General Introduction

Highlight

This chapter elucidates the preparation, characterization, property evaluation and applications of polyurethane and its nanocomposites of carbon-based nanomaterial(s) (CBN), in a nutshell. Most prominently, CBN like graphene, graphene oxide, carbon dot, reduced graphene oxide, etc. are discussed herein. A concise account is presented on different analytical and spectroscopic techniques employed in the characterization of polyurethane, nanomaterials, nanohybrids and polyurethane nanocomposites. In view of the importance of polyurethane nanocomposites based on different CBN, their fabrication methods, properties and prospective applications in diverse spheres of material science and technology are furthermore discussed. Last but not the least, the chapter comprises scopes, objectives and plan of research for the current study.

1.1. Introduction

During the past few years, nanoscience and nanotechnology has revolutionized the paradigm of scientific and industrial research, supported by the increasingly extensive spectrum of applications of nanomaterials [1]. This advancement fundamentally depends on the potential to manipulate materials and exploits their unique properties at nano-dimensional scale [2]. Development of nanomaterials results in the appearance of unique optical, electrical, magnetic and other attributes which have the prospective to modernize industry including electronics, medicine and consumer products. In this milieu, carbon-based nanomaterial(s) (CBN) have attracted significant interest owing to their exceptional amalgamation of chemical, thermal, electrical, mechanical and optical properties [1, 2].

With deeper appreciation and development of nanofabrication techniques, different types of CBN, including fullerenes, nanodiamonds, carbon nanotube(s) (CNT) such as multi-walled CNT (MWCNT), single-walled CNT (SWCNT) and graphene have been widely employed in various modern fields [3]. Furthermore, CBN as nanoscale fillers during fabrication of polymer nanocomposite(s) (PNC) have witnessed a huge development in current years due to utilization in various industries. The synergistic amalgamation of polymer matrix and nanofillers presents the materials with outstanding and improved mechanical, thermal, electrical, etc. properties which are unattainable by the individual components [4]. In this context, the choice of graphene as a reinforcing filler in the fabrication of PNC has received considerable interest of researchers due to its excellent electrical, mechanical and thermal properties which are significantly better than the used inorganic fillers [5]. However, the high surface energy and hydrophobic nature of bare graphene results in poor dispersion and seldom allows compatibility with the available polymer matrix. Thus, graphene based materials such as reduced graphene oxide (RGO) and graphene oxide (GO) are used as apt alternatives. The large number of oxygeneous functional groups like hydroxyl, carbonyl, carboxyl and epoxy of GO allows compatibility with most polar organic polymers [6]. Again, reduction of GO offers partial recovery of the graphene-conjugated structure which results in accomplishing unique properties as well as attaining a material that resembles graphene. RGO contains fewer oxygeneous groups, thus making it compatible with non-polar or extremely less polar organic polymeric system. However, the reduction of GO by hazardous chemicals (hydrazine, hydroquinone, sodium borohydride, etc.) and methods (thermal, chemical,

hydrothermal, etc.) are detrimental, both in terms of human health and environmental issues [7]. Although, sustainable alternatives of such reducing agents are available, but large-scale production of GO from graphite is very tedious and hazardous [7, 8]. Thus, one of the most recent addition to the family of CBN, carbon dot(s) (CD), proves to be an effective reinforcing nanomaterial in the fabrication of PNC owing to its advantages like easy functionalizability, remarkable aqueous solubility and biocompatibility as well as interesting luminescence property [9]. Moreover, the preparative methods of CD are facile as non-toxic chemicals, renewable precursors and environmentally benign solvents are used and thus the fundamentals of green chemistry are followed [9, 10].

Again, in the domain of nanotechnology, such CBN containing PNC including epoxy, polystyrene, polyaniline, polyurethane (PU), etc. based nanocomposites have grown to be a major area of development and research [5]. In the course of which, PU, being the most versatile, has gained tremendous recognition in a diverse field of applications including coating, adhesive, leather, composite, biomedical, etc [11]. Thus, an accurate scheme of PU with proper composition and structure of the constituents might consequence in exceptional and practical attributes for modern applications [11, 12]. In addition, hyperbranched polyurethane (HPU) with its unique architectural features might enhance the dispersion of CBN, to achieve unique rheological properties such as higher solubility, lower hydrodynamic diameter and lower solution as well as melt viscosity, as compared to conventional linear PU [12]. Such attributes assists in the mixing process through diverse physicochemical interactions and proves to be valuable for numerous applications besides single-step preparative methods.

Again, the emergent alarm for long term ecological and waste management problems, polymer industry aspires to utilize renewable resources for advancement of sustainable polymers as substitutes for petrochemical derivatives. In this milieu, sincere initiatives are undertaken to produce naturally renewable substitutes to minimize the dearth of raw materials and to reduce the risk of detrimental effects of the non-biodegradability of discarded materials to health and the environment. Vegetable oil (coconut oil, castor oil, sunflower oil, etc.), starch, soy protein and cellulose have been used as renewable feedstock to produce applicable polymers with economical and environmental values [13]. In this context, starch (second largest occurring biomass) may provide a cost effective and eco-friendly technique to form blends with synthetic polymers like PU with not only noted biodegradability and biocompatibility but also

remarkable elasticity [14]. However, till date, no research on starch-based HPU nanocomposites with different CBN has been found in literature. Therefore, exploration on starch-based HPU nanocomposite with different CBN like RGO, CD, etc. may present as an appropriate research to take on the current ecological, economic and environmental concern associated with the traditional polymeric materials. Thus the present thesis attempted to investigate starch modified HPU nanocomposites with CBN.

1.2. Historical background

The earliest work on PNC was conducted in 1980's by the Toyota research group which was based on the fabrication of polyamide nanocomposites and opened an innovative aspect in the discipline of material science [15]. A huge number of CBN like CNT, graphene, CD, etc. have been utilized thereafter in the fabrication of novel PU nanocomposites (PUNC). The rediscovery and isolation of graphene in 2004 by two renowned physicists Andre Geim and Konstantin Novoselov [16] of Manchester University proved to be a breakthrough in the domain of material science. In 2010, Khan *et al*. [17] studied the reinforcement of elastomeric PU with pristine graphene by solvent exfoliation which exhibited high modulus, toughness and ductility. In 2012, Nawaz *et al*. [18] fabricated thermoplastic PU (TPU) with functionalized GO and investigated the importance of network formation in the strengthening of elastomeric materials. In 2012, Chen and Lu [19] prepared PUNCs with graphene sheets for the development of mechanical characteristics without losing the toughness and ductility of the ultimate product. Ever since the discovery of CNT by Iijima [20] in 1991, they have been employed in several parts of science and engineering suitable to their exceptional properties. In 2005, Chen *et al*. [21] fabricated thermoplastic PU using SWCNT with improvements in electrical and mechanical properties. On the other hand, CD was accidentally discovered by Xu *et al*. [22] in 2004 during the purification of SWCNT which triggered widespread studies to exploit their fluorescence properties. In 2015, Gogoi *et al*. [10] developed a fluorescent and cytocompatible tannic acid based waterborne HPU nanocomposite with CD. However, art of literature reveals merely a few PUNC with CD as the reinforcing nanomaterial.

Again, PU was discovered by Otto Bayer *et al*. [23] around 1930s in Leverkusen, Germany. In 1993, HPU was initially prepared by Spindler and Frechet [24] with AB_2 monomers (A = hydroxyl group and B = blocked isocyanate group). Kumar and

Ramakrishnan [25] synthesized HPU by *in situ* generated 3,5-dihydroxyphenyl isocyanate (AB_2 monomer) from the equivalent precursor of carbonyl azide, during the same year. Hong *et al.* [26] reported a one-pot procedure for the preparation of HPU by employing the *in situ* generated dihydroxy isocyanate monomer. In 2007, Petrovic *et al.* [27] reported the first vegetable oil based HPU, using soybean oil modified polyol as the branching moiety. In this regard, naturally available polyphenolic compounds hold great promises towards the development of sustainable PU. In 1997, starch based PU foams were first synthesized where the effects of starch on its thermal and mechanical properties were studied [28]. Again, Wu *et al.* [29] reported the cross-linking of TPU micro-particles through urethane linkages using starch for the enhancement of mechanical strength of the final thermoplastic material. Inspite of using starch for modification of PU, the consequential products presented inferior properties in general, not to mention processing difficulties due to plasticization, hydrophilicity, brittleness and solubility difficulties in organic solvents [30]. **Table 1.1.** represents the continual improvements of various properties of starch based PU systems for different applications. Furthermore, starch modified HPU nanocomposite reinforced with CBN has not been reported, till date.

Thus, starch modified HPU nanocomposites with CBN such as GO, RGO, and their diverse nanohybrids demonstrated a promising field of research for their advanced applications.

1.3. Materials and methods

1.3.1. Materials

The advancement of PNC based on CBN has attracted researchers due to the combination of exceptional attributes which are advantageous in order to fulfill the demands of advanced materials. As mentioned earlier, various polymers are employed for the fabrication of PNC with CBN. In this milieu, segmented PU establishes as a valuable material due to its extensive gamut of properties which can be effectively modified by varying the basic building structures and compositions. Again, incorporation of CBN such as GO, RGO, CD, etc. into the PU matrix is a potential way to efficiently augment the different attributes of PUNC for advanced applications. The judicious selection of raw materials and variation of chemical constituents is significant in

dictating the final performance and applications of the nanocomposite with desired attributes. In the following section of the chapter, a broad review on the diverse materials employed during the preparation of PU and the fabrication of PUNC with CBN is made.

Table 1.1. Different applications and properties of starch based PU and PUNC

Type of PU	Type of starch	Unique properties	Ref.
Polyester based PU	Potato starch	Water resistant PU with improved mechanical properties.	[31]
PU	Corn starch	Cross-linked starch based PU with reduced hydrophilicity.	[32]
PU	Corn starch	Hydrophobic PU with strong adhesion between PU and starch granules	[33]
Waterborne PU (WPU)	Thermoplastic starch (TPS)	Enhancement of mechanical properties	[34]
WPU foams	TPS	Tough WPU foams with high tensile strength, contact angle and elongation at break.	[35]
WPU nanocomposites	Starch nanocrystals	High elongation at break, glass transition temperature (T_g) and tensile strength.	[36]
PU films	Corn starch	Improvement of mechanical properties	[37]
WPU	Pea starch	High amorphous character, hydrophobicity and tensile strength.	[38]
WPU nanocomposite	Starch nanocrystals	High elongation at break, Young's modulus and tensile strength.	[39]

1.3.1.1. Polyurethane

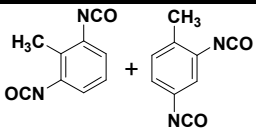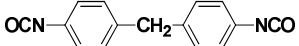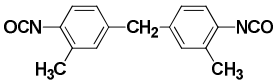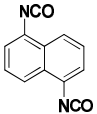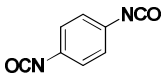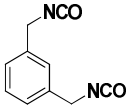PU is a linear polymer formed by the rearrangement reaction among di/polyol and di/poly-isocyanate, in presence of a chain extender with or without suitable catalyst [11]. The urethane group (also called carbamate group, -NH-COO-) is the repeating group in PU, though additional linkages such as urea, ester, ether, etc. are also found in their backbone [40]. In general, PU comprises of two incompatible structural segments, specifically, hard and soft segments [13]. The long-chain diols/polyols (known as

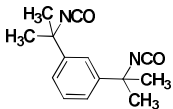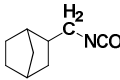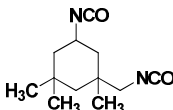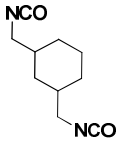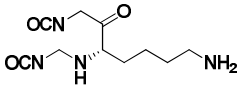macroglycols) built the flexible soft segments (weakly polar or non-polar) while the chain extender molecules (diols or diamines) and diisocyanate (aliphatic or aromatic) built the stiff and rigid hard segments (highly polar) [11, 41]. A large number of literatures cite that the incompatibility of the hard and soft segments enhances the desired properties of PU [12, 13, 41, 42]. Thus, the synthesis of PU entails the use of a di/poly-isocyanate, a chain extender and a macroglycol. A concise description on the three basic components is presented below.

(a) Diisocyanate

Aromatic or aliphatic di/polyisocyanates are the basic building block of segmented PU (**Table 1.2**).

