General Introduction

Highlights

In this chapter, a general introduction of the present investigation is highlighted. It contains a brief report on polyurethane (PU) and graphene based PU nanocomposites. The role of graphene, especially reduced graphene oxide (RGO) based nanomaterials in the property improvement of PU is encompassed in this chapter. Moreover, materials and methods for preparation of PU, RGO and PU nanocomposites are discussed herein. Various analytical, spectroscopic, microscopic techniques, such as FTIR, XRD, TGA, DSC, SEM and TEM are described for characterization of PU, RGO and PU nanocomposites. Various properties such as mechanical, thermal, electrical, especially smart properties like shape memory, self-healing, self-cleaning, etc. of RGO based nanocomposites are also discussed. This chapter further describes the applications of PU nanocomposites in different advanced fields. The scopes, objectives and plans for the present investigation are included in this chapter.

Parts of this chapter are published in

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1.1. Introduction

Over the last two decades, the domain of nanoscience boosted remarkably with an explosive growth in miscellaneous areas, such as computing, sensors, biomedical science and many others. Development of nanoscience basically depends on the ability to synthesize nanomaterials of various sizes and shapes, as well as to proficiently assemble them into complex architectures.[1,2] Nanomaterials are used in a numerous advanced applications due to their unique structural features. In this context, the discovery of graphene is a crucial addition in the domain, as it plays a vital role in modern science and technology.[3]

Graphene, a two-dimensional atomic thick structure of sp^2 carbon atoms, engraves a distinct niche in material science due to its excellent electrical, thermal and mechanical properties.[4-6] Incorporation of graphene to pristine polymers improves the mechanical, electrical and thermal attributes of the resulting nanocomposites.[7] Thus, recent research concentrated on the development of high performance polymer nanocomposites to achieve novel materials for a wide range of advanced applications with the help of graphene based nanotechnology. Here, it is pertinent to mention that graphene dramatically enhances the properties of the pristine polymer at a very low loading which is another advantage of it.[7] Carbon nanotube (CNT) is also a very effective reinforcing nanomaterial for such purposes.[1] Even though, graphene possesses a higher aspect ratio compared to CNT due to the unique sheet structure of it and the inner tube surface of CNT also inaccessible to polymer.[8] This makes graphene potentially more propitious to improve the properties of the polymer. Thus, graphene-based polymer nanocomposites are attracted the interest of both industry and academia.

In this context, it is imperative to mention that homogeneous dispersion of graphene in the polymer matrix is a critical challenge as restacking or aggregation of graphene sheets commonly takes place owing to the π-π stacking and hydrophobic interactions among the sheets.[9] Again, the weak interactions between graphene and the polymeric matrix result in the interfacial slippage on application of external stress which limits the improvement in properties.[10] In this milieu, graphene oxide (GO) and reduced graphene oxide (RGO) are the valuable alternatives of graphene which contain lots of polar functionalities that aid in dispersing them within the polymer matrix.[11-13]

Recently, various GO/RGO based polymer nanocomposites are fabricated with epoxy, polystyrene, polyaniline, polyurethane (PU), poly(vinylidene fluoride), polycarbonate, etc.[14-20] Amongst the various types of polymers used for the fabrication of

GO/RGO based polymer nanocomposite, PU is one of the most versatile one. It is used in a diverse field of applications including coating, adhesive, leather, composite, biomedical, etc. The repeating unit in PU is covalently connected with the urethane linkages (also called carbamate groups, -NH-COO-), though other linkages such as urea, ester, ether, etc. may also present in the structure.[21] PU generally contains two incompatible structural units *viz.* soft and hard segments. The soft segments are made up of linear long-chain diols or polyols and diisocyanate, whereas the hard segments form from diisocyanate and short chain extender molecules such as diols or diamines (**Figure 1.1**).[22] Therefore, the soft segments are flexible and weakly polar or nonpolar in nature, whereas the hard segments are rigid and highly polar. A wide range of physico-chemical properties of PU can be tailored just by judicious variation of the composition and structure of the three basic building blocks, *viz.* macroglycol, diisocyanate and chain extender.[22-24] So, proper design of PU with appropriate structure and composition of the components may result in unique and useful properties for different end applications.

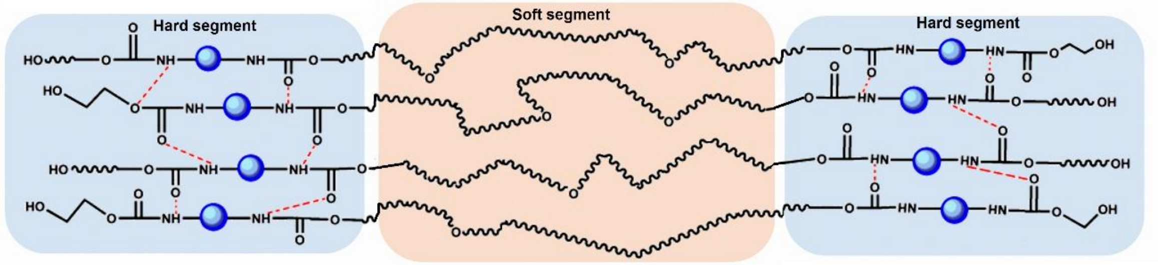


Figure 1.1 Representative structure of PU with soft and hard segment

Further, hyperbranched polymers offered their candidatures as advanced polymeric materials over the last two decades. These polymers are highly functionalized three-dimensional globular, non-entangled inimitable architecture.[25,26] Therefore, these polymers exhibited many desirable properties like high solubility, low melt and solution viscosity, high reactivity and so on.[27] Such properties are useful for different applications in addition to their single-step preparative techniques. Therefore, such novel polymers may be the right choice for the present research.

Moreover, depletion of petroleum resources, growing environmental concerns and waste disposal problems redirect material scientists to use bio resources such as vegetable oils as raw materials for the preparation of polymeric materials.[28] Vegetable oils possess many advantages like biodegradability, sustainability, non-toxic nature and the most importantly environmentally benign attributes.[28-30] Hydroxylation of vegetable oils is one of the good tactics to obtain the required polyols to be used as a chain extender for the preparation of hyperbranched PU (HPU). Thus, the versatility of HPU becomes much significant when it is synthesized from vegetable oils. In spite of such advantages, vegetable oil-based HPU suffers from poor mechanical properties. The presence of long hydrocarbon chains in the fatty acid moiety of vegetable oils provides plasticizing effect in HPU and deteriorates the mechanical strength.

As mentioned earlier, incorporation of a small amount of GO or RGO in the vegetable oil-based HPU may effectively tackle this challenge. But till date, research on vegetable oil-based PU/RGO nanocomposite is rare to find out. Thus, studies on vegetable oil-based HPU nanocomposite with GO, RGO and their nanohybrids are going to be a good proposition in the current scenario of polymer research.

