SiO$_2$. Notably, char residue (% mass) of PUNC at 600 °C vastly improved from 3.4 to 12.7 upon loading of 12% SiO$_2$. Simultaneously, thermal transition behavior like glass transition (T_g), crystallization temperature (T_c) and melting temperature (T_m) are also affected by fabrication of PUNC. Generally, the nanomaterial functions as a nucleating entity which confines the mobility of polymeric chains within the matrix. Wang et al. [64] recorded an initial increase of 1.3 °C in T_g upon incorporation of 6% nano-SiO$_2$ in castor oil-based PU, which gradually improved to 3.4 °C increase upon doubling the content of nano-SiO$_2$. Strankowski et al. [59] reported PUNCs with high enhancement of T_c with graphene (~ 40 °C enhancement) and rGO (~ 14 °C enhancement).

Likewise, flame retardancy of PU can be improved by fabrication of PUNC. Inorganic nanomaterials like clay, silica and metallic nanomaterials are useful in this regard. Kadam et al. [63] reported improvement in flame-retardant behavior of phosphate-containing bio-based PU by incorporation of bentonite clay.

1.6.4. Chemical

Chemical properties of PU are described by their stability and reactivity towards chemicals like acid, base, salt, etc. This chemical reactivity depends upon chemical composition and presence of free reactive functional groups in the polymer matrix [16]. The chemical properties of PU can be exploited for their modification and tailoring to obtain newer properties. However, in hindsight, such reactivity is mostly undesirable and detrimental for their long term application. Generally, PUNC exhibits superior resistance to chemicals, compared to the pristine PU. This chemical resistance is mostly attributed to the nature, distribution and interactions of the nanomaterial with the PU matrix [138]. Carbon nanomaterials like GO, rGO, etc. and inorganic nanomaterials like clay and silicates are instrumental in enhancing the chemical resistance of PUNC. Wang and co-workers [172] showed excellent chemical stability of PU/rGO nanocomposite foams in acidic (pH~2) and

alkaline (pH~10) medium after 24 h. Ahmadi and Ahmad credited superior chemical resistance of PU/GO nanocomposite as key factor for its anticorrosive behavior [173].

1.6.5. Optical

Common optical properties of PU usually include color, gloss, transparency, etc [16]. Color of PU mostly depends upon the monomers, with additional aspects like transparency and gloss depending upon their nature. PU mostly retains or changes its color and additional aspects on formation of PUNC, depending upon the features of the nanomaterial like nature, dispersion, loading and light scattering ability [138]. Ghosh et al. demonstrated that the fabrication of bio-based waterborne HPU with quantum-sized CD led to the preservation of original color and transparency of the nanocomposite films [100]. However, prominent changes are noticeable in case of PUNC with carbon based nanomaterials like graphene and CNT where there may have loss of color as well as transparency. Mahapatra et al. [174] demonstrated loss in transparency of HPU/SWCNT nanocomposite films with higher concentrations of SWNCT. Apart from these usual ones, PUNCs may exhibit special optical properties such as fluorescence, phosphorescence, non linearity, etc [54, 138]. These special properties are prominently observed in case of PUNC with quantum nanodots. Chen et al. [175] described the fabrication of transparent PUNC with quantum-sized CdS nanocrystals that exhibit good optical property like fluorescence. Tan et al. [176] reported the fabrication of PUNC with N-doped CQD that shows multiple mode of emission like fluorescence, delayed fluorescence and phosphorescence.