Table 1.2. List of some commonly used diisocyanates in PU synthesis

Type	Diisocyanate	Applications
Aromatic diisocyanate	 TDI	Flexible PU foams, sealants, coating, etc.
	 MDI	Rigid PU with good thermal insulation.
	 3,3′-Dimethyl diphenyl methane diisocyanate (DDI)	Rigid PU foams and elastomers.
	 Naphthalene diisocyanate (NDI)	Tough PU elastomers with temperature resistance and wear resistance
	 p-Phenylene diisocyanate (PPDI)	Provides a compact hard segment and phase separation in PU formulation
		For production of PU elastomers.

	m-Xylylene diisocyanate (XDI)	
		For preparation of PU elastomers
	Tetramethyl-m-xylylene diisocyanate (TMXDI)	
Aliphatic diisocyanates	 1,4-Diisocyanatobutane	For preparation of biocompatible PU
	  Hexamethylene diisocyanate (HDI)	PU for special coating like enamel coating, UV resistance coating, etc.
	  Norbornane diisocyanate (NBDI)	Flexible PU foams
	  Dicyclohexyl methane diisocyanate (H$_{12}$MDI)	Two component PU coating
	  IPDI	PU enamel coatings with resistant to abrasion and degradation from ultraviolet light
	  Hydrogenated xylene diisocyanate (HXDI)	Non-discoloring PU.
	  (*S*)-Lysine diisocyanate (LDI)	PU for biomedical applications.

Earlier reports have suggested that aromatic isocyanates are more reactive than aliphatic isocyanates [43]. Methylene diphenyl diisocyanate (MDI) and tolulene diisocyanate (TDI) are most important aromatic diisocyanates, whereas isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI) are two major aliphatic diisocyanates

employed in industry. The reactivity of the isocyanate group is largely determined by the steric effect, structure, substituent and stereochemistry of the isocyanates. For instance, in TDI, the *para*-NCO group is 25 times more reactive than the *ortho*-NCO group [44]. Generally, TDI is employed as a combination of 2,6- and 2,4- isomers in the mole ratio of 80:20. Likewise, among the three isomers of MDI, specifically, 2,2-, 2,4- and 4,4-diisocyanates, 4,4-isomer is normally employed for commercial PU. The preference of the isocyanate for PU production is controlled by the attributes essential for final applications [43-45]. Aromatic diisocyanates are preferred over aliphatic ones as the obtained PU using former exhibits superior mechanical and thermal properties. Conversely, aromatic diisocyanate derived PU suffers from poor ultraviolet and oxidative stabilities. On the other hand aliphatic diisocyanate (e.g. HDI), or cycloaliphatic diisocyanates (e.g. IPDI) can offer better ultraviolet stability, transparency and phase separation behavior over the corresponding aromatic isocyanates [43-45]. Hence, with respect to the type of development of PU for certain applications, a suitable diisocyanate can be selected.
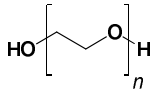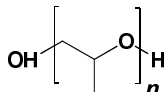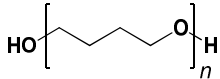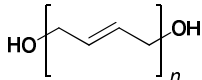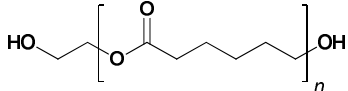
(b) Macroglycol
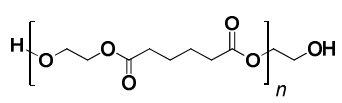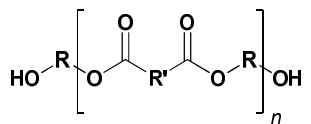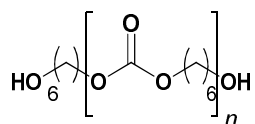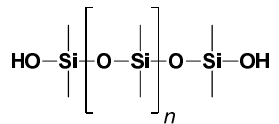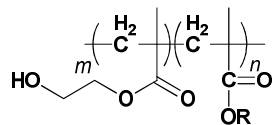
Most important part of PU comprises of polyol with molecular weight of 400-5000 g mol^{-1}, which strongly influences its ultimate properties. A variety of polyols have established PU as the most resourceful family of polymeric materials. These polyols contain two or more hydroxyl groups which react with diisocyanate to form PU polymer. The short chain polyol containing high functionality forms rigid PU, whereas long chain polyol with low functionality provides elastomeric soft PU [45]. Different kinds of polyols are employed for the synthesis of PU as shown in **Table 1.3**. Polyols such as hydroxyl terminated polyester polyols, hydroxyl terminated polyether polyols and hydroxyl terminated polybutadienes are usually used. The choice of polyols and their chemical nature primarily determines the physical behavior and end use of PU [43]. Basically the soft and hard segments of PU are developed with the aid of polyols. The ester bond in the soft segment of polyester-based urethanes imparts good material properties due to the presence of ester which is liable to hydrolyze. On the other hand, polyether based PU is relatively resistant to hydrolytic attack. Polydiene-based soft segment serves as an ideal candidate when the applications involve good environmental stability [46]. Again, hydroxyl and ester groups are comprised in a single backbone in

polyester polyol(s) (PEP). Moreover, highly branched PEP consequence in rigid, chemical and heat resistant PU, while less branched PEP impart remarkable flexibility and low chemical resistance to PU [44, 45]. Likewise, high long chain polyols with high molecular weight produce flexible PU whereas polyols with low molecular weight produce rigid PU. Castor oil occurs naturally as PEP, whereas other can be generated by chemical transformation of different vegetable oils. Moreover, polyols and fatty amide diols derived from vegetable oils serve as exceptional starting materials for the PU production. The amide group present in the backbone of the polyol provides good hydrolytic resistance and thermal stability [46, 47]. Again, the crystalline polycaprolactone diol (PCL) is the most suitable diol to develop shape memory PU [12].

Table 1.3. List of some bio-based and commercial macroglycols used in PU synthesis

Polyol	Characteristic	Application	Ref.
Polyethylene glycol (PEG)	Molecular weight 400-6000 g mol^{-1}, soluble in water, biocompatible, etc.	Imparts flexibility to PU for applications like elastomeric fibers and foam cushions.	
Polypropylene glycol (PPG)	Viscosity 100-1000 cp, molecular weight 400-4000 g mol^{-1}.	Formulations for PU as a dispersant in leather finishing, wetting agent for surfactants, etc.	[43]
Poly(tetramethylene ether) glycol (PTMEG)	Molecular weight 400-4000 g mol^{-1}.	Elastic fibers for stretchable fabrics and for PU resins.	
Hydroxy terminated polybutadiene glycol (HTPB)	Translucent liquid with variable properties	Highly elastic or tough and rigid PU.	[43]
	Polyester with low melting point	Production of PU with good resistance to water,	[12, 13]

PCL	(around 60 °C), low T_g and biodegradability.	oil, solvent and chlorine.	
Polyethylene adipate (PEA)	Melting point 55 °C, forms monoclinic crystals.	Used in preparation of PU with high mechanical and thermal properties.	[44]
Polyester diol where R/R´ = hydrocarbon part that may contain ether linkages also	Low molecular weight with narrow molecular distribution	Employed in production of high quality PU products with superior heat and light stability.	[46]
Poly(carbonate diol)	High performance polyols which provide tremendous hardness and weatherability to PU systems.	Fabrication of durable PU that can withstand extreme environmental conditions (temperature highs and lows, humidity, stain and chemical aggressions).	[47]
Polydimethylsiloxane glycol (PDMS)	Flexible and soft in nature, transparent to UV light and permeable to oxygen.	Used in fabrication of PU elastomers and is suitable for cell culture.	[48]
Acrylic polyol (ACPO)	Molecular weight 8000-13000 daltons, amorphous polyols.	Used in production of PU with superior solvent and chemical resistance.	[49]

(c) Chain extender

Chain extenders are diol/polyol (di/polyamine in case of poly(urethane-urea)) with low molecular weight (typically, less than 500 g mol^{-1}) which are used to bond with the pre-polymer species during PU synthesis (**Table 1.4**) [50-52].

Table 1.4. List of some chain extenders used in PU synthesis
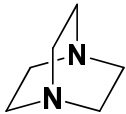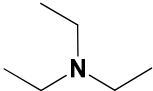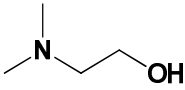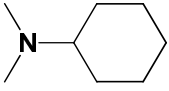
Type	Chain extender	Chemical Structure
Hydroxyl based chain extenders	Ethylene glycol	
	1,6-Hexanediol	
	1,4-Butanediol	
	1,4-Cyclohexane dimethanol	
	Glycerol	
	1,2,3-Propanetriol	
	Trimethylol propane	
	Triethanol amine (TEA)	
	N,N,N,N-tetrakis (2-hydroxyethyl)ethyl diamine	
Amino based chain extenders	Ethanolamine	
	Diethanol amine (DEA)	
	Diethylene triamine	
	Ethylene diamine	
	4,4-Methylene bis(2-chloroaniline) (MOCA)	
	4,4′-Methylene bis(cyclohexylamine)	

Di-functional compounds (1,4-butanediol, cyclohexane dimethanol, hydroxyl-amines, etc.) are regarded as chain extenders, whereas poly-functional compounds (hyperbranched polyol, triglyceride ricinolate, etc.) are employed as branch generating unit in case of HPU [53]. PU chain extenders are classified into two classes: linear and branched. Usually, PU chains are extended with an aliphatic diol or diamine which is introduced into the hard segments that eventually controls the thermal, mechanical and hydrolytic stability of the end products [53].

(d) Catalyst

In general, urethane reaction using aromatic isocyanates is feasible in absence of catalysts. However, in order to perform PU synthesis at a rapid rate and a low temperature, catalyst is regularly used (**Table 1.5**).

Table 1.5. List of some catalysts used in PU synthesis

Type	Structure/Name	Salient feature	Ref.
Amine compounds	Triethylenediamine (TEDA/DABCO)	Balances and controls the formation of gas, foam and gel during the production of PU foam. Normally, (0.1 - 5.0) % of a PU formulation are employed.	[44, 54]
	Triethylamine (TEA/TEN)		
	Dimethylethanol amine (DMEA)		
	Dimethylcyclohexyl-amine (DMCHA)		
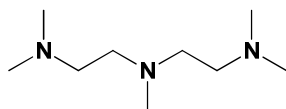
	N,N,N′,N′,N″-pentamethyl diethylenetriamine (PMDTA)	
Metal complexes	Dibutyltindilaurate (DBTDL)	Used to promote the most desired reactions in the PU formulation to influence the fluidity of reacting mixture, the size of bubbles and the finished properties of the product. Can be incorporated into the PU matrix. [44, 54]
	Stannous octoate $R_nSnX_{(4-n)}$ Tetravalent tin compounds where R=alkyl, aryl, etc. and X= halogen/ carboxylate group. Phenylmercury neodecanoate (Thorcat®)	Employed in PU production. For example in seals and gaskets, water resistant coatings and concrete sealants, shoe soles, in vibration dampers, as encapsulant for electronic assemblies etc. [44, 55]
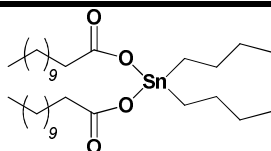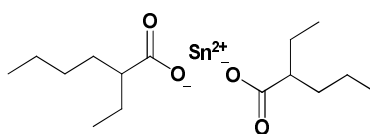
In PU synthesis, the catalysts typically used are organometallic salts of Hg, Sn and Pb, tertiary amines and carboxylic salts [45, 54]. Tertiary amines are the most reactive and react vigorously with water as compared to polyols. Moreover, amines are suitably employed for production of PU foams as blowing catalyst. Alternatively, organometallic salts of Hg and Pb are used in spray foams and PU synthesis, respectively. Nevertheless, the toxicity of Hg and Pb catalysts renders to the use of alternatives [44]. Organometallic salts of Sn are widely used as catalysts owing to their capability to activate the hydroxyl

groups of polyol. Yet again, in isocyanurate, quaternary ammonium, sodium and potassium carboxylic acid salts are generally used. Some of the widely used catalysts for the successful synthesis of PU are mercaptide oxides (dibutyltindilaurate (DBTDL), alkyl tin carboxylates, stannous octoate, dioctyltin mercaptide, dibutyltin oxide, etc), zinc and bismuth oxides and carboxylates [54].