1.2. Background

Graphene is the basic structural unit of some carbon allotropes, including graphite, CNT and fullerene. In 1940, it was established theoretically that graphene was the building block of the graphite structure.[31] Even though the existence of graphene itself was controversial at that time due to the thermodynamically unstable nature of two dimensional material under ambient conditions. However, in 2004, Geim and Novoselov from Manchester University successfully identified the free-standing graphene from graphite by using a scotch tape only.[32] Then onwards, extensive research is enduring on graphene and graphene based polymer nanocomposites. In 2010, Liang et al. reported three types of PU nanocomposites which were prepared by a solution mixing process.[33] They incorporated isocyanate modified graphene, sulfonated graphene and RGO as nanoreinforcing agents. Wang et al. prepared PU/graphene nanocomposite by an *in situ* polymerization. The nanocomposite demonstrated enhanced mechanical and thermal properties.[34] In 2012, Chen et al. developed a novel approach to prepare strong, tough and highly ductile PU/graphene nanocomposites.[35] In another study, Wu et al. reported PU graphene nanocomposites which showed high modulus, high tensile and yield strength, high permittivity and low loss tangent.[36] Here, it is noteworthy to mention that the term ‘nanocomposite’ was first devised by Theng in 1970.[37] Albeit, polymer nanocomposites were developed in both commercial and academic research since late 1980s.

Whereas, PU was first time invented by Otto Bayer in the I.G. Farben industry in 1937.[38,39] After a decade of the discovery, development of PU chemistry starts rapidly with toluene diisocyanate (TDI). On the other hand, the hyperbranched polymer was first designed by DuPont researchers, Kim and Webster in late 1980s.[40] However, HPU was first successfully prepared by Spindler and Frechet in 1993 by using AB_2 monomers which contained one hydroxyl group (A) and two blocked isocyanate groups (B).[41] Following this initial study, HPU was synthesized via the *in situ* generated AB_2 monomer (3,5-dihydroxyphenyl isocyanate) from the corresponding carbonyl azide precursor by Kumar and Ramakrishnan in the same year.[42,43] Another one-pot approach for the preparation of HPU was proposed by Hong et al. by taking the *in situ* generated dihydroxy isocyanate monomer.[44] Again, the potential of vegetable oils for industrial purposes was first presented by J. G. Kane who is known as the father of vegetable oil-based polymer.[45] In 1925, Kienle and Hovey synthesized a series of alkyd resin from vegetable oils which was the exact beginning of vegetable oils based polymer.[45] However, vegetable oils based PU was rapidly developed in early 2000s in both industry and academia. In 2008, a soy-based PU was used by Ford Motor Company in automobile interiors such as dashboards, side-panels, etc.[46] Whereas, Petrovic et al. first reported vegetable oils based HPU which was prepared by using soybean oil based polyol as branching moiety.[47]

Thus, research on vegetable oil-based HPU nanocomposites with graphene based materials such as GO, RGO, and their different nanohybrids showed an emerging background to be studied for their advanced applications.

1.3. Materials and methods

In this section, different types of materials generally used in the graphene based polymer nanocomposite as well as the preparative methods of PU and graphene based nanocomposites are discussed.

1.3.1. Materials

Graphene based polymer nanocomposites are gaining much interest in recent time over the others polymeric nanocomposites. Different types of polymers are utilized to obtain a variety of graphene based polymer nanocomposites as mentioned earlier. As the present investigation deals with PU and graphene based nanomaterials, so the discussion is restricted within these materials only.

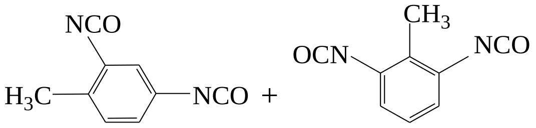
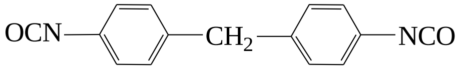
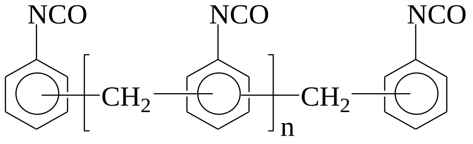
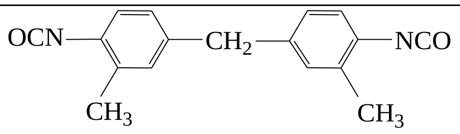
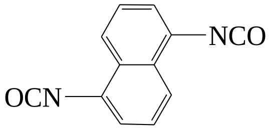
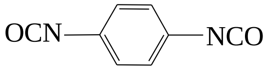
1.3.1.1. Polyurethane

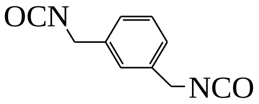
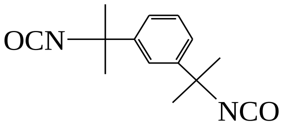
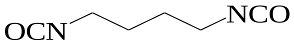
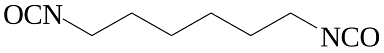
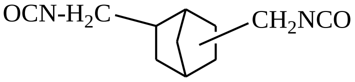
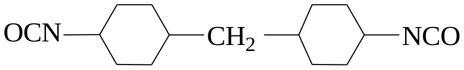
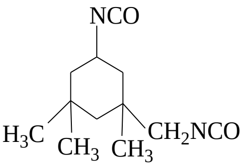
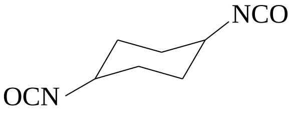
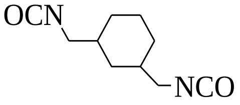
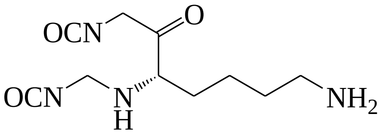
PU is an important subclass of polymers and segmented PU contains multi-disperse blocks of soft and hard segments in an alternative fashion. The urethane linkage (-NHCOO-) is produced through a rearrangement reaction between a diisocyanate and a polyol. The common raw materials used for PU synthesis are categorized into macroglyol, diisocyanate and chain extender. The brief descriptions of these components are presented below.

Diisocyanate

It is a fundamental precursor for the synthesis of PU. Although, both type of diisocyanate *viz.* aromatic and aliphatic are used but aromatic diisocyanates are most commonly used for this purpose. Properties of PU greatly depend on the structure of diisocyanate component. Thus, appropriate selection of diisocyanate component envisages the properties of PU. The most commonly used diisocyanates are listed in **Table 1.1** with their chemical structures.