1.6.6. Electrical

Electrical properties of PU concern its insulating or conducting behavior on application of electric current. Generally, pristine PU possesses poor electrical conductivity and behaves as an insulating material [138]. However, it is possible to induce conductivity in PU by fabrication of PUNC with appropriate nanomaterials. The development of conductive pathways (conductive network of nanomaterials) enabling electron or charge transfer induces electrical conductivity in PUNC [177]. Carbon nanomaterials like CNT, graphene, GO, rGO, etc. enjoy excellent electrical conductivity and are employed in fabrication of electroconductive PUNC [178]. Kim et al. demonstrated that incorporation of even 1 wt% of GO and rGO in PU matrix introduces electrical conductivity [96]. Likewise, Wang et al. [179] reported MWCNT/PUNC with saturated direct electrical conductivity as high as 839 ± 72 S cm^{-1} at nanomaterial loading of ~31 wt%. Pokharel and co-workers reported a hierarchical hybrid assembly of graphene nanoplatelets, carbon black and MWCNT in PU matrix at 1:1:2 mass ratio and loading of 2 wt% that shows low surface resistivity ~10$^{6.8}$ Ω/sq, pointing

towards electrically conductive network structure [180]. In recent times, it has been observed that graphene nanomaterials facilitate better electrical conductivity in PUNC at significantly low loadings compared to other carbon nanomaterials [181].

1.6.7. Biological

Biological activity is one of the most sought-after attributes of PU. PU is known to show biodegradability, biocompatibility, anti-microorganism activity and many more biological attributes [11, 12]. Biodegradability is an important trait of PU. Mostly, biodegradable PUs are polyester-based, that are susceptible to degradation upon exposure to different external bio-conditions and microbes like bacteria, fungi, etc. or enzymes. Presence of hydrolysable chemical linkages like ester, amide, urea, etc. augments the biodegradation process of PU [13, 17]. However, there is no general trend regarding the effect of PUNC fabrication on biodegradability of PU. State-of-art literature on biodegradability of PUNC shifts accountability on the bio-conditions and nature of nanomaterial used. Nanomaterials like GO, rGO, clay, HAp, Fe_3O_4, CQD, etc. are employed for fabrication of PUNC based biomaterials. Gu et al. [182] reported rapid *in vitro* degradation of PU/Fe_3O_4 nanocomposites in PBS solution (pH~7.4 at 37 °C) during first 3 weeks, following steady decline in degradation enduring 67% weight loss after 13 weeks. Biswas et al. [183] reported the profound biodegradation of organically modified nanoclay/PUNC in enzyme media (lipase; *P. cepacia* at 37 °C and pH~7.4), manifested in significant weight loss of 50% in only 12 days. Oprea et al. [184] demonstrated accelerated fungal biodegradation of castor oil-based PU upon incorporation of cellulose derivatives, as confirmed from SEM, FTIR and mechanical performance analysis. However, as a synthetic matrix, PU lacks target-specific bioactivity and invites the risk of host reaction due to its xenobiotic nature. Fabrication of PU with suitable nanomaterials enhances its inherent bioactivity and biocompatibility. Incorporation of GO, Ag, ZnO, TiO_2, Fe_3O_4, etc. imparts anti-microbial or biocidal activity [185]. Ahmadi and Ahmad reported the surface antibacterial activity of PU/GO nanocomposites against bacterial strains of *E. coli* and *S. aureus* with 100% reduction in viability after 24 h incubation [173]. Similarly, HAp, layered silicates and nanoclay exhibit osteogenic activity [186]. Ni and co-workers developed a porous shape memory PUNC scaffold containing nano HAp that promotes bone tissue engineering. Nano-HAp improves the biological performance of the PU scaffold by promoting bone cell growth [187]. In recent times, bio-functionalized nanomaterials have been used fabricated to biocompatible polymers. These bio-functionalized nanomaterials bear bio-active motif like peptide, protein, enzyme or any drug molecule, which imparts target-specific bioactivity. Zhang et al. [65] reported the modification of a shape memory PU/HAp/rGO

nanocomposite using RGD peptide to recuperate its cellular adhesion towards promoting neo-tissue formation and integration with the targeted bone tissue in rabbit bone stem cells.

1.6.8. Smart

Smart polymers are advanced materials that respond to any suitable external stimuli like temperature, light, moisture, electric or magnetic fields, pH, chemical compounds, etc [188]. Generally, minor changes in the environments are enough to induce large changes in the polymer structure-property essence. Polymers demonstrate smart attributes like shape memory, self healing, self cleaning, etc. which have important implications in the polymer domain.