(e) Bio-based resources

With the increase in fossil fuel consumption, there has been a rise in global warming in recent times, by release of greenhouse gases like CO_2. Hence, the reliance on fossil fuels for generating chemicals and products should be replaced and reduced with suitable alternatives like renewable resources [55]. In the last few decades, petrochemical based coatings have been extensively replaced by bio-based, biodegradable PU, due to their versatility in structure, eco-friendly, easy availability and biodegradability [56, 57]. Bio-based material (starch, vegetable oils, cashew nut shell liquid (CNSL), lignin, etc.) serve as rich sources of precursors for polyol since they are easily available, versatile in structure and have low ecological impact. Further, diisocyanate can also be synthesized from them and hence facile green production of PU is possible from them [58]. Among these, two of the major renewable resources based on bio-based resources are vegetable oils and cellulose. Vegetable oils find their utilization in the preparation of polymeric binders for flooring materials, coating formulations and resin applications. On the other hand, the use of cellulose is mainly restricted in polymeric coatings [56, 58]. Generally, vegetable oils are modified to derivatives such as alkyd based polyols and resins. In the past and present, vegetable oil based PU from plant seeds (castor, soybean, sunflower, etc.) have been reported [57-60]. Moreover, literature not only cites the use of bio-based polyols, but also bio-based isocyanates for the development of PU. There have been reports of use of different bio-based polyols developed by Palaskar *et al.* [61] from castor oil, cotton, ricinoleic acid and oleic acid. Bueno-Ferrer *et al.* [62] prepared polyol from dimer fatty acids. Kiatsimkul *et al.* [63] reported the preparation of polyols by initiating ring-opening of epoxidized soybean oil with ricinoleic acid, linoleic acid and ricinoleic acid estolide. Moreover, PU blending with starch has attracted great attention in PU chemistry which generated immense attention among the researchers. Literature cites variety of starch modified PU materials (composites, nano-composites, copolymers, grafts, blends, etc.) and their latest developments [64]. Thus, bio-based PU has gained

the attention of researchers for the chemical modification of renewable resources to the bio-based products for diverse applications.

1.3.1.2. Nanomaterials

In principle, nanomaterials are described as materials of inorganic or organic origin with at least one external dimension of 100 nanometers or less. Over the last two decades, various novel nanomaterials were investigated by the material scientists through extensive research. In general, they are categorized as zero dimensional (0-D), one dimensional (1-D) and two dimensional (2-D). O-D nanomaterials have all their dimensions measured in the nanoscale [65, 66]. The most widespread representations of O-D nanomaterials are nanoparticle, nanocluster and nanocrystal that fall within this group. Different metal, metal oxide based nanoparticles, quantum dot, etc. include as 0-D nanomaterials. 1-D nanomaterial possesses two dimensions in the nano range while its third dimension lies in several hundred nanometers to micrometer range which include nanotubes, nanorods, nanowires, nanospindle, etc. Some examples consist of CNT, cellulose nanofiber, polyaniline nanofiber (PANi), etc. [66]. 2-D nanomaterials possess only one dimension in nano scale regime, whereas the other two dimensions differ in between several hundred nanometers to micrometer range. They exhibit lamellar or plate like structures where the thickness lies in the nanoscale which includes nanofilms, nanolayers and nanosheets, for example, graphene based nanomaterials (GO, RGO, etc.), layered silicates, etc. [67]. Most interestingly, all of these three types of nanomaterials are employed for the fabrication of PUNC which leads to some excellent attributes owing to their high surface to volume ratio and exceptional physico-chemical properties. Distribution of the nanomaterials in the polymer matrix along with their size and shape chiefly define the properties of the PNC [68]. In this context, CBN exhibit extraordinary chemical and physical attributes (remarkable resistance to corrosion, high strength) and outstanding thermal and electrical stability and conduction. Such distinctive characteristics lead to their utilization in various fields such as medicine, biology and energy storage. Some of the current CBN are described below [69].

CBN

CBN have established an exceptional position in nanoscience due to their remarkable, mechanical, thermal, electrical attributes which find applications in drug delivery, energy

conversion and storage and composite materials. Conjugated CBN cover the areas of CNT, fullerenes and graphene [70]. Such CBN have garnered widespread attention in different applications like electronics and tough composite materials attributed to their excellent thermal, electrical and mechanical properties. With the development of innovative nanofabrication techniques, the employment of various CBN in advanced applications has progressed in recent times [70, 71]. Moreover, the technique for the advancement of CBN modified PNC has gained immense interest to acquire innovative materials with superior functional and structural properties as compared to pure components and previous nanocomposites [72]. Thus a brief overview of such CNB is narrated below.

(a) Graphene

Graphene is a novel poly-aromatic 2-D sp^2 hybridized carbon with a monolayer hexagonal honeycomb crystal lattice structure [73]. The consequent growth of graphene-based PNC (GPNC) is poised to participate as a vital position in modern science and technology. Indeed, GPNC is an emergent domain of nano-engineered materials, presenting light-weight alternatives to CNT-based PNC with added functionality connected to value-added and nanoscale specific properties. The high surface-to-volume ratio of graphene sheets in comparison to CNT possibly makes them more beneficial for altering the attributes of GPNC (mechanical, thermal and rheological properties [74]. The fabrication of GPNC develop the outstanding attributes of the polymer host and graphene displaying improved performance in various applications such as hydrogen storage, memory devices, semi-conductive sheets in transistors, etc. For the utmost improvement in the end properties of GPNC, homogeneous dispersion of graphene in the polymer matrix should be achieved which consequences in the efficient transfer of the external load *via* tough polymer-nanomaterial interfacial interactions [75].

(b) GO

The dispersion of graphene in most polymers is difficult due to its efficient interaction with just a limited number of polymers with aromatic rings. In addition, the low solubility of pristine graphene also limits its applications [76]. In this context, chemical modification of graphene is necessary by introduction of functional groups which can increase the number of interfacial interactions and thus confers effective compatibility

and dispersion of graphene in polymer matrix [77]. In this context, GO proves to be a chemist's chief tool for modification of graphene. GO was investigated as far back as 1840s [78]. Exhaustive oxidations of graphite leads to the formation of GO containing various peripheral oxygeneous functional groups, which assists in its additional functionalization. The oxygeneous functional groups are typically phenol, carbonyl, carboxyl, etc. at the edges of the sheets and epoxy and hydroxyl groups on the basal plane [79]. The electrochemical, mechanical and electronic attributes of GO are strongly affected by its oxygeneous groups and thus, accounts for its disparity with graphene [80]. It is pertinent to mention that, structural defects of GO associated with loss of some electrical conductivity, thus limiting the use of GO in electrical devises and materials. However, the presences of the oxygeneous groups endows with prospective benefits for utilizing GO in applications that supply provides enormous scope in electrochemical applications [80, 81].

(c) RGO

A growing area of science is the use of RGO in different polymeric materials owing to its unique electronic, optical, mechanical and catalytic properties. RGO can display high moduli (208 GPa to over 650 GPa), high electrical conductivities and easy functionalization to modify their compatibility with the polymer matrix [82]. RGO provides an appropriate resolution for applications like energy storage due to its easy large scale production. RGO is predominantly sp^2 hybridized few atoms-thick 2-D carbon layers with a few oxygen containing functional groups at the edges. GO can be reduced by various ways like chemical, thermal or electrochemical techniques or through infrared (IR) or ultraviolet (UV) irradiation to obtain a powder form [74, 82, 83]. Although, chemical reduction of GO is a scalable technique, RGO produced by this technique often displays substandard properties [82-84]. However, its excellent electrical conductivity allows the product to be used in a number of research projects. Moreover, by treating RGO with other chemicals or by creating new materials by combining RGO with other nanomaterials, the properties can be enhanced to suit advanced commercial applications [85, 86]. However, high toxic nature of the employed reducing agents (hydrazine, sodium borohydride, etc.) may have injurious effect, particularly for bio-related applications. In this context, various environment-friendly methods are employed for the GO reduction by using amino acid, vitamin C, polyphenol alcohol, reducing

sugar, glucose, photocatalytic reduction, phytochemical reduction, etc. are also worth mentioning. RGO is also treated as nano-reinforcing agent in fabrication of nanocomposites due to its enthralling physical and chemical properties such as extraordinary electrical, mechanical and thermal properties [7, 8]. Tkacheva *et al*. [87] prepared RGO by reaction with alcohols *via* novel technique. The obtained RGO platelets were range in the range of one to several nanometers in thickness and up to few microns in lateral size. In 2014, Yan *et al*. [88] realized a polystyrene and RGO based PNC with high electromagnetic interference shielding by solid-phase compression molding under high pressure. Thus, RGO has been widely studied in the various fields of science and technology.

(d) CD

CDs are quasi-spherical, discrete particles (size below 10 nm) with a sp^2 conjugated core, comprising of numerous oxygeneous groups like hydroxyl, carboxyl, aldehyde and epoxy [9]. In 2004, Xu, *et al*. [22] reported the isolation of fluorescent CD (1 nm size) by electrophoretic fractionation of arc-discharge soot. Nevertheless, Sun's group claimed this CBN as CD, or carbogenic quantum dots or carbon nanodots after two years later [89]. The predominant property of CD is photoluminescence (PL) which greatly influences the researchers. They also demonstrated excitation wavelength-dependent PL behaviors. Ever since 2006, scientific publications on CD significantly increased attributed to low cost, simple synthesis and remarkable biocompatibility of CD [90, 91]. CD has found extensive application in nanomedicine, sensing, catalysis, bioimaging energy storage/conversion, etc. Moreover, the low toxicity, high photostability and photoluminescence of CD serve them as prospective alternatives to semiconductor quantum dots presently employed [10]. Again, a nanocomposite containing highly dispersed CD modifies the refractive index and improves the photoconductivity of pristine polymer. Several methods have been developed to fabricate CD based PNC [92]. Lee *et al*. [93] reported the achievement of almost complete color emission using CD-polymer composites. Again, in 2015, Zhuo *et al*. [94] prepared RCD by reducing the solution of cysteine based CD with NaBH₄ which acts as a reducer for synthesizing Au nanoparticles. In 2013, Xu *et al*. [95] synthesized RCD which was used for cell imaging due to their strong blue PL. Thus, such investigations can unlock innovative scopes for advanced applications of CD.

(e) Nanohybrid of CBN

Nanohybrid is a composite system consisting of two or more different nanomaterials where often one is organic and the other is inorganic in nature. Usually, 0-D nanomaterials are decorated on the surface of 1-D or 2-D nanomaterials to obtain such nanohybrids. In this context, CNB nanohybrids are interesting materials employed in the fields of chemical gadgets, mechanics, electronic and electrical devises due to their remarkable chemical, electrical, mechanical properties [96]. Metals, inorganic fibers, polymeric fibrils, etc. enhance the attributes of graphene upon formation of CNB nanohybrids. Typically, 0-D nanomaterials such as Pt, Ag, Cu, ZnO, CuO, TiO_2, Fe_3O_4, NiO_2, etc. are used to prepare graphene-based nanohybrids [75, 94]. The large surface-to-volume ratio, high electrical conductivity and outstanding chemical tolerance of graphene serve it as a suitable matrix for PUNC. Therefore, in recent years, integration of inorganic materials (metal, metal oxides and metal sulfides) to graphene significantly attained huge focus for multi-functional attributes [96]. In 2017, Zhan *et al*. [97] prepared and studied cobalt sulfide-RGO nanohybrid as an anode material for sodium ion batteries. Again in 2017, Su *et al*. [98] synthesized variety of iron oxide-GO nanohybrids for removal of arsenic as high-performance adsorbents. Furthermore, current investigation on CD-metal modified nanohybrids has also dominated the fields of electrochemical and photochemical devices due to their fascinating down- and up-conversion features of PL along with charge or electron transport attributes [99]. Supported on the up-conversion luminescence attributes of CD, Li *et al*. [100] designed photocatalysts based on nanohybrids of SiO_2/CD and TiO_2/CD to harness the complete spectrum of sunlight. In 2015, non-enzymatic electrochemical sensors were designed which were based on CD/octahedral cuprous oxide nanohybrid for detection of hydrogen peroxide and glucose [101]. The formation of nanohybrid of CBN offers numerous physicochemical functions and attributes which prove to be beneficial for bio-applications as compared to the individual material. Such nanohybrids of CBN exhibit synergistic and individual attributes of the nanoparticles which significantly enhances their prospective applications [75, 94, 96, 102].

1.3.2. Methods

Preparative methods for PU, CBN, nanohybrid of CBN, and PUNC with CBN are described in this section.