Table 1.1 Structures of a few commonly used diisocyanates in PU synthesis

Type	Name	Structure
Aromatic diisocyanates	Toluene diisocyanate (TDI)	
	4,4-Diphenyl methane diisocyanate (MDI)	
	Polymeric methylene diphenyl diisocyanate (PMDI)	
	3,3-Dimethyl diphenyl methane diiscocyanate (DDI)	
	Naphthalene diisocyanate (NDI)	
	p-Phenylene diisocyanate (PPDI)	

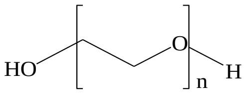
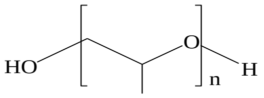
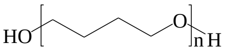
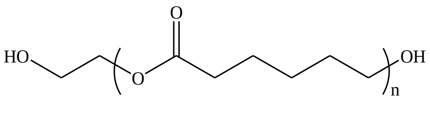
	m-Xylylene diisocyanate (XDI)	
	Tetramethyl-m-xylylene diisocyanate (TMXDI)	
Aliphatic diisocyanates	1,4-Diisocyanatobutane	
	Hexamethylene diisocyanate (HDI)	
	Norbornane diisocyanate (NBDI)	
	Dicyclohexyl methane diisocyanate (H_{12}MDI)	
	Isophorone diisocyanate (IPDI)	
	Cyclohexyl diisocyanate (CDI)	
	Hydrogenated xylylene diisocyante (HXDI)	
	Lysine diisocyanate (LDI)	

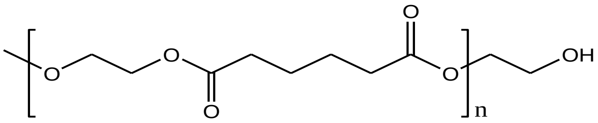
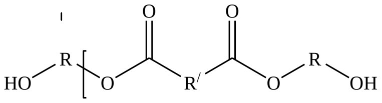
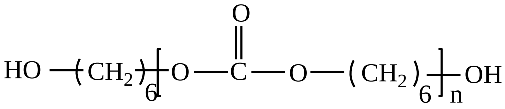
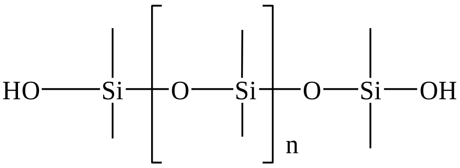
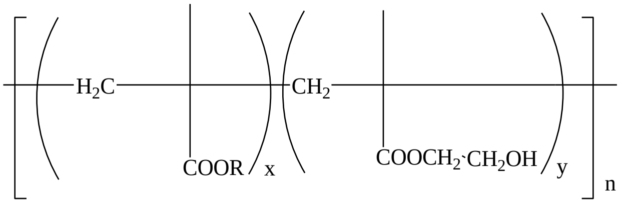
Amongst them, TDI and MDI are widely used in the preparation of PU.[48,49] In most of the cases, TDI is used as a mixture of the 2,4- and 2,6- isomers in 80:20 mol ratio.[48] Similarly, MDI also has three isomers namely 4,4-, 2,4-, and 2,2-diphenyl methane diisocyanates. However, 4,4-isomer is used in most of the commercial PU.[48] Though aromatic diisocyanates have higher reactivity than aliphatic ones and obtained PU exhibited good thermal and mechanical properties, but the former PU also suffer from a few inadequacy such as lower oxidation and weaker ultraviolet stabilization.[50] Therefore, the use of aliphatic diisocyanates is required, where color and transparency are important.

Macroglycol

In the synthesis of PU, the aliphatic diols or polyols with molecular weight 400 to 5000 g mol^{-1} are mainly used as macroglycols. The long chain macroglycol containing low functionality provides elastomeric soft PU, whereas the short chain macroglycol with high functionality forms rigid PU.[50] Various types of macroglycol such as polyester, polyether, polycarbonate, hydrocarbon, etc. are used in the synthesis of PU and these are tabulated in **Table 1.2**. However, the polyester and polyether macroglycols are mostly used among them. Polyester macroglycol provides high flexibility, heat stability and adhesion to PU, though it suffers from poor chemical resistance.[51] The ester groups are easily hydrolyzed by alkali and thereby weakening the performance of PU. Even though, a few of polyester polyol macroglycols such as polycaprolactone, polycarbonate, etc. demonstrate high hydrolytic stability in alkaline condition too.[51] On the other hand, polyether macroglycol contributes some specific properties such as metal chelation, hydrophillicity, crystallinity, surface activity, etc. In addition to that different dendritic or hyperbranched polyols are also used to prepare HPU. Among all, the crystalline polycaprolactone (PCL) diol is the most convenient one for smart PU as shape memory material.

Table 1.2 Structures of a few commonly used macroglycols in PU synthesis

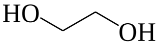
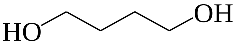
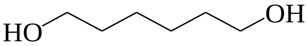
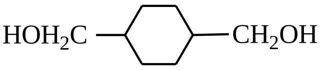
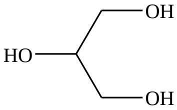
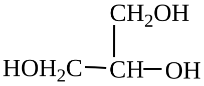
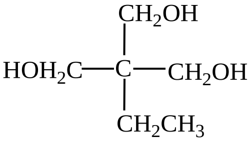
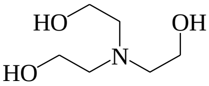
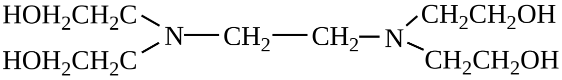
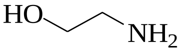
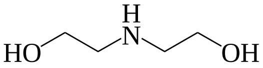
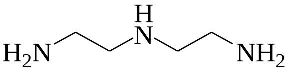
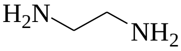
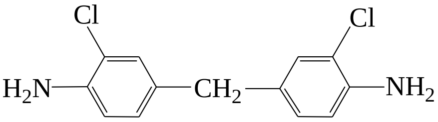
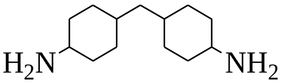
Type	Name	Structure
Polyether macroglycols	Polyethylene glycol (PEG)	
	Polypropylene glycol (PPG)	
	Poly(tetramethylene ether) glycol (PTMEG)	
Hydrocarbon macroglycol	Hydroxy terminated polybutadiene glycol (HTPB)	$HO-\left[CH_2-CH{=}CH-CH_2\right]_n-OH$
Polyester macroglycols	Polycaprolactone diol (PCL)	

	Polyethylene adipate (PEA)	
	Polyester diol	 where R = hydrocarbon part that may contain ether linkages also
Polycarbonate macroglycol	Polycarbonate diol	 $HO-(CH_2)_6-[O-\overset{\overset{O}{\|}}{C}-O-(CH_2)_6]_n-OH$
Siloxane macroglycol	Polydimethylsiloxane glycol (PDMS)	
Acrylic macroglycol	Acrylic polyol (ACPO)	

Chain extender

Chain extenders are low molecular weight (generally, below 500 g/mol) diols, diamines and amino alcohols.[51-53] The most commonly used chain extenders are presented in **Table 1.3**. The chain extender is generally used to increase the chain length and the molecular weight of PU. The amine chain extender reacts rapidly and increases the crosslinking density of PU by bridging with biuret linkages in case of PU thermoset, whereas diol chain extenders sometimes required organometallic catalysts to obtain PU. On the other hand, multi-functional and highly branched chain extenders like trimethylol propane, glycerol, triglyceride ricinolate, hyperbranched polyol, etc. are used to prepare HPU or as crosslinking agents for the thermosetting PU.[51]