(a) Shape memory property
Shape memory property stems from the shape memory effect (SME). Some of the key parameters that define SME are shape recovery, shape fixity and shape recovery time. PU is an inherent shape memory polymer (SMP), due to its hard-soft segmental composition in the polymeric chains. As a result, PU possesses a broad-ranged transition temperature for shape recovery, high recovery strain (up to 400%), high control on the softening, favorable and tunable physical properties, and so on [189]. SME in PU is mostly governed by the hard and soft segment morphology and its reception to external stimuli. The hard segments embolden the permanent shape of PU, while the soft segment facilitates the transition from permanent to temporary shape or vice-versa. It is seen that SME in PU can be enhanced by formation of PUNC using suitable nanomaterials. In this regard, carbon nanomaterials like graphene, CNT, etc. have been found to perform exceptionally well. Patel and Purohit reported shape memory thermoplastic PU/graphene nanocomposite with improved shape recovery (90% in 30s), recovery strength (150%), constrain strain recovery (50%) under MW irradiation [57]. Thakur and Karak fabricated a tough elastomeric HPU/rGO nanocomposite that exhibited outstanding multi-stimuli responsive shape memory behavior under direct sunlight, MW and thermal energy [99]. Mahapatra et al. [168] demonstrated excellent photothermal shape recovery (99.1%) and very fast shape-recovery actuation (9 s) in nanodiamond-grafted HPU/MWCNT nanocomposite using laser irradiation.

b) Self healing property
Self healing is a smart property that enables repairing of any micro-scale damages in the polymeric material by either intrinsic or extrinsic factors [190]. Such healing occurs autonomously or by action of a specific stimulus like temperature or light or chemical

reactions, etc. PU is considered to be an appropriate polymeric system for self healing materials, due to its structural inhomogeneity borne out of hard-soft segments in the polymer backbone and tunable properties. Several techniques are employed to tune healing tendency in PUs such as microencapsulation, microvascular network formation, supramolecular assembly and reversible bond formation [191]. Fabrication of PU with suitable nanomaterials enhances self healing tendency. Especially, carbon based nanomaterials have been found to improve the self healing behavior of PUNCs. Wan and Chen demonstrated that the self healing efficiency of waterborne PU/GO nanocomposite containing disulfide bonds reached a value of 85% for 0.5 wt% GO [58]. Li et al. reported the synergistic effect of graphene/CNT heterostructures in achieving a healing efficiency of $\sim$127% under microwave in PU/graphene/CNT nanocomposites [192]. Jin and co-workers reported near-infrared light triggered self healing behavior of PU/functionalized GO nanocomposite with improvement upto 90% healing efficiency and healing efficiencies maintained above 75% even after five cycles [193].

c) Self cleaning property

Self cleaning is a fascinating smart property that showcases inherent ability to remove any debris or microbes from material surfaces in a variety of ways. Such materials are specialized in self decontamination or purification by a cleaning medium like liquid (primarily water) [194]. The self cleaning phenomenon is controlled by two key parameters: surface free energy (γ_s) and surface roughness. Based on these two parameters, surface with contact angle (θ)>90° is considered as hydrophobic and θ<90°is hydrophilic. Consequently, self cleaning behavior is primarily obtained from hydrophobic (low γ_s and θ>90°) surface or hydrophilic (high γ_s and θ<90°) surface. Hydrophobic self cleaning involves sliding or rolling of water over the surface, carrying away dirt or debris with them. On the other hand, hydrophilic self cleaning involves covering the surface with water and removing dirt and debris by breaking them down *via*. chemical or photochemical techniques [195]. PU, owing to its inherent material property can be devised to show self cleaning property. Control and manipulation of the surface free energy and surface roughness by various techniques in PU imparts hydrophobicity or hydrophillicity that offers self cleaning behavior. Fabrication of PUNC with suitable nanomaterials like nanosilica, nanoclay, etc. can alter the surface properties of PU which can help in introducing hydrophobicity/hydrophillicity. Seyfi et al. [196] reported that surface modification of hydrophilic PU by nanosilica can introduce superhydrophobicity ($\theta$$\sim$160°) in PU/silica nanocomposite. Olad and co-workers demonstrated PU/montmorillonite/TiO$_2$

nanocomposite with enhanced hydrophillicity ($\theta \sim 10°$) for photocatalytic self cleaning towards degradation of malachite green dye (70% efficiency) [197].