1.3.2.1. Preparative methods of PU

The polymerization among the three chemical components namely diisocyanate, macroglycol and chain-extender lead to the production of segmented PU. Primarily the following two methods, namely, (a) pre-polymerization technique (two-step process) and (b) one-shot process are used to synthesize such PU (**Scheme 1.1**) [92]. In the first step of the pre-polymerization technique, macroglycol is reacted with diisocyanate to form an isocyanate or hydroxyl terminated pre-polymer of relatively high molecular weight, depending upon the molecular weight of the polyol and the ratio between the two reactants. In the second step, a chain extender, including branch generating unit is added to the pre-polymer at a definite temperature, to achieve a regular chain sequences of high molecular weight PU. Common solvents like dimethylacetamide (DMAc), dimethylformamide (DMF), tetrahydrofuran (THF), xylene, etc. are used in such polymerization process. On the contrary, the one-shot process which involves the addition of all the three reactants *viz*. diisocyanate, macroglycol and chain-extender at the same time, is rapid and tough to control. Moreover, when a branch generating moiety with more than two functionalities is incorporated during the polymerization reaction, the controlling of reaction is very important. Thus the pre-polymerization approach which is far more accurate, reproducible and consistent, and offers more variables to control the reaction, is used for the synthesis of HPU. In the second step, the multifunctional moiety is added slowly under dilute condition to better control the reaction without gel formation. Furthermore, literature cites a number of reports on the synthesis of HPU [44, 92, 103]. In 2006, Cao and Liu [104] prepared a series of HPU using hyperbranched polyester polyol as a chain extender *via* pre-polymerization technique which proved to be a superior solid-solid phase change heat storage polymeric material. In 2016, Zou *et al*. [105] prepared HPU with flexible poly(tetrahydrofuran) segments between the branching points by a one-shot method and used as a toughener for diglycidyl ether of bisphenol A/amine system. Stanzione *et al*. [106] synthesized bio-based PU foams using succinic acid as one of the bio-based polyol which exhibited good thermal stability and tensile strength. In 2016, Patil *et al*. [107] synthesized PU coatings using dicarboxylic acids and *Gossypium arboreum* plant oil as raw materials. In 2012, Thakur and Karak [12] reported the synthesis of HPU by $A_2 + B_3$ technique by employing castor oil or its monoglyceride as the hydroxyl containing B_3 reactant.
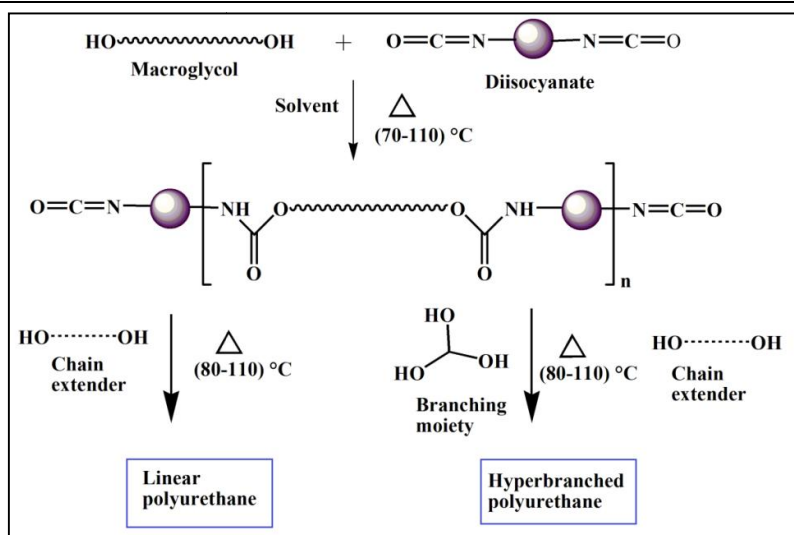
Scheme 1.1. Synthesis of PU and HPU.

1.3.2.2. Preparative methods of CBN

The typical preparative methods of some CBN are described below.

(a) Graphene

Over the last few decades, a range of methods have been reported for synthesis of graphene. The most frequently used techniques for synthesis of graphene are chemical synthesis, mechanical cleaving (exfoliation), chemical exfoliation and chemical vapor deposition (CVD) [108]. Some other reported techniques for graphene synthesis are microwave (MW) synthesis and unzipping of nanotubes. In the chemical exfoliation technique, exfoliation of dispersed graphite is done by inserting alkali ions between the graphitic layers [109]. Chemical synthesis involves the synthesis of GO, followed by dispersion in a solution and finally reduction with hydrazine [74, 75]. On the other hand, CVD method produces high quality graphene on a large scale for various applications. Again, another method for graphene synthesis is thermal graphitization of a SiC surface to produce epitaxial graphene. However, this technique is limited to merely high process temperature and is not capable of transferring on to any other substrate. Consequently, thermal CVD method is distinctive due to the production of uniform layer of thermally and chemically catalyzed carbon atoms that can be transferred over a wide range of substrates and deposited onto metal surfaces. Recent reports demonstrated graphene production in bulk using CVD for facile transfer of graphene which has made

advancement in semiconductor industries by providing new prospects to scientists and engineers [109, 110].

(b) GO

The preparation of GO primarily involves two major steps. Initially, graphite oxide is produced by oxidizing graphite powder which readily disperses in polar solvents owing to the presence of oxygeneous functional groups. In the second step, monolayer, bilayer or multi-layer GO sheets in colloidal suspensions can be formed by exfoliation of bulk graphite oxide by sonication, in various solvents. Moreover, the important points of GO preparation lies in selecting appropriate oxidizing agents for oxidation of graphite. GO is primarily synthesized by chemical oxidation of natural graphite. However, few reports on the electrochemical oxidation of graphite are found [110, 111]. Brodie [112] first reported graphite oxide preparation by addition of $KClO_3$ into graphite slurry in fuming HNO_3, in 1859. 40 years later, Staudenmaier [113] improved the method by adding concentrated H_2SO_4 in place of two thirds of fuming HNO_3 and supplying the chlorate in batches. Then in 1958, Hummers and Offeman [114] developed Hummers' method, an alternative oxidation technique, supported by the above investigations. In this technique, concentrated H_2SO_4 is used to dissolve $KMnO_4$ and $NaNO_3$ for oxidation of graphite to graphite oxide in a few hours. Consequently, Hummers' method was extensively adopted to prepare GO, owing to short time and ease of execution. However, the Hummers' method still suffers from some disadvantages like low yield, residual nitrate, generation of toxic gases (NO_2, N_2O_4), etc. Thus, over the last two decades, different modifications on Hummers' method have been made [115]. In recent times, Gao *et al*. [116] reported an oxidation technique based on K_2FeO_4 as an alternative to $KMnO_4$, and acquired a single-layer GO at room temperature. Marcano *et al*. [117] established another technique, "improved Hummers' method" where MWCNT led to the formation of GO nano-ribbons on addition of H_3PO_4. Again, Li *et al*. [118] reported the preparation of GO *via* improved Hummers' method under moderate condition, which led to the achievement of high rate of poly (L-lactic acid) (30.8%) grafting.

(c) RGO

Diverse reduction techniques are employed to obtain RGO from GO. Stankovich *et al*. [74] reported one of the commonly employed method of chemical reduction, using

hydrazine hydrate ($N_2H_4 \cdot H_2O$) as the reducing agent. Hydroquinone, hydrazine, dimethyl-hydrazine, and $NaBH_4$ are some other reducing agents which are utilized for preparation of RGO [7, 85, 116, 117]. It is pertinent to mention that, chemical reduction methods allow the introduction of heteroatom nitrogen which results in affecting the electronic structure of RGO. Again, thermal reduction of GO by heating it above 1000 °C is another generally used technique. Moreover, plant extract method, photo-catalytic method, supercritical fluid method, biomolecule-assisted methods and electrochemical method are some novel methods employed for GO reduction [118-120]. Su *et al*. [120] reported the production of RGO with exceptional electrical conductivity by using high-temperature alcohol vapor as a reducing agent of GO. Again, keeping into consideration the damaging effects of the chemical reduction methods, vitamin C, amino acid, polyphenol alcohol, tea solution, wild carrot root, melatonin, reducing sugar, glucose, bovine serum albumin and bacteria are employed in the reduction of GO [7, 8]. Moreover, innovative techniques are explored by researchers under the dictates of green chemistry doctrines by using natural polyphenol compounds such as plant extract mediated preparation of RGO is of primary importance.

(d) CD

Advancement of synthetic techniques for large-scale production of CD is essential to their applications. Xu *et al*. [22] first discovered fluorescent CD accidentally when they were purifying SWCNT from arc-discharged soot. Literature cites cost-effective, facile, large scale and size-controllable techniques for the synthesis of CD aimed advanced applications with varied structures and compositions. A majority of the present synthetic techniques for bulk production of CD are employed despite the inherent nature of the raw materials. However, very few works have been conducted for the mass scale production [9, 22]. Yang *et al*. [121] reported the production of 120 g of CD in a facile one pot synthesis using Chinese ink as raw material. Although carbon materials prove to be preferably appropriate precursors for the CD synthesis in macro-scale, the use of strong acids may cause pollution. In this context, biomass appears to be suitable alternative to carbon materials [122]. Sahu *et al*. [123] reported the preparation of CD by mixing ethanol with orange juice by hydrothermal treatment for 2.5 h at 120 °C. Wang *et al*. [124] reported the synthesis of CD using used chicken eggs by plasma-induced pyrolysis. Most recently, Park *et al.* synthesized CD by using harmful cyanobacteria and

food wastes in large scale [125]. However, as the high oxidation form of CD does not assist the emission of fluorescence, developing reduced CD (RCD) can widen their range of applications. Zhuo *et al.* [94] prepared cysteine based CD and successfully prepared RCD by reduction of CD with $NaBH_4$, which were employed for preparation of Au nanoclusters and nanoparticles. In 2013, Xu *et al.* [95] synthesized RCD with strong PL by a carbonization-extraction strategy.

(e) Nanohybrid of CBN

Literature reports several techniques to synthesize nanohybrid of CBN. In CVD method carbon nanoparticles can be produced by using silica matrices. In order to construct the carbon system in the initial step, the nanoparticles are introduced into the pores of the system by wet impregnation and subsequently the nanohybrids are treated with heat [126]. Conversely, the carbon matrix and the nanoparticles can be produced *in situ* by the polymeric precursor method, used for both types of matrices, silica-based and carbon-based [127, 128]. Among such nanohybrids of CBN, the fabrication methods of graphene based nanohybrid are generally categorized as the *ex situ* and *in situ* growth approach [129]. In the first technique, dispersion of RGO sheets in an appropriate solvent is mixed with a dispersion of pre-synthesized or commercially available nanomaterial. Prior to mixing, surface modification of the nanomaterial and/or RGO sheets is generally carried out for obtaining strong non-covalent and covalent interactions between them. As an alternative of just decorating nanoparticles on the surface of RGO, such sheets can also wrap around the nanoparticle for definite applications like the Li-ion battery. Moreover, the *ex situ* approach suffers from a few limitations such as low density, non-uniform coverage of the nanoparticles on the RGO surfaces, etc [130]. Contrary to the *ex situ* technique, the *in situ* growth approach can control the nucleation sites on RGO by providing a homogeneous distribution of the nanoparticles on the surface. As a result, the continuous decoration of nanoparticles on RGO surfaces is achievable [131]. Again, three fundamental techniques are employed to prepare CD-metal based nanohybrids *viz.*, (a) physical mixing method, (b) chemical reduction method and (c) hydrothermal/solvothermal technique. In the first technique, a dispersion of metal nanoparticles was added to CD solution, followed by mechanical shearing and sonication, which led to the formation of CD-metal based nanohybrids [132]. Li *et al.* [100] reported the preparation of TiO_2/CD nanohybrid from an aqueous CD solution with a dispersion of

TiO$_2$ nanoparticles stirred steadily for 10 min and subsequently vacuum dried at 80 °C for 12 h. In 2015, Bhattacharya *et al.* [133] prepared CD decorated Fe$_3$O$_4$ nanohybrid via ultrasonic treatment. In the second technique, CD was used as the reducing agent to prepare CD-metal nanohybrid. The peripheral polar oxygeneous groups like carboxylic acid, hydroxyl, carbonyl and epoxy groups on CD are able to reduce metal ions to metals by transfer of electrons [134, 135]. In 2011, Mitra *et al.* [136] prepared Ag and Au nanoparticles (from their corresponding salts) by using CD as the reducing agent under MW irradiation, in presence of PEG. Currently, this method extensively utilized one pot and facile to prepare CD-metal based nanohybrids. In the third method, preparation of nanohybrids was conducted by incorporation of CD or its precursors with the aqueous solution of the metal salts, prior to hydro/ solvo-thermal treatment [137]. The technique helps to control the shape and size of the nanohybrids and create strong interfacial interactions between CD and metal nanoparticles. The hydrothermal preparation of Fe$_2$O$_3$/CD nanohybrid was reported by Zhang *et al.* [138] by means of an aqueous solution of FeCl$_3$·6H$_2$O and (NH$_2$)$_2$CO in presence of CD at 180 °C.