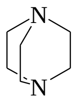
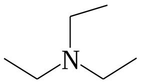
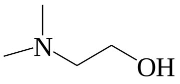
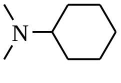
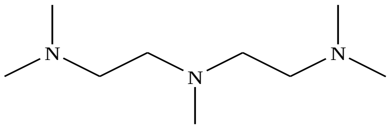
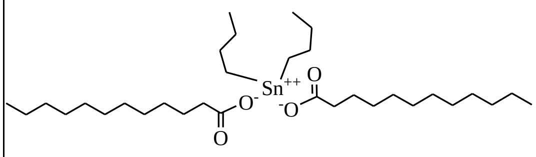
Table 1.3 Structures of a few commonly used chain extenders in PU synthesis

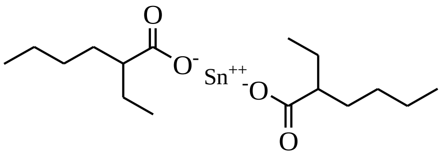
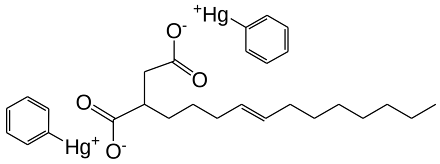
Type	Name	Structure
Hydroxyl based chain extenders	Ethylene glycol	
	1,4-Butanediol	
	1,6-Hexanediol	
	1,4-Cyclohexane dimethanol	
	Glycerol	
	1,2,3-Propanetriol	 $HOH_2C-\overset{CH_2OH}{CH}-OH$
	Trimethylol propane	 $HOH_2C-\underset{CH_2CH_3}{\overset{CH_2OH}{C}}-CH_2OH$
	Triethanol amine (TEA)	
	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)	

Catalyst

The isocyanates especially the aromatic ones are highly reactive, but for synthesis at low temperature and aliphatic isocyanate containing PU required the use of catalyst.[50] Also, the reaction rate rapidly decreases when the steric hindrance increases, mainly on the substitute in higher alcohols. In such cases, catalyst is required. A list of commonly used catalysts is given in **Table 1.4**. These catalysts are mainly divided into two categories *viz.* amino (basic) and organometallic compounds. The commonly used amine catalysts are triethyl amine, triethylenediamine (TEDA), dimethylethanolamine (DMEA), dimethylcyclohexylamine (DMCHA), etc. Similarly, organometallic catalysts are mercury, lead, tin, bismuth and zinc based organo-complexes. However, these catalysts are toxic and hence, they have disposal problems which hinder their uses. Nowadays, bismuth and zinc carboxylates, alkyl tin carboxylates, oxides and mercaptide oxides such as dibutyl tin dilaurate (DBTDL), dioctyltin mercaptide, stannous octoate, dibutyltin oxide, etc. are used successfully.[54]

Table 1.4 Structures of a few commonly used catalysts in PU synthesis

Type	Name	Structure
Amine compounds	Triethylenediamine (TEDA/ DABCO)	
	Triethylamine (TEA/TEN)	
	Dimethylethanol amine (DMEA)	
	Dimethylcyclohexyl-amine (DMCHA)	
	N,N,N',N',N''-pentamethyl-diethylenetriamine (PMDTA)	
Metal complexes	Dibutyltindilaurate (DBTDL)	

	Stannous octoate	
	Tetravalent tin compounds	$R_nSnX_{(4-n)}$ where R=alkyl, aryl, etc. and X= halogen/ carboxylate group
	THORCAT	

Vegetable oils

The global focus on sustainable environment and depletion of petroleum based resources entail the use of renewable resources. Thus vegetable oils, the eminent green resources are extensively researched to synthesize PU. The presence of different types of fatty acids result in different triglycerides in the oil, but the fatty acid composition is fixed for a particular oil. Vegetable oils used for synthesis of PU have been derived from castor, soybean, linseed, palm, kernel, sunflower, *Mesua ferrea* L. seeds and so on.[30] Generally, vegetable oils are not used directly in the synthesis of PU, as most of them don't contain free hydroxyl groups for the reaction. Thus, vegetable oils are usually converted into monoglyceride/polyol then it is utilized for this purpose. Although, *Ricinus communis* oil (castor oil) is a triglyceride of fatty acids with 92–95% ricinoleic acid. Further, secondary hydroxyl group is present in its fatty acid chain, so it can be used directly as chain extender.[55] Karak et al. prepared a series of HPU using direct castor oil as chain extender.[55] Kalita and Karak prepared vegetable-oil-based HPU using castor, sunflower and *M. ferrea* L. seeds oils.[29] They found that castor oil based HPU exhibited better mechanical proprieties and *M. ferrea* L. seeds oil based HPU possessed higher thermal stability. It is found that the biodegradability of HPU improved after incorporation of vegetable oil moiety.[56] Other properties like the flexibility of HPU is also enhanced due to incorporation of oil based hyperbranced polyol. Tan et al. prepared PU with soybean oil-based polyol which exhibited good gas barrier properties.[57]

1.3.1.2. Nanomaterials

The presence of nanomaterials in polymeric nanocomposite provides some exceptional attributes due to their high surface to volume ratio and unique physico-chemical properties.

Different novel nanomaterials are explored in the last two decades through extensive research by the material scientists. The properties of the polymer nanocomposite mainly depend on the size, shape and distribution of the nanomaterials within the polymer matrix. Generally, nanomaterials are categorized into three classes, *viz.* zero, one and two dimensional nanomaterials (**Figure 1.2**).

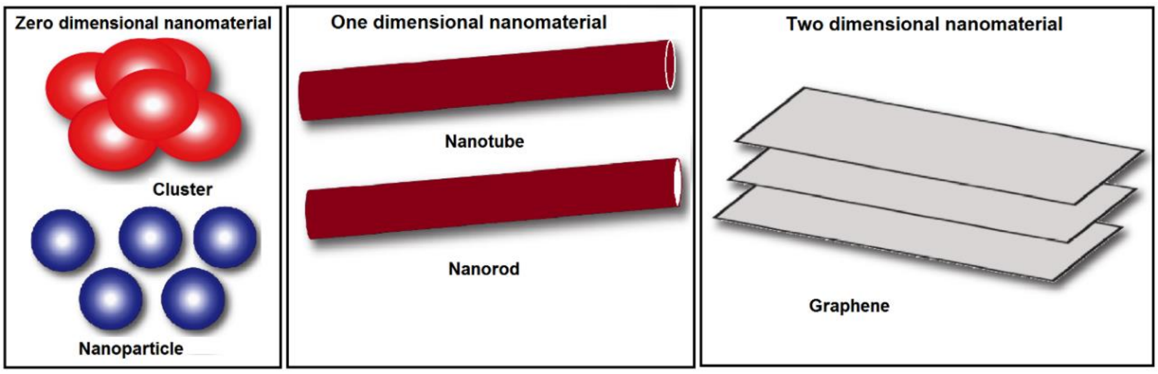


Figure 1.2 Types of nanomaterials

Nanoparticles, quantum dots and nanoclusters with all the three dimensions in nanometer range are considered as zero dimensional nanomaterials. This type of the nanomaterial may possess different shapes, with amorphous or crystalline structure as well as they may be composed of different chemical elements too. Several zero dimensional metal nanoparticles such as silver, gold, iron, copper, sulfur, etc. and different metal oxides such as TiO_2, ZnO, CuO, SnO_2, Fe_3O_4, etc. are widely used in polymer nanocomposites for antimicrobial, catalysis, sensor, optical, photonic and electronic applications.[58] These nanoparticles are synthesized by different methods such as co-precipitation, sol-gel, hydrothermal, microwave, sonochemical, wet chemical reduction, reverse micelles, electrochemical, template synthesis, etc.[58-60] The properties of the nanomaterials depend on the size, shape and distribution, which can be tuned by changing the reaction parameters.