1.6.9. Catalytic

Catalytic property is one of the emerging facets of polymer nanocomposites, which is gaining immense appeal in recent years. As discussed in the materials section (Section 1.3.1, Sub-section 1.3.1.4), a large variety of nanomaterials including metal, metal oxides, carbonaceous, semiconductor quantum dot, etc. possess remarkable catalytic activity. These nanomaterials are exploited towards introducing catalytic properties in PUNC. However, mostly photocatalytic properties have been explored till now. In particular, metal/metal oxides of Ti, Zn, Ag, etc., semiconductor quantum dots like CdS, carbon nanomaterials like CQD, g-CN, etc. and their nanohybrids possess light-harvesting activity, which is applied for photocatalytic purposes. Thakur and Karak demonstrated the photocatalytic attribute of TiO_2-rGO nanohybrid in HPUNC towards degradation of methylene blue (within 2-3 h) under sunlight [198]. Mosconi et al. [199] explored the potential of N-doped CQD with different polymer nanocomposites to achieve UV-light induced H_2 generation, photo-reduction of Ag ions to Ag nanoparticles and visible light-driven selective photo-oxidation of benzyl alcohol to benzaldehyde. Budimir and co-workers achieved upto 97% efficiency in photocatalytic degradation of organic dye Rose Bengal using Gamma-rays modified CQD in PUNC [60]. Recently, Duarah and Karak demonstrated the utility of rCD-ZnO in HPUNC for photocatalytic degradation of commercial detergent ($\sim$95% degradation in 2.5 h) under sunlight [200]. On the contrary, the utility of PUNC in synthetic catalysis and transformations have been very elusive. These PUNCs possess better mechanical stability and shelf life, which makes them useful for catalytic purposes. Das et al. [201] reported a waterborne HPU/CQD nanocomposite as promising catalyst for selective *para*-hydroxylation of various aromatic hydrocarbons using UV light. Lately, Janiak and co-workers reported the catalytic activity of Pd nanoparticle immobilized porous PUNC for Suzuki-Miyaura cross-coupling reaction at room temperature [202].

1.7. Applications

Applications of PU and PUNC span a wide spectrum due to their unique and tunable range of properties. Some of these applications are discussed in this section.

1.7.1. Surface coating

PU is extensively employed for surface coating application. As a coating material, PU provides several advantages like high shelf life, superior physical and chemical resistance to corrosive environments, strong adhesion, transparency, ease of application, etc [138]. PU coating is applicable on different surfaces and objects which include building materials, furniture, floor, coating on metal surface, oil and gas pipeline, exterior and interior coating in automobiles and many more. Additionally, formation of PUNC improves the coating performance of PU and introduces several unique attributes which are useful for advanced applications. In recent times, PUNCs have been developed as antibacterial coating, UV resistant coating, self healing coating, self cleaning coating, anticorrosive coating, etc. Charpentier and co-workers developed PU/nano-TiO_2 nanocomposite as an antibacterial and self cleaning coating [203]. Ghosh et al. [100] showed the utility of bio based waterborne PU/CD nanocomposite as visibly transparent and photoluminescent surface coating material. Yu et al. reported self healing PUNC coating with recoverable surface hydrophobicity [204]. Tran et al. [205] showed the fabrication of PUNC with silanized-graphene and hexagonal boron nitride and their utility as UV resistant coating. Ahmadi and Ahmad developed bio based PU/GO nanocomposite as antimicrobial and anti-corrosive coating [173].