1.3.2.3. PU nanocomposite fabrication with CBN

PUNC are mainly fabricated using mainly three different preparative approaches, specifically, (a) *in situ* polymerization, (b) melt mixing and (c) solution techniques, which allow the homogeneous dispersion of the nano-reinforcing material in the polymer matrix. A brief overview of these approaches is given below.

(a) *In situ* polymerization technique

The fabrication of PUNC can be conducted by the *in situ* polymerization technique which is an efficient and simple route. This technique involves an *in situ* generated polymer in presence of the nanoparticles or corresponding precursors by a single-step synthetic procedure where the nanoparticles grow within the polymer matrix [139]. This route averts agglomeration of particles and maintains a homogeneous distribution of nanoparticles within the polymer matrix. Moreover, *in situ* polymerization establishes a tough polymer-nanomaterial interaction devoid of using additional solvent. However, the drawback of this method is that the un-reacted reactants may hamper the ultimate attributes of the material. Extensive mixing, interaction and distribution of CBN within the polymeric matrix is allowed by this method. The presence of diverse secondary interactions between the CBN and polymer matrix assists in the formation of well

dispersed and stable PUNC. Basically, prior to dispersion into the pre-polymer or monomeric precursors, the nanomaterial is swollen and finally treated to polymerization reaction in order to obtain the PUNC. In comparison to solution technique, the extent of interaction between CBN and polymer is high due to the lower viscosity of pre-polymer or monomeric precursors as compared to the individual polymers [140, 141]. Very often, *in situ* polymerization is employed for the formation of exfoliated PUNC. The nanomaterial can take part in the cross-linking process and therefore influences impact the final attributes of the nanocomposite and for the fact that the nanomaterial is added well before the polymerization reaction [141]. In 2014, Reid *et al*. [142] reported a PU-TiO$_2$ nanocomposite with uniform dispersion of nanoparticle *via in situ* synthesis of TiO$_2$ nanoparticles in a solution of the hydroxyl-terminated polybutadiene pre-polymer. Khwanmuang *et al*. [143] developed and optimized the *in situ* synthesis of antimicrobial Ag/PU nanocomposites.

(b) Solution technique

In solution technique, the nanomaterial is dispersed in an appropriate solvent or solvent mixture and subsequently mixed with the polymeric solution by means of strong mechanical shear force followed by ultrasonication. The choice of solvent is deemed to be very important along with its amount for the successful preparation of the PUNC by this method. Eventually, the nanocomposite is obtained by evaporation of the solvent or precipitation subsequent to accurate mixing. The proper dispersion of the nanomaterials in this approach is attributed to its swelling by the solvent molecules. Consequently, the solvent molecules are replaced by the polymeric chains resulting in the formation of stable nanocomposite [144]. In addition, the confinement of the polymeric chains decreases the overall entropy of the system which is compensated by solvent desorption. This results in the intercalation of the PUNC. Not only most intercalated nanocomposites but also partially exfoliated structures are prepared through this method [145]. In 2006, Nanda *et al*. [146] prepared uniform dispersions of aqueous PU in acetone using 4-10 wt% functionalized polyhedral oligomeric silsesquioxane (POSS), followed by solvent exchange with water. In 2008, Mishra *et al*. [147] prepared thermoplastic PU-clay nanocomposite by solution mixing technique for engineering applications. Again, chitin based PU/clay nanocomposites were fabricated by the emulsion polymerization

technique [148]. Recently, in 2017, Wu *et al.* [149] produced porous conductive PUNC using the conventional solution-casting method.

However, it is pertinent to mention that, in spite of the easy and simple execution; this technique involves large quantity of volatile organic solvents that hinder its industrial effectiveness. Moreover, discharge of toxic waste to the surroundings is an associated disadvantage [144, 145].

(c) Melt mixing technique

Melt mixing technique is a widespread approach employed for fabrication of thermoplastic PNC. During this technique, mixer, twin screw intender, injection molding, rollers, etc. are used in order to mix the nanomaterial with the molten polymer. This mixing is attained above the softening point of the polymer under shear force. Semi-crystalline polymers are processed above their melting temperature (T_m), whereas amorphous polymers are mainly processed above their T_g [150, 151]. In 2007, Chun *et al.* [152] prepared PUNC with montmorillonite (MMT) under melt mixing condition which exhibited higher complex modulus and storage modulus. In 2016, Tayfun *et al.* [153] prepared PUNC reinforced with CNT by melt mixing which led to the improvement of tensile strength. Cruz *et al.* [154] prepared multifunctional and modified TPU elastomers with carbon nano-sized particles *via* melt mixing technique. The degree of interaction between the polymer matrix and the nanomaterials is not immense which leads to the formation of only intercalated PNC in most of the cases. Yet, melt mixing is the most preferred technique commercially even from an ecological point of view as it does not require any solvent or additional process [150].

1.4. Characterization and testing

The characterizations of pristine HPU, CBN, nanohybrid of CBN and HPU nanocomposites are generally performed by various analytical, microscopic and spectroscopic techniques which are summarized below.

1.4.1. *Spectroscopic techniques*

(a) UV-visible spectroscopy

UV-Visible spectroscopy is one of the important analytical tools for the characterization of materials such as polymers, nanomaterials, nanocomposites, etc. This technique

detects the functional groups of HPU, CBN and HPU nanocomposites of CBN that demonstrate absorption due to n-π* and π-π* transitions in the UV-visible region. GO displays a near 228 nm that undergoes a red-shift near 271 nm upon its reduction. This specifies the restoration of electronic conjugation. The absorbance values can also be used to determine the band gaps of the nanomaterials [7, 8]. In cases of PUNC, the varied doses of nanomaterials determine the nature, intensity and position of their peaks. Meera *et al*. [155] reported that the transmittance of PU/silica nanocomposites decreased upon increasing the concentration of silica nanoparticles. The visible to near IR region (NIR) radiations absorbed by plasmonic nanoparticles depend upon the shape and size of nanoparticles. This characteristic is known as SPR which is related to the resonant oscillation of the surface conduction electrons. The peaks displayed by the dispersed nanoparticles due to SPR in the UV-visible spectra, provide valuable information pertaining to the distribution, size and shape of the nanoparticles. Hence, UV-visible spectroscopy is employed to characterize PUNC loaded with plasmonic nanoparticles [156]. Soares *et al*. [157] reported the UV-visible spectral analysis of PU/ZnO nanocomposite which absorbs strongly near 275 nm on addition of ZnO nanoparticles, thus demonstrating the interfacial interaction of ZnO moieties within the PU matrix.

(b) Fourier transform infrared (FTIR) spectroscopy

FTIR study is utilized to identify different chemical linkages and functional groups present in nanomaterial, HPU and PUNC. Carbonyl stretching (–C=O) vibration near (1630-1750) cm^{-1} range (amide-I) and amine (-N-H) stretching vibration near (3400-3500) cm^{-1} region are the most important FTIR bands for PU. The emergence of these bands confirms the formation of urethane (-NHCOO-) linkage [158]. Moreover, this technique also assists in the examination of hydrogen bonding (H-bonding), existing within the structure of PU. Normally, formation of H-bonding can be identified from the shift of amide-I and -N-H bands towards lower wave number region. H-bonding is also indicated by broadening in intensity of transmittance band. In the same manner, diverse nanomaterials can be identified from their characteristic IR frequencies [12]. Mohammadi *et al*. [159] reported that the carbonyl band shifted to 1731 cm^{-1} as the hydrogen bonds in the polymer chains are disrupted by Fe_3O_4 nanoparticles in the PNC. FTIR proves to be a vital tool as disappearance of the band corresponding to -NCO group at around 2270 cm^{-1} can confirm the completion of the PU reaction [56,158].

(c) Nuclear magnetic resonance (NMR) spectroscopy

NMR is a commonly used technique for the structural characterization of polymers. ^{13}C NMR and ^{1}H NMR spectral analyses help to identify the presence of various types of carbons and protons in different chemical environment [12]. Again, NMR spectroscopy serves as a significant tool for meticulous structural analysis of HPU including information about its degree of branching (DB). Previous reports demonstrate the determination of DB from the peak area of the dendritic, linear and terminal units. Moreover, the formation of isomeric urethane linkages can be validated by NMR. For instance, ^{1}H-NMR spectroscopy can confirm the formation of two isomeric di-urethanes (*Z* or *E*). Moreover, DB of HPU can also be estimated by proper analysis of NMR spectrum [12, 56]. The structural study of the nanohybrids of CBN and its polymeric nanocomposites can also be done by ^{1}H and ^{13}C NMR spectral analysis. Huang *et al*. [160] reported the characterization of alkyne-containing PU and sulfobetaine-containing PU using NMR analyses.

1.4.2. Scattering techniques

(a) X-ray diffraction (XRD)

XRD is employed to determine the degree of crystallinity, crystal structure and crystal size of polymeric materials. Predominantly helpful for study of nanomaterials, this technique also discloses important information regarding crystal structure and crystallinity of nanomaterial. It helps to classify different diffraction planes from the intensity, shape of diffraction peaks and diffraction angles (2θ values) [161]. This technique also provides the scope to establish the inter-layer spacing in a nanostructure, calculated from Bragg's equation as given below.

$$n\lambda = 2d\sin\theta \dots\dots\dots\dots\dots\dots\dots\dots \textbf{(Eq. 1.1)}$$

where, n = order of diffraction, λ = wavelength of X-ray, θ = diffraction angle and d = inter-planar distance. Shift of diffraction peak towards lower diffraction angle indicates increase in interlayer distance. These frequently occur as a result of intercalation of polymer chains in between the layers of nanomaterial subsequent to the formation of PNC. Therefore, the observation of the position of diffraction peaks helps to attain ideas regarding the nature of interactions between nanomaterial and PU matrix [162]. Hence, XRD is also a crucial tool to investigate the interlayer distance. Pristine graphite display a basal reflection (002) peak at 2θ = 26.6º and the peak shifts to a lower angle upon

oxidation due to increase in interlayer distances [7, 8, 13]. Definite crystallographic peaks of metal and metal oxide nanoparticles from XRD analysis can confirm their formation. Normally, XRD techniques are of two types, specifically, small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD). SAXS is employed to determine nanoparticle size distribution, presence and shapes of voids, and dimension of small crystalline regions like lamellae whereas WAXD provides the orientation of crystalline region, nature of ordering structure and degree of crystallinity. The collective study of WAXD and SAXS demonstrated the quantitative characterization of PUNC [163]. Hezma *et al.* [164] reported the XRD pattern of PU/PVC blend displaying a sharp peak at 21.7° and a small peak at 22.4° due to semi-crystalline nature of pristine blend.

(b) Raman spectroscopy

Raman spectroscopy is frequently employed to examine the rotational, vibrational and other low-frequency modes in CBN such as graphene, RGO, GO, CD, etc. This technique provides a structural fingerprint by which molecules can be identified for structural characterization of such nanomaterials. Basically, the inelastic scattering of monochromatic light obtained from the materials is determined by Raman spectroscopy. This technique commonly employs a laser in the near infrared or near UV range as the light source. This technique is extremely susceptible to the material crystallinity, orientation and temperature and thus practical for analysis of molecules without permanent dipole moment [165, 166]. All allotropic CBN exhibit G band (near 1580 cm^{-1}), which represents sp^2 hybridized graphitic structure and D band (near 1350 cm^{-1}) indicates disorderliness in the graphitic structure. Moreover, 2G band (near 2800 cm^{-1}) indicates multilayered graphitic carbon nano-structure [7, 8]. Strankowski *et al.* [167] reported the Raman spectra of graphite, GO, and RGO. The most significant signals for GO appear as strong G band and D bands at 1550 and 1350 cm^{-1}, respectively. Further, the extent of disorder can be determined from the relative intensities of D and G bands (I_D/I_G ratio). High value of I_D/I_G ratio signifies high degree of disorder [13]. Moreover, Raman analysis also helps to characterize certain metal/metal oxide nanomaterial and nanohybrid of CBN.

1.4.3. Microscopic techniques

(a) Scanning electron microscopy (SEM)

SEM is a visual microscopic technique which scans the surface of with a beam of focused high energy electrons and generates its images from the back scattered electrons [163]. Further, this technique divulges information concerning surface topology of nanomaterial, PU and PUNC. The inhomogeneity and the surface morphology of nanomaterial (size and shape) can be studied with SEM. SEM also serves as a visual mode for information about the orientation and distribution of nanomaterial in polymeric matrix. SEM, in conjugation with Electron Dispersive X-ray (EDX) technique is useful for the elemental analysis of PU and nanomaterials. Ansari *et al*. [168] shows a SEM microphotograph of the PU/clay nanocomposite which showed approximately 3-5 nm thick and well dispersed nanolayers on the PU surface. The SEM images demonstrated the homogeneous dispersion of the MMT particles in the PU matrix.