One dimensional nanomaterials are those, which have two dimensions in nanometer and one in micrometer range. They include nanofibers, nanotubes, nanorods, nanowires, etc. Amongst them, nanotubes with hollow tubular structures are most exciting materials and CNT is the most promising one. It is widely used in polymer nanocomposites due to its extraordinary mechanical, electrical and physico-chemical properties.[61] These nanotubes are composed of single and multiple numbers of sp^2 hybridized graphitic carbon layers and classified as single walled (SW), double walled (DW) and multi-walled (MW) CNT respectively. Different nanofibers such as carbon nanofiber, cellulose nanofiber, etc. are quite well-known in polymer nanocomposites.

Two dimensional nanomaterials with only one dimension in nanometer range are one of the most popular nanomaterials in the arena of polymer nanocomposite. Such materials include nanoclay, nanofilms, graphene, GO, RGO, etc. Nanoclays are layered silicates, with tetrahedrally bound Si atoms to an octarhedrally shared edge of $Al(OH)_3$ or $Mg(OH)_2$. Layered nanosilicates possess very high aspect ratio with about 1 nm thick layers.[62] These layers are stacked by weaker physical forces like van der Waals to form a gallery.

Graphene

Graphene, a newly discovered two dimensional carbon allotrope engraved tremendous attention in field of polymer nanocomposites for its unique and fascinating electronic, mechanical and thermal properties.[63] Since the discovery of graphene, a number of studies are carried out on graphene based polymer nanocomposites in a short span of time. Graphene is made of an atomic thick sheet of carbon atoms where the carbon atoms are compactly packed in honeycomb fashion with sp^2 hybridization. Each atom contains four bonds, three σ bond with three neighboring atoms in the plane and one π-bond with carbon atom out of the plane. Carbon-carbon bond length is about 1.42 Å. Every carbon atom present in the graphene sheet is accessible for chemical reaction from two sides (upper and lower sides). Atoms present at the edges of the sheet show unusual chemical reactivity. Graphene contains the highest edge atoms compared to any other carbon allotropes.

Graphene based nanohybrid

Nanohybrid, a special nanomaterial consisting of two or more different nanomaterials, is widely used in recent times as it provides many unusual properties. Generally, zero dimensional nanomaterials are decorated on the surface of one dimensional or two dimensional nanomaterials to obtain such nanohybrids. Recently, a large number of graphene based nanohybrids are studied for different applications. Most of the cases, zero dimensional nanomaterials such as Ag, Pt, Cu, CuO, ZnO, TiO_2, Fe_3O_4, NiO_2, etc. are used to prepare graphene based nanohybrids. Further, one dimensional nanomaterials such as CNT also used to prepare CNT-graphene nanohybrid.[64] In graphene-based nanohybrid, graphene is used either as a functional material or a substrate for immobilizing the other nanomaterials.[65] Although, graphene itself possesses many fascinating properties as discussed in earlier section, a few special properties such as magnetic, photocatalytic, etc.

can also be achieved by proper choice of additional nanomaterial in the nanohybrid.[64] The graphene based nanohybrids are extensively used in diverse fields such as electrochemical energy conversion, optics, electronics, and solar energy harvesting, etc.

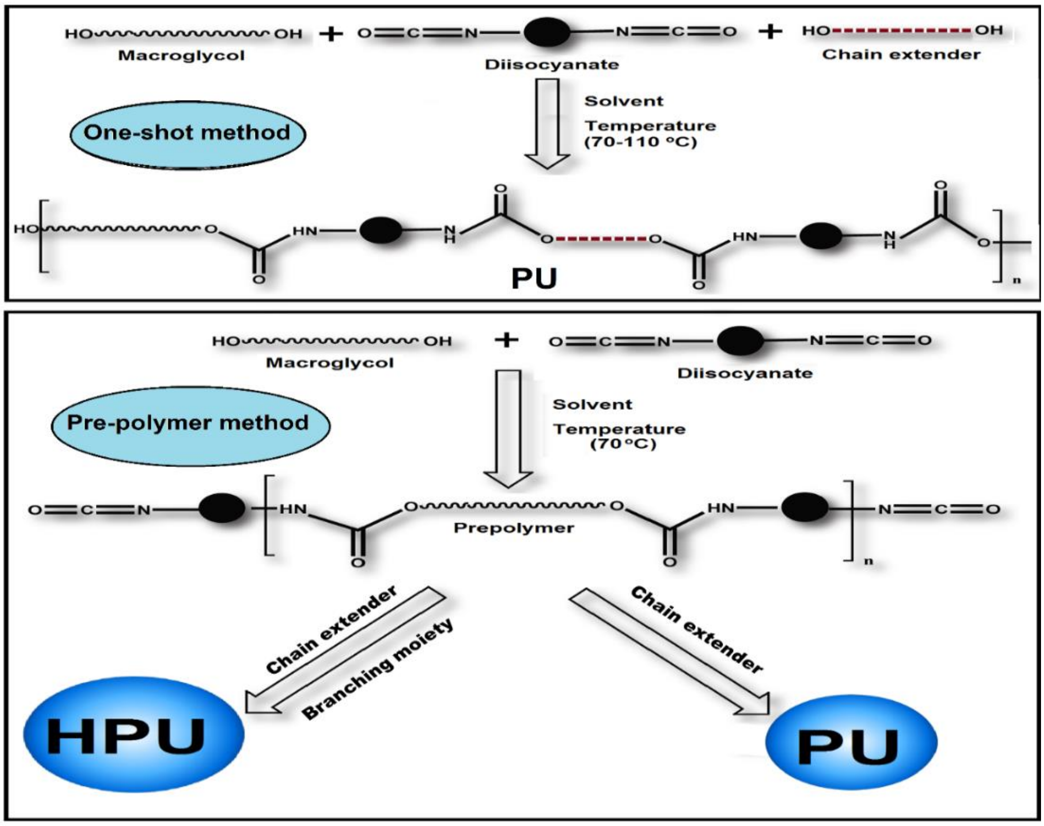
1.3.2. Methods

Preparative methods for PU, graphene, graphene based nanohybrid and graphene based polymer nanocomposites are discussed in this section.