1.7.2. Construction material

PU is fervently used in manufacturing construction and building material like artificial walls, roof, furniture, floor, decorative items, home appliances, sculptures, etc [206]. Rigid PU foam is useful for making wall, ceilings and roofs of modern houses. Compared to traditional building materials, rigid PU foam is light-weight, shows high water and chemical resistance, structurally stable and easy to install. On the hand, flexible PU foam is employed in furniture and furnishing appliances like seat cushions, mattress padding, carpet cushions, etc. Flexible PU foam is easy to mold into different shapes, provides better durability and comfort, and more cost effective compared to leather furnishing products. In addition, PU foam is also used as electrical and thermal insulator in home appliances [207]. PU resin is utilized as an aesthetic wall painting and flooring material. Such PU resin is seamless, water resistant and offer high longevity than concrete/stone flooring and solvent based paints [208]. In hindsight, PU and its nanocomposites provide good service and shelf life as construction and building materials.

1.7.3. Biomaterial

PU and its nanocomposites are widely used as biomaterials for medical applications such as anti-microbial coating, tissue engineering, wound healing, surgical sutures, drug delivery,

artificial muscle, medical implants, etc. PU possesses good biocompatibility and biodegradability, which makes it suitable for such applications [12, 13]. PU and its nanocomposite are used as 3-D scaffold matrix for tissue engineering with target-specific bioactivity [186]. PU/HAp nanocomposites show good osteogenic activity, and perform exceptionally well towards bone tissue regeneration [65, 155]. PUNCs with metal/metal oxides like Fe_3O_4, ZnO, TiO_2 and Ag exhibit profound anti-microbial activity and are used as infection resistant coatings and wound dressing materials [185]. Recently, a biodegradable starch-based PU/rCD nanocomposite is demonstrated to exhibit self-tightening behavior at body temperature, which can be used as a surgical suture [61]. PU and its nanocomposite can be used for targeted delivery or controlled release of drugs and therapeutic agents. Biodegradable LDI-based PU exhibited controlled release of anti-cancer drug, 7-tertbutyldimethylsilyl-10-hydroxy-camptothecin [209]. In another instance, PU-grafted chitosan nanocomposite exhibited effective capability for controlled and sustained release of anti-bacterial drug, tetracycline hydrochloride [210]. Since the last decade, PU and its nanocomposites are also employed for manufacturing biodegradable appliances for common day-to-day uses, in a bid to replace single-use plastic materials [10, 11].

1.7.4. Smart material

In modern times, PUNCs are in massive demand for advanced applications like smart materials. Smart materials are futuristic commodities designed to possess one or more properties that can be tuned or customized by application of external stimuli such as temperature, stress, radiation, pH, etc [188]. PU is considered to be an ideal polymer matrix for imbuing smart attributes [189]. These smart attributes are better defined and projected in PUNC fabricated with different nanomaterials, showing advanced features like shape memory, self healing, self cleaning, wear resistance, UV-resistance, etc. PUNC bearing carbon nanomaterials exhibit excellent efficiency as multi-stimuli responsive shape memory materials [57, 65, 87]. Similarly, PUNC with carbon nanomaterial perform well as self healing materials, as supported by various healing techniques [58, 62, 193]. PUNC with nanomaterial-induced surface or matrix modification demonstrate self cleaning attribute *via.* water repellency or photocatalysis [197, 198, 203].

1.7.5. Miscellaneous

PU and its nanocomposites are designed for variety of common day-to-day applications. PU is very commonly applied as adhesive and sealant [211]. PU adhesive is used to bind non porous surfaces like metal, wood, glass, etc. PU sealant is used to obstruct gaps and orifices to prevent air and water leakage. PU in various form is also used in automobile industry to

manufacture various interior components like seats, arm rest, head rest, dashboard, etc., as well as exterior parts like bumpers, roll panes, wiper cowls, etc [212].