(b) Transmission electron microscopy (TEM)

TEM is considered as the basic instrumentation for characterization with detailed study of internal structure of nanomaterials and their distribution in PUNC matrix [163]. TEM employs a highly energetic electron beam that passes through an ultra-thin film of the specimen which allows the electron beam to interact with the sample. The sample then transmits electrons which reveal details about the internal structure of the specimen. The shape, size and distribution of nanomaterial in the polymeric matrix can be disclosed from the TEM images of the nanomaterials. Moreover, High Resolution TEM (HRTEM) image offers information about inter-planar distance within a nanostructure. Selected Area Electron Diffraction (SAED) pattern confirms the crystallinity of a nanomaterial, assisted by Inverse Fast Fourier Transform (IFFT) and Fast Fourier Transform (FFT) images. The chemical composition of nanomaterial can also be studied using TEM associated with EDX. Moreover, the fact that TEM offers visual confirmation, the exact distribution of nanomaterial in a PUNC matrix can be determined. Therefore, TEM supplies straight examination of dispersed CBN and nanohybrid of CBN. Presence of diverse metallic nanomaterials on CBN surface can be effortlessly explored in nanohybrids of CBN by this technique. Strankowski *et al*. [167] reported the presence of RGO in PU matrices from TEM analysis.

(c) Atomic force microscopy (AFM)

AFM is a powerful and versatile scanning probe microscopy (SPM) to study samples at very high resolution at nanoscale. It has a sharp tip which helps to determine the tunneling current and tip sample interaction. This microscopy proves to be very important for nanohybrids and nanocomposites of CBN [161]. AFM supplies information about surface roughness, and layer thickness as well as mechanical attributes of the tested sample. Moreover, it serves as a significant tool to note the number of layers present in CBN such as graphene, GO, RGO, etc [169].

1.4.4. Optical techniques

(a) Photoluminescence

Some CBN and their nanocomposites like CD reveal extraordinary optical attributes like PL. The spectrophotometer (Fluorimeter) is used to study the precise PL performance of CD. This method utilizes an excitation source to pass the light through a monochromator or filter that strikes the surface of the sample. The sample absorbs a section of the incident light which allows some of the molecules to undergo fluorescence and the fluorescent light is emitted in every direction. Again, a second filter or monochromator allows the passage of a quantity of this fluorescent light to reach a detector, positioned at 90° to the incident light. LED, lasers, mercury-vapor lamps, xenon arcs are the different light sources employed as excitation sources. Extraordinary PL behavior of CBN such as up-conversion of CD can also be investigated with the aid of PL spectroscopy [10, 170].

1.4.5. Biological techniques

(a) Cell viability test

The viability of PU, PUNC and nanomaterial with any mammalian cell is tested by the broadly adopted technique, MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] assay. This technique is supported by the fact that 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (yellow) is reduced to insoluble 3-(4,5-dimethylthiazol-2-yl)-1,3-diphenylformazan (formazan) (purple) in living cells, under the action of mitochondrial reductase. The extent of reduction reflects the viability of the cells, which can be quantified by calorimetric method. In real practice, formazan is dissolved in a solvent (generally dimethyl sulfoxide, acidified ethanol or sodium dodecyl sulphate diluted with hydrochloric acid). Wavelength of 500-600 nm is used to measure the absorbance which is directly proportional to the number of viable cells [171].

(b) Cell proliferation

One of the most frequently used techniques for cell proliferation study is Alamar Blue assay which provides a sensitive, rapid and simple determination for estimation of mammalian cell viability [172]. A non-toxic, weakly fluorescent dye called resazurin is present in Alamar Blue which acts as a redox indicator and undergoes change in color under cellular metabolic reduction. The intensity of fluorescence of the reduced resazurin (resofurin) is directly proportional to the number of living cells. Thus, the rate of cell proliferation can be quantified by measuring the absorption of resofurin (at wavelength 500-600 nm), over a period of time.

(c) Antimicrobial test

Antimicrobial test of PUNC is chiefly carried out by the well diffusion technique [173]. In this process, test microbes are initially taken on Petri dishes and spread on the surface of potato dextrose agar or Muller-Hinton agar. Subsequently, the dispersed PNC are poured into the wells (6 mm diameter) on the solidified agar. For the positive control, a standard antibiotic is used in one well. Consequently, diameter of the zone of inhibition is calculated by a zone scale reader subsequent to incubation at 37 °C for (24-48) h.

(d) Hemolytic test

The quantifying of red blood cell(s) (RBC) lysis stimulated by polymeric samples is evaluated by hemolytic activity [174]. Porcine whole blood is collected in heparin containing vial and centrifuged to separate the RBC from the plasma (yellowish upper layer) which is discarded. The bottom layer containing the RBC is washed twice with NaCl buffer and diluted 20 times. An amount of diluted blood is incubated with the polymeric films at room temperature for specific amount of time. For positive and negative controls, tritonX-100 and NaCl buffer is used, respectively. The film treated blood is centrifuged to obtain undamaged RBC. Hemotytic activity is then quantified by noting the absorbance of the supernatant at 540 nm in a multiplate reader.

(e) *In vitro* degradation study

ASTM F 1635-04 is the standard method used to conduct the *in vitro* degradation of polymeric films [175, 176]. 0.1 M phosphate buffered saline (PBS) is used for the incubation of the films at 37 °C over a period of time at 30 rpm in a shaking incubator

set. PBS to film weight ratio is maintained at 3:1 ratio and the experiment is performed in triplicates. The films are washed with deionized water after being taken out of PBS and subsequently dried at 37 °C, at regular time interval of test. The mass loss (%) is calculated from the following equation.

$$Degradation\ (\%) = [(W_0 - W_1)/W_0] \times 100 \ \ldots\ldots\ldots\ldots.. \textbf{(Eq. 1.2)}$$

Where, W_0 = original weight of the film and W_1 = ultimate weight of the dry film.

(f) Biodegradation

The biodegradation of polymeric sample is studied as per the ASTM D6691-09 standard method [56, 174]. In such method bacterial culture is maintained in a medium consisting of $H_3BO_3.5H_2O$ (10 mg), Na_2HPO_4 (2.0 g), $(Fe_2SO_4.7H_2O$ (1 mg), $MgSO_4.7H_2O$ (1.2 g), KH_2PO_4 (4.75 g), $CaCl_2.2H_2O$ (0.5 mg), $ZnSO_4.7H_2O$ (70 mg), $MnSO_4.5H_2O$ (100 mg), $CuSO_4.7H_2O$ (100 mg), $(NH_4)_2SO_4$ (2.0 g) and MoO_3 (10 mg) in 1 L distilled H_2O. For a specific time polymeric films are kept in this medium. By measuring calorimetric estimation of bacterial growth and change in weight at regular intervals of time, the rate of biodegradation is determined.

1.4.6. Other testing techniques

(a) Thermogravimetric Analysis (TGA)

TGA helps to determine the pattern of thermal degradation, on-set and end-set temperature of degradation, etc [13, 56]. TGA offers data in terms of change in weight of the sample as a function of temperature due to loss of volatiles (such as moisture), decomposition or oxidation. This technique is extensively employed for analysis of reaction kinetics, degradation mechanism, degradation patterns, and determination of inorganic and organic content of the sample.

(b) Differential Scanning Calorimetry (DSC)

A fundamental instrument, DSC is used to study the thermal attributes of polymers. DSC is used to measure the T_m, T_g, cross-linking kinetics, crystallinity, amount of exothermic or endothermic energy. Gogoi and Karak reported the increase in T_g with increase in wt% of tannic acid in the polymer [174].

(c) Mechanical test

Different mechanical attributes like tensile strength, tensile modulus and elongation at break of HPU and its nanocomposites are evaluated by Universal Testing Machine (UTM). ASTM D 882-12 is the standard test used to perform the tensile test on polymeric film samples (rectangular shaped) of HPU and PUNC [177]. Diversely, impact resistance is measured by impact tester which follows the standard falling weight method of ASTM D1037-16a [178]. Scratch resistance of the film samples is measured by following the standard ASTM D7027-13 protocol [179].

(d) Chemical resistance test

Chemical resistance analysis of PU and its nanocomposites is conducted to determine their resistance to diverse chemicals under different chemical environments (acidic, alkaline or saline). ASTM D543-14 is the standard technique which is commonly adopted to study chemical resistance of polymers [180]. Thakur and Karak used the standard ASTM D 543-67 method to perform the chemical resistance test by determining weight of a small amount of the polymeric film in various chemical media for a specific time period [12].

(e) Shape memory test

Different testing techniques are used to evaluate the shape memory behavior of PU and their nanocomposites which are described below.

    (i)   Stretching technique

The polymeric film is first heated above its T_m and subsequently expanded to twice its original length (L_0) which is calculated and denoted as L_1. Instantly, the stretched samples are immersed at low temperature (greatly below T_m) which fixes the temporary shape for a specific time period. On release of the stretch, the length of the sample is measured as L_2. The fixed sample is activated with diverse stimuli like MW, heat, electricity, light, etc. and the resulting length is designated as L_3. Consequently, shape fixity and shape recovery of the polymeric films are determined from the equations below [181].

$$\text{Shape fixity (\%)} = \frac{(L_2 - L_0)}{L_0} \times 100 \qquad \text{------------------ (Eq. 1.3)}$$

$$\text{Shape recovery (\%)} = \frac{(L_1 - L_3)}{L_0} \times 100 \quad \text{------------------ (Eq. 1.4)}$$

(ii)   Bending technique

The polymeric film is heated above T_m for a specific time period and afterward folded to a ring shape. In order to fix the temporary shape of the folded film, it is then instantly immersed into low temperature bath. The fixed folded film is activated with diverse stimuli like MW, heat, light, electricity, etc. In the same manner as above, shape recovery and shape fixity of the polymeric films are determined from the equations below:

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

$$\text{Shape fixity (\%)} = \frac{\theta}{90} \times 100 \qquad \text{------------------ } \textbf{(Eq. 1.6)}$$

Where, θ (degree) = angle between the tangential line at the midpoint of the sample and the line connecting the midpoint and the end of the curved sample. Additionally, cyclic thermo-mechanical test is also used to resolve the shape memory behavior of polymers [13].

(f) Self-tightening test

The polymeric film is heated above T_m for a certain time period and stretched to twice their original length, and immediately immersed at low temperature for the fixing of its shape. External stimuli like heat, light, etc. was used on the film which helped to note the time required for self-tightening [182].

(g) Self-healing test

For the self-healing test, a razor blade is used to cut the polymeric films in oblique direction and using various stimuli the cracked films are healed. The shortest time necessary in each case for best healing efficiency is ascertained as optimal healing time. The healing efficiency is calculated using the following equation [183].

$$\text{Healing efficiency} = \frac{\text{Tensile Strength}_{after\ healed}}{\text{Tensile Strength}_{before\ healed}} \times 100 \qquad \text{------------------ } \textbf{(Eq. 1.7)}$$

1.5. Properties

The principal purpose of producing PNC with CBN or their nanohybrids is to enhance the mediocre properties of the pristine polymers without affecting their advanced ones. The degree and nature of development depend on the interfacial interactions that exist between the CBN and polymer matrix which lead to fascinating properties. The

following section describes some of the general properties of PU and their subsequent improvement with the development of nanocomposite.

1.5.1. Physical

The physical properties of PU which comprise of viscosity, molecular weight, solubility, etc. are determined by its composition of soft and hard segments and its molecular weights. The degree of solubility is controlled by polarity of the solvent and molecular weight of PU. Although, conventional solvent borne PU are soluble in common polar organic solvents (THF, acetone, DMAc, DMSO, etc.), they are insoluble in aqueous medium and alcohols. Nevertheless, aqueous PU dispersion can be obtained by incorporating an appropriate emulsifier into the polymer matrix. The solubility factors of the pristine polymeric system are not interfered by the fabrication of nanocomposites. Thakur and Karak reported a castor oil modified HPU that is soluble in DMSO, DMAc, THF, etc. [12]. The physical properties of PU are considerably influenced by its architectural features. HPU is more soluble as compared to its linear analogs. Similarly, HPU acquires significantly low solution viscosity as compared to the pristine even with the similar molecular weight. Moreover, the solution viscosity tends to decrease on increasing the degree of branching. In general, solution viscosity increases depending upon the nature of nanomaterial used. Kumar and Ramakrishnan reported that the solution viscosity of HPU indicated that they were of plausibly high molecular weight [25].