1.3.2.1. Preparative method of PU

PU is produced by a rearrangement polymerization of three chemical constituents namely diisocyanate, macroglycol and chain-extender. PU can be synthesized by both one-shot and pre-polymer methods but pre-polymerization technique is mostly used in preparation of HPU.[66] In this case, hydroxyl or isocyanate terminated prepolymer is first prepared by reacting macroglycol with diisocyanate. In the second step, a chain extender, including branch generating unit is added to the pre-polymer to obtain high molecular weight PU. The obtained PU contains regular chain sequences and common solvents like xylene, dimethylformamide (DMF), dimethylacetamide, etc. are generally used in the polymerization process. In contrary, all reactants are added at same time in one-shot technique. This technique is easier, faster and more reproducible. The obtained PU also possesses high crystallinity but controlling of reaction is very tough. A branch generating moiety with more than two functionalities is incorporated as multifunctional unit during polymerization process to synthesize HPU. As multifunctional unit contains more than two functionalities, controlling of reaction is very important. Therefore, pre-polymerization technique is used and the multifunctional unit is added slowly under dilute condition in the 2nd step of the polymerization process to avoid gelation. The general schemes for synthesis of PU (both linear and hyperbranched) using both the processes are shown in **Scheme 1.1**.

In this context, plentiful literature is found for the synthesis of vegetable oil-based HPU using different approaches. Vegetable oil-based HPU are usually synthesized by using A_2+B_3 approach. Kalita and Karak synthesized *M. ferrea* L. seed oil based HPU using this approach where triethanol amine was used as a branch generating unit.[66] Deka and Karak also prepared *M. ferrea* L. seed oil based HPU using glycerol as a B_3 moiety.[67] Again, sunflower oil based HPU was prepared by using pentaerythritol as a branch generating unit by the same approach.[68,69] HPU was also synthesized utilizing the castor oil directly as a B_3 monomer and isocyanate terminated pre-polymer as a A_2 monomer.[55]



Scheme 1.1 Synthetic schemes of PU and HPU

1.3.2.2. Preparative methods of graphene

Now-a-days, graphene can be produced by a variety of procedures such as mechano-chemical ball-milling, micro-mechanical exfoliation, epitaxial growth of graphite, unzipping of MWCNT, chemical vapor deposition (CVD) of combining gases (H_2 and CH_4) and chemical reduction of GO (**Figure 1.3**).[5,64,70-73] The obtained graphene possesses a relatively perfect structure and excellent properties. Amongst the mentioned approaches, chemical reduction of GO is one of the most advantageous routes for the mass scale preparation of graphene which was proposed by Ruoff and co-workers.[74] Although, graphite oxide is acknowledged as an oxygen containing and water-dispersible material over long time. Only in 2006 scientists understand that it can be exfoliated and well suspended in water even down to the single layer level, i.e. in the form of GO. Thus, GO becomes a tactical starting point for the mass scale preparation of solution dispersible graphene. The reduction of GO possesses two amazing features; (i) it can be prepared using a cost-effective raw material, graphite with a high yield, and (ii) it contains highly oxygen containing groups to form stable aqueous dispersion.

Despite the unique advantages of chemical route for reduction of GO, the obtained RGO tends to form irreversible aggregation which limits its processability. However, this limitation may be tackled by chemical modification of RGO using small organic molecules, bio-molecules and polymers.[75-78] Another negative aspect of the reduction method is the use of toxic reducing agents such as hydrazine, di-methylhydrazine, hydroquinone, sodium borohydride, etc.[79] The presence of trace amount of such toxic agents results detrimental effect, especially for bio-related applications. In this context, employment of green nanotechnology can overcome the above problem. Various reports on the reduction of GO are found in literature by using vitamin C, amino acid, polyphenol alcohol, tea solution, wild carrot root, melatonin, reducing sugar, glucose, bovine Serum albumin and bacteria.[79] Hence, newer methodologies are explored by researchers under the dictates of green chemistry tenets. In this vein, plant extract mediated synthesis of RGO is of prime interest.

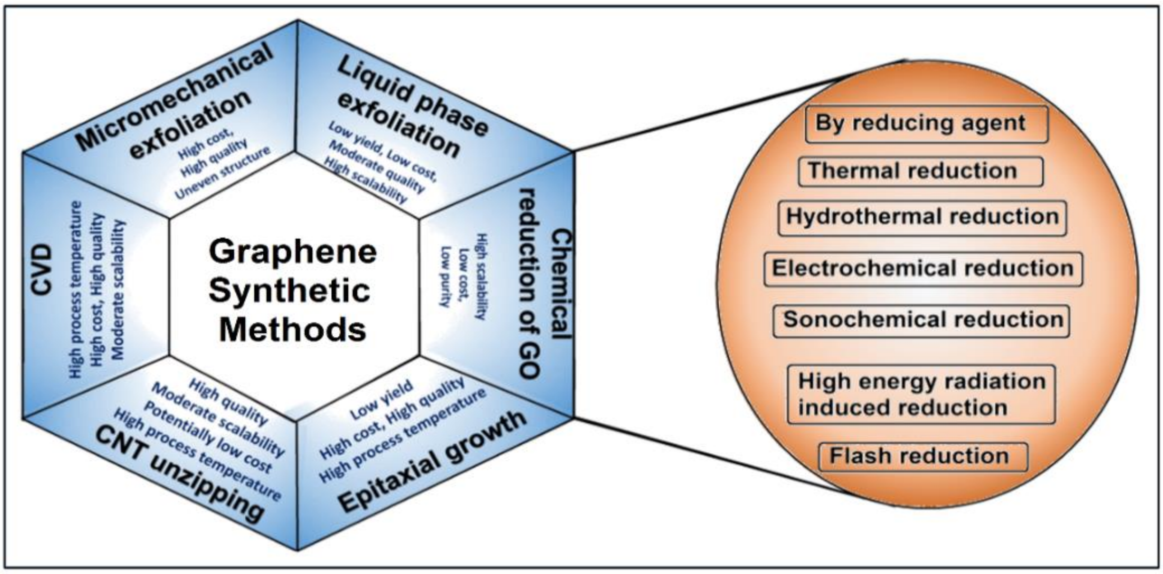


Figure 1.3 The conventional methods used for the synthesis of graphene along with their key features

1.3.2.3. Preparative methods of graphene based nanohybrid

The fabrication methods of graphene based nanohybrid are generally categorizes as the *ex situ* and *in situ* growth approach. The typical preparative approaches for graphene based nanohybrids and their related applications are summarized in **Table 1.5**.