Apart from common applications, PU and its nanocomposites are also used in designing materials for advanced applications. PU is used in electrical and electronic appliances as an encapsulator to seal and insulate fragile and pressure sensitive microelectronic components, printed circuit boards, transistors, underwater cables and wires, etc [213]. In similar vein, PUNC is used in optoelectronic applications like electrical conductors [180], sensors and actuators [214], electromagnetic shielding [215], light emitting diodes [216], etc. In recent times, PUNC is successfully used as 3D printed structural material [217], anti-counterfeiting material [139] and catalyst [201].

1.8. Scopes and objectives

State of art literature discussed in the prior sections provides an overview of the recent trends in PU research. It clearly reveals the efforts devoted to the development of eco-friendly PUs and their nanocomposites with unique properties for advanced applications. Apparently, there is a pertinent demand for shifting the focus of PU synthesis from conventional petroleum based feedstocks to renewable ones. Since the range of renewable resource based raw materials being utilized for development of polymeric materials is not yet sufficiently explored. Hence, the development of renewable resource based PUs demands sustained efforts and exploration in the current times. Literature reports discuss the utility of vegetable oils as the prime renewable source in this matter. However, there is scope for further development of vegetable oil based PUs by modification and innovation, in order to improve their material aspects and at the same time meet the environmental demands. Design of HPUs provides an inimitable approach for realizing this goal. Hence, modifications of vegetable oils like castor oil and their utilization towards development of renewable resource derived HPUs may provide an opportunity to meet the requirements of an eco-friendly and purposeful polymeric material. Simultaneously, it is equally vital to improve the property aspect of these eco-friendly polymers by fabricating their nanocomposites to address the contemporary demands. In this regard, carbon based nanomaterials, with their set of myriad properties (structural, thermal, electrical and optical) are in the forefront of research in polymeric nanocomposites. For the fact of the matter, the fabrication of HPUNCs with carbon based nanomaterials can provide the opportunity to improve the material properties as well as cultivate advanced attributes like shape memory, self healing, self cleaning, etc., which are still under developing stages. Thus, development of renewable resources derived HPUNCs using carbon based nanomaterials may form the suitable research proposition to reinvigorate a fresh perspective towards

diverse advanced applications like shape memory, self healing, self cleaning, catalysis, anti-counterfeiting, etc.

Thus, taking into consideration the aforementioned perspectives, the following objectives are earmarked for the proposed study:

i)   To synthesize, characterize and evaluate the properties of HPU containing modified renewable resource

ii)   To prepare carbon based nanomaterials by simple routes

iii) To characterize the prepared nanomaterials using various spectroscopic, microscopic and analytical techniques

iv)   To fabricate and characterize the nanocomposites of HPU with carbon based nanomaterials at different compositions

v)   To gauge the performance of the fabricated nanocomposites for their potential applications, and

vi)   To optimize the composition of the nanocomposites to obtain the best performance.

1.9.   Plan of research

In a bid to accomplish the objectives of the proposed study, the following strategies are adopted:

i)   A thorough literature survey on the field of renewable resource derived HPU, carbon based nanomaterials and their nanocomposites will be conducted.

ii)   HPU will be prepared by using multi-functional moieties derived from renewable resources like vegetable oils; diisocyanate like IPDI along with other conventional reactants. Characterization will be done by using different analytical and spectroscopic techniques such as FTIR, NMR, TGA, DSC, etc.

iii) Carbon based nanomaterials like GO, rGO, CQD and their nanohybrids will be prepared through simple orthodox methods.

iv)   The prepared nanomaterials will be characterized by different spectroscopic and microscopic techniques such as FTIR, XRD, SEM, TEM, TGA, etc.

v)   HPUNCs will be fabricated by the standard techniques as reported in literature using above nanomaterials.

vi)   The fabricated nanocomposites will be characterized by using FTIR, UV, XRD, SEM, TEM, etc.

vii) The performance of the HPUNCs will be investigated.

viii) The fabricated nanocomposites will be utilized for potential applications.

ix)   Optimization of composition of the nanocomposites will be performed to achieve the best performance.

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