1.5.2. Mechanical

It is eminent that the integration of even a small quantity of CBN into a pristine PU matrix can help to improve the mechanical attributes, considerably. Mechanical properties comprise of toughness, tensile strength, scratch hardness, impact resistance, elongation at break, elastic modulus, etc. Generally, the development in tensile strength upon fabrication of PUNC is dose dependent and the degree of improvement is determined by the distribution and nature of nanomaterial in the polymer matrix. Proper dispersion of nanomaterial supports high tensile strength whereas agglomerations tend to diminish the same [13, 181]. In the same manner, exfoliated PUNC demonstrates improved strength in comparison to intercalated ones. Contrarily, elongation at break of PU and flexibility values decrease upon formation of PUNC. Although, it is pertinent to

mention that, flexibility of PU also depends on the nature of the nanomaterial employed. In the last decade, formation of PUNC has been reported with enhanced mechanical properties like impact resistance, elastic modulus, scratch hardness, etc. [183]. Most of the reported PUNC, like PU/RGO, PU/MWCNT, etc. exhibit overall increase in mechanical performance in comparison to their pristine form [13, 176, 183]. Inspite of the numerous structural defects of RGO as compared to graphene, it also possesses high elastic modulus (0.25 TPa). Thus, integration of nanohybrids of CBN like GO, RGO and CD based nanohybrid in pristine polymer matrix efficiently enhances the mechanical attributes of the polymer system [183, 184]. Xiong *et al*. [185] reported the increase in modulus and tensile strength in a PUNC by incorporating 2 wt% to the polymer matrix. Li *et al*. [186] also showed the enhancement of tensile strength, Young's modulus and flexibility of liquid crystalline PU upon incorporation of GO. Besides CBN or their nanohybrid, other nanomaterials are also used to enhance the mechanical properties of PUNC. Hamedi *et al*. reported that the elastic modulus, hardness and scratch resistance of the nanocomposites were improved dramatically on addition of nanoclay [187].

1.5.3. Thermal

Thermal properties (thermal transition performance, thermal degradation stability, T_m, T_g, etc.) are improved, in general, by the formation of PUNC. Frequently, metallic nanomaterials generate an obstacle and prevent the volatile decomposed product from escaping. This results in slowing down of the decomposition process that eventually imparts better thermal stability to the polymer. CBN like graphene, GO, RGO, CD, MWCNT, etc. are efficient for the improvement of thermal stability of PUNC [10, 13, 184]. The char that is formed at the end of thermal degradation acts as thermal insulator and slows down the rate of degradation. Both T_m and T_g of PU tend to increase upon formation of nanocomposites. The nanomaterial acts as a nucleating agent which restricts the molecular chain orientation within the polymeric matrix. Bocchio *et al*. [188] reported that the addition of nanoclay significantly increased the decomposition temperature of the PUNC, thus improving its thermal stability. Several studies have been reported on the increase in thermal stability of PU after incorporation of CBN and their nanohybrids. Wang *et al*. [189] reported that with the incorporation of 2 wt% graphene nano sheets, the temperature for 5% weight loss of PUNC is increased by 40 °C. During the process of combustion, a blocked network of char layers is produced by the

nanomaterials which obstruct the transport of the products of decomposition. Even GO, which is thermally unstable itself, can improve the overall thermal stability of the resulted PNC compared to the pristine polymer. Yu *et al.* [190] reported PU acrylate nanocomposites which demonstrated an increase in initial degradation temperature from 299 °C to 316 °C on incorporation of 1.0 wt % functionalized GO.

1.5.4. Electrical

The incorporation of certain CBN (MWCNT, RGO, etc.) during fabrication of nanocomposite can impart polymeric products with electrical conductivity. The development of penetrable pathways (conductive network of nanomaterials) for electron transfer presents the nanocomposites with electrical conductivity [191]. The scope of applications of PU can be additionally enhanced by incorporation of CBN. This augments the mechanical properties and increases conductivity for novel applications, for instance, electromagnetic interference (EMI) and electrostatic discharge (ESD) shielding materials [192]. Comparable results can be obtained with CBN such as CNT, carbon nanofibers, conductive carbon black and graphene. Xu *et al.* [22] reported CNT based PU foams and investigated their conductivities for a fixed loading of 2 wt% CNT at different densities. However, even at low loading of graphene, the properties of PNC is noticeably improved and its high surface conductivity facilitates in achieving electrically conductive polymer materials. Graphene modified PNC have been broadly useful in anti-static materials, EMI shielding, bipolar plates for fuel cells, etc. The transition from insulator polymer to conductor occurs at appreciably lower loading of graphene in comparison to CNT. Shamsi *et al.* [193] reported that electrical conductivity of the nanocomposites improved on increasing the wt% of GO in PU matrix. Literature cites that incorporation of 0.5 wt% of RGO formed electrically conductive PUNC. Yousefi *et al.* [194] fabricated PU/RGO nanocomposites with higher electrical conductivity with a percolation threshold of 0.078 vol%. Yang *et al.* [195] incorporated polydopamine coated graphene sheets in PU and investigated the EMI shielding performance. In another study, Hsiao *et al.* [196] reported water based PUNC modified with exfoliated graphene with shielding effectiveness of 32 dB in the frequency range of 8.2-12.4 GHz at 7.7 wt% of the reinforcing agent. Swain *et al.* [197] also reported that the percolation threshold was much higher in PU/functionalized RGO nanocomposite in comparison to PUNC with functionalized MWCNT. The electrical conductivity of the

graphene based HPU nanocomposites shows a significant anisotropy with high RGO contents as conductive networks along the in-plane direction is formed.

1.5.5. Optical

Optical properties of PUNC primarily include gloss, color, transparency, etc. The transparency, color and gloss of majority of PUNC are unaffected upon their fabrication. This is due to low level light scattering, nano-size dimension and small amount of nanomaterial loading. However, CBN like MWCNT, RGO, etc. may lead to loss of original color and transparency. PUNC may also display special optical properties like luminescence, fluorescence, non-linearity, etc. in addition to these common behaviors. The excellent optical features of CBN distinguish them from conventional luminescent materials and make them prospective candidates for diverse exceptional applications such as catalysis, bio-imaging, capacitors, medical diagnosis and photovoltaic devices [198]. Owing to their early discovery and adjustable parameters, luminescent CD attracted great attention from researchers for fabrication of PUNC. In 2007, Chen *et al.* [199] fabricated PU with CdS quantum dot which displayed enhanced optical properties. Gogoi *et al.* [10] reported fluorescent waterborne HPU/CD nanocomposite which exhibited remarkable behavior of luminescence and thus established the polymer matrix to be efficient in preventing the solid state quenching.

1.5.6. Catalytic

Different semiconductor nanomaterials like ZnO, SnO$_2$, TiO$_2$, etc. have found widespread applications as photocatalysts in recent times. Nanomaterials containing metal, metal oxide, quantum dot, CD, etc. have profound catalytic activity. In the early 1970s, Honda and Fujishima [200] first began the pioneering work of using TiO$_2$ as a semiconductor photocatalyst in the early 1970s by investigating the splitting of water into oxygen and hydrogen by UV light. Particularly, ZnO, semiconductor based quantum dots, TiO$_2$, CD act as photocatalyst due to their light harvesting activity and thus exhibit catalytic activity. In 2016, Hazarika and Karak [201] reported hyperbranched polyester/CD nanocomposite which resulted in photocatalytic degradation of methylene blue and formaldehyde. Thus, such materials have the potential to be used as a self-cleaning and eco-friendly material. However, requirement of UV light to activate such photocatalysts considerably restricts their practical applications since UV light content

makes up merely (2-3)% in the solar spectrum. In this context, RGO based semiconductor nanohybrids like RGO-TiO$_2$ and RGO-ZnO exhibited remarkably improved visible light assisted photocatalytic performance [202]. Conversely, bare nanomaterials cause problems in recyclability of the photocatalyst which gives way to the employment of PNC as heterogeneous catalysts for such purposes [203].

1.5.7. Flame retardant behavior

PUs containing halogens, phosphorus, metal, etc., in general, exhibit flame retardant behavior. Such materials retard or inhibit heating, decomposition or degradation, explosion of flammable gases and combustion with production of heat throughout the burning process. Fabrication of PUNC with silica, clay, carbon nanofiber, CNT, RGO, etc. enhances the flame retardant performance of pristine PU. Such nanomaterials disintegrate to form non-flammable char throughout the burning process and consecutively reduce the rate of heat release [204]. The spreading of fire is also prevented the structural integrity of PU. Jin *et al*. [205] utilized expandable graphite (EG) with aluminum hydroxide in the production of polyisocyanurate-PU foams with improved flame retardant behavior.

1.5.8. Smart behavior

Smart polymers have the ability to change according to the external stimuli like humidity, temperature, pH, wavelength/intensity of light, etc. Minor environmental changes are enough to stimulate huge modifications in the polymer properties. Smart polymers are employed for the production of hydrogels, biodegradable packaging and to a huge extent in biomedical engineering such as in drug delivery.

(a) Shape memory property

One of the most important smart properties is shape memory effect (SME). PU is an imperative class of shape memory polymer(s) (SMP) due to the presence of hard and soft segments in the polymeric chains. Zhang *et al*. [206] reported that PU exhibiting SME has the capability to present different mechanical behavior related to soft and hard segment morphology. The hard segment is accountable for permanent shape whereas the soft segment permits the transition from permanent to temporary form or vice-versa. On application of heat, the soft segment is frequently utilized for molecular switching which

is responsible for SME in PU. In this context, it is observed that shape memory performance can be enhanced using various CBN as conductive reinforcing agent. Some of the key parameters to illustrate SME of a polymer are shape recovery, shape fixity and recovery time. Shape fixity or strain fixity is the extent of fixation of the temporary shape of SMP. The percentage of the ratio of fixed deformation to total deformation by the sample is equal to shape fixity. Alternatively, the capability to retain the original shape of a polymeric material from its temporary shape is defined as shape recovery. Thus, the percentage of ratio of deformation recovered to the deformation taken place by the sample is equal to shape recovery. The recovery rate from a fixed temporary shape to its original shape throughout the recovery process is expressed by the recovery rate parameter of the polymer upon exposure to an appropriate stimulus. HPU/RGO nanocomposites demonstrated good multi-responsive shape memory behavior [13]. Again, Jana *et al*. fabricated reported PUNC with poly(ε-caprolactone)-grafted CNT which exhibited improved shape memory attributes [207].

(b) Self-healing property

Self-healing polymers (SHP) are categorized as smart polymers which possess the capability to repair/heal the damage (micro-cracks) caused by mechanical strain throughout their service time [183]. Wang *et al*. fabricated PUNC with improved self-healing ability by a SME [208]. Huang *et al*. [209] reported repeated healing efficiency of a graphene modified PUNC upon application of suitable stimuli like MW energy, IR light and electricity. Thakur and Karak [183] reported a HPU nanocomposite modified with sulfur nanoparticle decorated RGO nanohybrid which demonstrated remarkable repeatable healing capability on application of sunlight and MW.

1.5.9. Biological

In today's world, PU is extensively used in various biomedical applications due to its biodegradability and biocompatibility. To improve its intrinsic bioactivity has always been a priority. In the recent past, suitable CBN like GO, RGO, MWCNT, CD, etc. have been reportedly used in the design of PUNC based biomaterials. This helps in achieving target specific bioactivity of PUNC and prevents related risks of host reaction owing to xenobiotic behavior. In this regard, incorporation of Ag, ZnO, TiO_2, etc. imparts antibacterial activity to the host PU [210, 211]. MWCNT and Fe_3O_4 are known to confer

wound healing ability. Recent research on biomaterial cites the use of various bio-functionalized nanomaterials with bioactive motif (protein, peptide, enzyme or any kind of drug molecule) for fabrication of biocompatible PNC which imparts target specific bioactivity [212]. Moreover, PU possesses an intrinsic bio-characteristic of biodegradability with polyester based PU being considerably vulnerable for biodegradation upon exposure of different microorganisms (enzyme, bacteria or fungi) as compared to polyether diols derived ones [213]. Nonetheless, it is fairly difficult to suggest a comprehensive idea about the impact of nanocomposite formation on biodegradability of a polymer. Okamoto *et al*. [214] fabricated trimethyl octadecylammonium modified MMT and poly(lactic acid) based nanocomposite with improved biodegradability. This is attributed to the heterogeneous catalysis of the matrix hydrolysis which results due to adsorption of water by hydroxyl groups of the intercalated silicate layers.