Ex situ approach

In this technique, dispersion of RGO sheets in a suitable solvent is mixed with other dispersion of commercially available or pre-synthesized nanomaterial. Before mixing, surface modification of the nanomaterial and/or RGO sheets is generally carried out for good covalent and non-covalent interactions between them. As an example, bovine serum albumin (BSA), a protein molecule is used for the RGO surface modification via the π–π interaction. Then, the modified RGO serves itself as an adhesive layer for absorption of Au, Ag, Pt and Pd nanoparticles.[80] Instead of decorating nanoparticles on the surface of RGO, such sheets can also wrap around the nanoparticle for specific applications such as the Li-ion battery.[81] Although, the *ex situ* approach provides the pre-determined nanostructures with desired functionalities, but a few limitations such as low density, non-uniform coverage of the nanoparticles on the RGO surfaces, etc. are present here.[64]

In situ growth approach

In this technique, nanoparticles are grown on the RGO surface by different techniques as shown in **Figure 1.4**. In comparison to *ex situ* technique, the *in situ* growth approach can provide uniform surface coverage of nanoparticles by controlling the nucleation sites on RGO. As a result, the continuous decoration of nanoparticles on RGO surfaces is possible.[64]

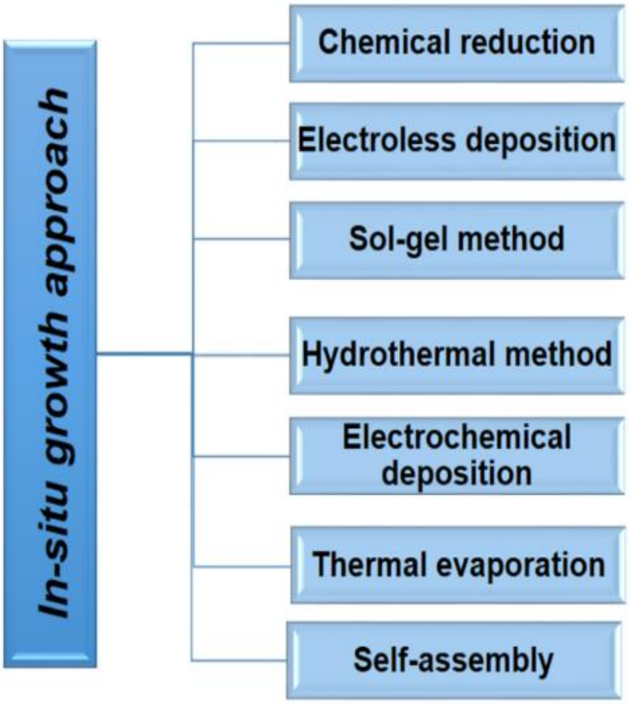


Figure 1.4 Different *in situ* growth approaches to prepare graphene based nanohybrids

Table 1.5 Typical synthetic methods for graphene based nanohybrid and their related applications

Materials	Preparative methods	Applications	Reference
Au/RGO	Through π–π interaction, *Ex situ*	Catalysis, SERS	80
	Photochemical reduction, *In situ*		82
	Chemical reduction, *In situ*	Raman enhancement	83
	Chemical reduction, *In situ*	Plasmonics	84
Ag/RGO	Through π–π interaction, *Ex situ*	SERS	80
	Electroless deposition, *In situ*		85
	Chemical reduction, *In situ*	Photocurrent generation	86
GO/Ag/AgX (X = Br, Cl)	Chemical reduction, *In situ*	Photocatalyst	87
TiO_2/RGO	Self-assembly, *Ex situ*	Photocatalyst	88
	Templated hydrolysis, *In situ*		89
	Hydrolysis, *In situ*	Li ion battery	90
ZnO/RGO	Electrochemical deposition, *In situ*	Photovoltaics	91
	Chemical reduction, *In situ*	Photocurrent generation	92
		Solid-state solar cell	93
	Self-assembly and reduction by UV light, *In situ*	Pollutant adsorbent	94
Fe_3O_4/RGO	Hydrolysis, *In situ*	Li ion battery	95
	Solvothermal, *In situ*	Supercapacitor	96
	Chemical reduction, *In situ*	Arsenic removal	97
Fe_3O_4/GO	Co-precipitation, *In situ*	Drug carrier	98
CdS/RGO	Chemical bath deposition, *In situ*	Solar cell	99
Cu_2O/RGO	Hydrothermal, *In situ*	Supercapacitors	100
	Chemical reduction, *In situ*	Li ion battery	101
	Chemical reduction, *Ex situ*	Electrocatalyst	102
Sulfur/RGO	Chemical method, *In situ*	Li ion battery	103
	Thermal method, *In situ*		104

1.3.2.4. Formation of graphene based polymer nanocomposites

Till date, various approaches are used for the formation of graphene based polymer nanocomposites. There are three main approaches for the formation of nanocomposites: *in situ*, melt mixing, and solution techniques. These approaches are briefly described below.

In situ technique

This is one of the most usually used techniques for the fabrication of graphene based polymer nanocomposites.[105,106] In this technique, prepolymer or polymer precursors are reacted in presence of graphene or other nanomaterials to form *in situ* polymer nanocomposite. Insertion of monomer/prepolymer chains into the layer of the multilayered graphene allows extensive mixing, interaction and distribution of it within the polymeric matrix. This method is widely adopted for preparing exfoliated graphene based polymer nanocomposite. Diffusion of pre-polymer or polymer precursors through nanomaterials and the presence of different secondary interactions forms stable and well dispersed polymer nanocomposite in this technique. High surface energy of the graphene helps in attracting the prepolymer chains of PU to diffuse through the layers of it. Then, the prepolymer chains start to grow within the graphene sheet and resulted a highly exfoliated nanocomposite. Wang et al. prepared PU/RGO nanocomposite by *in situ* polycondensation of MDI and poly(tetramethylene glycol) in presence of RGO sheets using ethylene glycol as the chain extender.[34] Chen et al. fabricated a PU/SiO_2 nanocomposite by the *in situ* technique. SiO_2 nanoparticles were reacted polyester polyol to form functionalized SiO_2 nanoparticles. Then the functionalized SiO_2 nanoparticles reacted with IPDI to get the nanocomposite.[107]

Solution technique

In solution technique, a suitable solvents is used to disperse the nanomaterial and then the dispersed nanomaterial is mixed with polymeric solution by vigorous mechanical shear force followed by ultrasonic energy.[1,108] Nanocomposite is obtained by precipitation or evaporation of the solvent after proper mixing. In this technique, the solvent molecules firstly swell the nanomaterials and help them to disperse. Then, polymeric chains replace the solvent molecules to obtain stable nanocomposite. The total entropy of the process decreases due to the confinement of the chains, which is again compensated by desorption of solvent molecules resulting in intercalated nanocomposite. Intercalated/exfoliated or partially exfoliated PU/graphene nanocomposites are reported through this approach. Chen et al. prepared PU/functionalized RGO nanocomposite by using DMF as a solvent and ultrasound treatment for 30 min.[35] Wu et al. also prepared PU/modified RGO nanocomposite by using this technique. They firstly prepared PU and the nanomaterial solutions in DMF. Then these solutions were mixed and stirred at 70 °C for 30 min to obtain the nanocomposite.[36]

In this technique, a large amount of volatile organic solvents is required which hamper industrial utility of this technique. Along with that, release of toxic waste to the environment is an allied disadvantage of it.