1.6. Applications

PU and their nanocomposites appear in highly specialized applications, in addition to their common applications owing to their broad range of properties. In this context, PUNC is already researched for a range of important applications which are discussed below.

1.6.1. Surface coating

Surface coating is a blend of polymers with pigments and other additives, which on application to a surface and cured/dried forms a thin functional or decorative film. It is used to protect the surface of substrates from damages by external causes and to decorate [215]. They are broadly used in different objects like ships, bridges, oil and gas pipelines and other facilities. Surface coatings are efficiently used owing to their outstanding performance and life resistance to high abrasion resistance, corrosive environments, strong adhesion, etc. [12]. Sabzi *et al*. [216] incorporated TiO_2 nanoparticles in a PU coating which enhanced their mechanical properties owing to sufficient interfacial interaction between titania and PU matrix. Mo *et al*. [217] reported the improvement of anti-corrosion attributes of a functionalized graphene based PUNC for its application as surface coating. Li *et al*. [218] established that the anti-corrosion attributes of PU were improved on addition of RGO (0.2 wt%).

1.6.2. Adhesive and sealant

PU is employed as adhesive and sealant to attach non-porous surfaces like metal, glass, etc. High chemical and water resistance are the advantages of PU adhesive [43, 44]. Conversely, PU sealant is used to fill up gaps to prevent water and air leakages. Its flexibility and resistance to chemicals, corrosion and moisture are important characteristics. Furthermore, PU offers resistance against physical forces and cracking and to the newly joint material due to its intrinsic flexibility. Normally, PU adhesive and sealant are accessible in both one as well as two component systems. Wang *et al.* reported a series of low viscosity and solvent free PU adhesives [219]. Cui *et al.* synthesized PU adhesives for applications of wood bonding using glycerol-based polyols [220].

1.6.3. Shape memory material

SMP have attracted raising interest in diverse fields such as textile engineering, packaging, aerospace engineering, automobile fenders, etc. Furthermore, they are widely employed in medical and biological domains, chiefly for biomedical devices like in minimally invasive surgery. Jiu *et al.* [221] demonstrated PUNC with graphene sheets with 95% shape recovery, 93% shape fixity and rapid electro-active rate of shape recovery. In 2014, Yoo *et al.* [222] reported shape memory PU nanofibers modified with functionalized-GO which exhibited improved mechanical strength and shape recovery speed. Thakur and Karak [13] reported HPU/RGO nanocomposite with outstanding multi-stimuli responsive SME under thermal energy (60 °C) and MW (360 W). In 2013, Kim *et al* [223] demonstrated enhanced shape recovery and shape fixity ratios of acrylate terminated PU with the addition of isocyanate modified graphene up to 1.5 phr.

1.6.4. Self-healing material

The lifetime of ceramics, metal, and polymer materials can be extended provided self-healing is achieved. Moreover, it reduces the economic loss caused by renewal of the materials. Such recovery can be triggered by a specific stimulant and can arise autonomously. Literature cites various PU based self-healing materials. Ling *et al.* [224] reported a linear PU based on disulfide linkage that can recover its mechanical strength over 90%, at moderate temperature within 10 min. Thakur and Karak [183] prepared HPU nanocomposites modified with sulfur nanoparticle decorated RGO which

demonstrated sunlight-induced self-healing attribute. Kim *et al.* [225] reported the fabrication of graphene based PUNC using 4,40-methylene diphenyl diisocyanate and poly(tetramethylene glycol) which demonstrated near IR induced self-healing attributes. The self-healing features of PUNC were investigated by means of intermolecular diffusion of the polymeric chains which was enhanced as a consequence of the thermal energy produced during NIR absorption.

1.6.5. Self-cleaning material

In recent years, coatings based on the technology of self-cleaning has garnered growing attention owing to their extensive range of impending applications, *i.e.* from window glass to cements and textiles. Self-cleaning materials possess the intrinsic capability to eliminate bacteria or any fragments from their surface. In this context, super-hydrophobic surfaces possess the most vital facets for a self-cleaning *i.e.*, low surface energy and surface microstructure [183]. Charpentier *et al.* reported a PUNC using functionalized TiO_2 which demonstrated the removal of stearic acid under UV light irradiation [226]. Thus, PUNC also exhibited good self-cleaning properties by degradation of organic contaminants. Zhang *et al.* reported PU foam which demonstrated super-repellency towards corrosive liquids, oil and displayed superior oil/water separation attributes [227]. Heo *et al.* designed two new PU with thermoresponsive self-healing property, supported by the Diels-Alder reaction between maleimide and furan moieties. SME assists in healing of the damaged PU by bringing the cracked surfaces into intimate contact [228].

1.6.6. Biomedical

With rising concerns on health care, at present, PU has aimed towards advancement of biomedical applications. PU is employed in different biomedical applications such as, drug delivery devices, antibacterial catheters, tissue engineering scaffolds, stents, surgical dressing, pressure responsive adhesives, etc. owing to its flexibility, bio-stability, biocompatibility, ease of fabrication into devices and good biodegradability [177, 229]. For several years, polyether-based PU has been employed as medical implants. However, in some cases the degradation of such PU leads to stiffening, deep or surface cracking, erosion or deterioration of mechanical strength which eventually causes implant malfunction [230]. Again, fabrication of PUNC with bioactive fillers, like

natural protein, polysaccharide and hydroxyapatite (HA) can endow it with exceptional features and assist in mimicking biological tissues. The incorporation of fillers not only imparts toughness to the PNC, but also enhances the surface bio-reactivity [177, 231]. Fabrication of PU with definite nanomaterials (*i.e.* clay, POSS and silver) can improve its biocompatibility. Despite controversies on safety issues, CBN like carbon fibers, CNT and graphene are utilized in the fabrication of functional PUNC for biomedical applications. Moreover, agglomeration of CBN can be evaded by pre-functionalization, such as amination and acidification treatment to get the modified carbon materials [232]. Patel *et al*. [233] fabricated graphene based PUNC which exhibited greater storage modulus and toughness. This assisted in the controlled release of the incorporated drug (tetracycline hydrochloride, an antibiotic) which proved to be more sustained than with pristine PU which had an exploded release. In this context, bio-based HPU and its nanocomposites are employed as scaffold materials owing to their favorable biocompatible and biodegradable attributes. Das *et al.* [234] reported HPU/functionalized MWCNT nanocomposite as a prospective biomimetic scaffold for bone tissue engineering. Alternatively, HPU nanocomposite modified with Fe_3O_4 decorated MWCNT nanohybrid displayed its efficiency in controlled drug release and antibacterial activity for application as a wound healing material [176].

1.6.7. Miscellaneous

Flexible PU foam is employed in a variety of furniture and furnishing applications including automotive seat cushions, furniture and carpet cushions, interior trim, mattresses, etc. [28]. Being soft, they endow with remarkable structural stability, durability and comfort. PU-based furniture cushion is cost effective in comparison to leather finished furniture [35]. Moreover, various PU foams are employed in automotive industry to construct different machinery. Flexible PU foams are employed while designing interior components like head rest, arm rest, dashboard, roof liners, etc. Moreover, they are extensively employed to build automobile seats. Being light weight, economical, resistant to corrosion, etc. polymeric materials offer improved flexibility and durability as compared to conventional fiber glass [44]. In this context, PUNC are employed in the automotive industries for development of diverse structural components like side skirts, bumpers, wiper cowls, roll pans, etc. PU/TiO_2 and PU/nanoclay nanocomposites are utilized by automobile manufacturers, worldwide [235, 236]. Also,

various building materials like decorative items, artificial wall, home appliances, sculptures, etc. are constructed with PU. PU foams also find applications as thermal insulator [237]. Conversely, PU resin can be used as an aesthetic flooring material. Being seamless and water resistant, such polymeric floor is getting substantial interest. PU possesses various benefits such as light-weight, high water and chemical resistance, easily installable moldable into desired size and shape [238]. PNC of CBN is also utilized as shielding materials for EMI and ESD materials [239]. This is attributed to intrinsic high conductivity and aspect ratio of graphene which enable to attain the percolation threshold at very low loading. Also, GPNC are used as super-capacitors, antistatic material, etc. depending on the loading amount of graphene. Verma *et al.* [240] reported graphene-based PUNC as new alternative candidates for ESD and EMI shielding applications attributed to their tunable electrical conductivity, easy processability and light weight. Valentini *et al.* [241] fabricated a PUNC modified with exfoliated graphite (20 wt%) which exhibited a shielding effectiveness of 20 dB in the X band for sample thickness of 4 mm. Hsiao *et al.* [242] fabricated electro-spun water based PU featuring sulfonate groups/ RGO and achieved 34 dB of EMI shielding effectiveness in the X-band for a sample thickness of 1 mm. An additional course of investigation by the same group prepared water based PUNC with non-covalently modified exfoliated graphene sheets with a maximum 32 dB shielding effectiveness at 7.7 wt% filler content in the range of frequency (8.2-12.4) GHz [243].

1.7. Scopes and objectives of the present investigation

State of literature presented in the above sections, offer a perception about the current drift in PU research. It evidently reveals the substantial amount of work conducted on eco-friendly PU and their nanocomposites with exceptional properties for advanced applications. However, renewable resource based HPU nanocomposites of CBN are sufficiently unexplored. Development of bio-based HPU nanocomposites contribute a noteworthy transformation from conventional petroleum based ones. CBN has received immense interest owing to its unique properties which may impart exceptional attributes to the resultant PUNC. Hence, the superiority of CBN along with starch modified HPU is yet to be explored comprehensively. The majority of the literature cited utilization of vegetable oils as the key bio-source. However, other renewable resources like starch have not been sufficiently investigated, yet. In most cases, starch has been merely used

as an additive or an auxiliary component to enhance the rigidity of flexible PU foam. Thus, the employment of starch modified polyol may endow with the exceptional scope for the designing of environmentally benign HPU. At the same time, it is equally important to improve various properties of these eco-friendly materials by preparing their nanocomposites to meet the modern day demands. In this regard, CBN, with their unique combination of physical and chemical properties (mechanical, thermal, electrical and optical attributes) have led to extensive research efforts for use in various advanced applications. Moreover, diverse applications such as shape memory, self-healing and self-cleaning are not yet concentrated on completely. Thus, development of starch modified HPU nanocomposites using CBN as nano reinforcing agents may form the appropriate research proposition to open a new avenue of research as self-cleaning, self-healing and shape memory materials for distinctive applications like biomedical, photocatalysis, optoelectronic, etc.

In this perspective, current investigation lays down the following objectives,

i) To synthesize hyperbranched polyurethane using bio-based multi-functional moieties.

ii) To characterize the synthesized hyperbranched polyurethane using diverse spectroscopic and analytical techniques.

iii) To evaluate the properties of the synthesized hyperbranched polyurethane.

iv) To fabricate nanocomposites of hyperbranched polyurethane using different carbon-based nanomaterial like carbon dot, reduced graphene oxide, etc. and their nanohybrids.

v) To characterize the fabricated nanocomposites by different spectroscopic and analytical techniques.

vi) To evaluate the properties of the fabricated nanocomposites by various methods.

vii) To optimize the performance of the prepared nanocomposites for their prospective applications.

1.8. Plan of research

In order to implement and achieve the objectives, the proposed work has been planned in the following manner,

i) A methodical literature review on hyperbranched polyurethane and their nanocomposites will be conducted.

ii) Hyperbranched polyurethane will be synthesized by $A_x + B_y$ (x, y $\geq$ 2) technique, using a bio-based multi-functional moiety along with the conventional reactants.

iii) The synthesized hyperbranched polyurethane will be characterized by using different analytical and spectroscopic techniques such as FTIR, NMR, TGA, DSC, etc.

iv) The hyperbranched polyurethane will be evaluated for its various properties like physical, mechanical, chemical, biological, etc.

v) The hyperbranched polyurethane nanocomposites will be fabricated by conventional literature reported techniques using carbon-based nanomaterials like carbon dot, reduced graphene oxide, etc. and their nanohybrids.

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

vii) Special properties like antimicrobial, self-healing, self-cleaning, etc. of the hyperbranched polyurethane nanocomposites will be assessed.

viii) The performance characteristics of the fabricated nanocomposites will be explored by determination of tensile strength, elongation at break, impact resistance, scratch hardness, chemical resistance, etc.

ix) The best studied nanocomposite, achieved by optimization of amount of nanomaterials and processing factors will be employed for further potential applications.

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