Melt mixing technique

Melt mixing technique is a common industry based method for the fabrication of thermoplastic polymer nanocomposites. In this technique, the nanomaterial is mixed with a molten polymer by twin screw intender, mixer, rollers, injection molding, etc. Mixing of the nanomaterial and the polymer is achieved under shearing force above the softening point of the polymer.[109] Amorphous polymers are mainly processed above their glass transition temperatures but the semi-crystalline polymers are processed above their melting temperatures. Zhang et al. prepared PU/MWCNT nanocomposite by using this technique.[110] They mixed MWCNT with molten PU at 190 °C in a N_2 atmosphere for 4 min at 50 rpm by a mini extruder. Barick and Tripathy reported the formation of PU/organoclay nanocomposite by employing melt mixing technique.[111] They reported that melt mixing is an efficient technique to disperse organoclay in the polymer matrix. Chun et al. also reported PU/montmorillonite (MMT) nanocomposite by this technique using twin screw extruder together with a compatibilizer to improve the dispersion of MMT.[112]

In case of graphene or graphene based nanomaterials, the polymer can penetrate into the interlayer space of it and form either an intercalated or an exfoliated nanocomposite. The level of interaction between polymer chains and nanomaterials is not as good as that of *in situ* technique. However, this technique is superior from the solution technique as it eliminates the use of hazardous solvents. Also, polymer nanocomposites are fabricated by few other techniques like solid-state mechano-chemical or twin-screw pulverisation processes, latex fabrication, template synthesis, coagulation spinning, sol-gel process, plasma treatment, thermal decomposition, etc.

1.4. Characterization and testing

The following section highlights different analytical, spectroscopic and microscopic techniques which are used for the characterization of HPU, GO/RGO, RGO based nanohybrids and HPU nanocomposites. Properties of the pristine HPU and its nanocomposite are evaluated by different testing methods which are also briefed here.

1.4.1. Spectroscopic techniques

UV-visible spectroscopy: This is one of the most commonly used cost effective, simple and fast tools to characterize HPU and nanomaterials especially GO and RGO. The functional groups present in HPU and the nanomaterials provides particular absorbance peaks in the UV-visible spectrum due to π-π* and n-π* transitions. Band gap of nanomaterials can also be determined from the absorbance values. GO shows a peak at 228 nm which is red-shifted to 271 nm after reduction of GO.[76] This indicates the electronic conjugation is restored. In polymer nanocomposite, the position, intensity and nature of the peaks appear differently with different doses of nanomaterials. Chen et al. reported that intensity of the absorbance band (around 290-400 nm) increased in polyester based PU nanocomposite with increase in the content of nano-SiO_2.[107]

Fourier transform infrared (FTIR) spectroscopy: This is a highly useful technique for identifying the presence of different types of functional groups and chemical linkages present in HPU, nanomaterials and HPU nanocomposites. Presence of urethane linkage, reduction of GO, etc. can be supported by this technique. The shifting of band position and broadening in intensity of transmittance band indicates the degree of hydrogen bonding present in the samples. Kalita and Karak reported that band position of the carbonyl group of HPU was shifted from 1728 to 1715 cm^{-1} with the loading of functionalized-MWCNT in the nanocomposites.[113] This indicates the presence of more secondary interaction in the nanocomposite. For the synthesis of PU, it is a very important tool as disappearance of the band at around 2270 cm^{-1} corresponding to –NCO group depict the completion of the reaction.[29,113]

Nuclear magnetic resonance (NMR) spectroscopy: NMR is a useful technique for structural characterization of polymer. Presence of different kinds of protons and carbons in different chemical environments is revealed from ^1H NMR and ^{13}C NMR spectral analyses. Again, NMR spectroscopy is an important tool for the characterization of HPU since detailed analysis of the spectrum permits extracting of information about degree of branching (DB). DB can be calculated from the peak area of the linear, terminal and dendritic unit as reported by Karak and co-workers.[29,69]

1.4.2. Scattering techniques

X-ray diffraction (XRD): XRD is used to study the degree of crystallinity, amorphousness, size of crystals and crystal structure of polymers. This technique is also used to investigate the structure of the nanomaterial and its polymeric nanocomposite. The crystal structure of the nanomaterial can be identified after measuring the angles and intensities of the diffraction peaks. Formation of metal and metal oxide nanoparticles is confirmed from their specific crystallographic peaks from XRD analysis. In case of GO and RGO, XRD is also a crucial tool to investigate the interlayer distance. Pristine graphite exhibits a basal reflection (002) peak at $2\theta = 26.6^{o}$ and the peak shifts to the lower angle upon oxidation due to increase in interlayer distances.[114] Generally, two types of X-ray diffraction techniques are used for polymers and its nanocomposites. These are wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS). WAXD provides the information about the degree of crystalinity, orientation of crystalline region and nature of ordering structure. On the other hand, SAXS is utilized to obtain information on the dimension of small crystalline regions as lamellae and the presence of voids and their shapes. The combined study of WAXD and SAXS presented the quantitative characterization of nanostructure and crystalline structure of polymer nanocomposites. Rana et al. reported that intensities of diffraction peaks at $2\theta = 21.2^{o}$ and 23.4^{o} of PCL moiety in vegetable oil based HPU nanocomposite were increased upon incorporation of MWCNT.[115]

Raman spectroscopy: Raman spectroscopy depend on the inelastic scattering of monochromatic light with materials. Commonly, a laser in the near ultra-violet, visible or near infrared range is used as the light source for this technique. This technique is highly sensitive to the material crystallinity, orientation and temperature. This is useful for analyzing molecules without a permanent dipole moment. This technique is mostly used for the study of carbon based materials such as CNTs, graphene, GO, RGO, etc.[114] It is used to determine the G band (generally observed at 1575 cm^{-1}) that represents the graphitic structure present in the carbon allotrope and the D band (at 1350 cm^{-1}) that indicates the presence of disorder in the structure.[114] Raman spectroscopy is also important for different metal/metal oxide nanoparticles and RGO based nanohybrid.

1.4.3. Microscopic techniques

Scanning electron microscopy (SEM): SEM provides surface images of a sample by scanning with focused beam of electrons. The electrons interact with atoms present in the sample that generates various signals by emitting secondary electrons which are detected by a detector. These secondary electrons give the information about surface topography and composition of the samples. Thus, the SEM micrograph is mainly used to visualize the surface morphology and dispersion patterns of different nanomaterials in the polymeric matrix.[62] Das et al. reported that the inhomogeneity in HPU structure can be visualized from SEM images.[69] Besides determining surface morphology and composition of nanomaterial, SEM is also frequently used to analyze nanomaterial core, and their size and shape.

Transmission electron microscopy (TEM): TEM is considered as the fundamental instrumentation for characterization of nanomaterial and polymer nanocomposite. This is commonly used to analyse the size, shape and aspect ratio of nanomaterials. It allows a beam of high energy electrons to transmit through a very thin specimen, which shows internal structure of the sample. Thus, TEM can provide direct observation of dispersed multi-layer GO/RGO and graphene-based nanohybrid.[114] Presence of different nanomaterials on the surface of GO/RGO can be easily investigated in the graphene based nanohybrid by this technique. It also an important technique to investigate the dispersion of nanomaterials in the polymer matrix.

Atomic force microscopy (AFM): AFM is a very high-resolution type of scanning probe microscopy (SPM), with demonstrated resolution on the order of fractions of a nanometer. It uses a sharp tip to determine the tunneling current and tip-sample interaction respectively. It is a very useful instrumentation for graphene based materials. AFM provides the idea about layers thickness, roughness of the surface and mechanical properties of the tested sample. Thus, it is an important tool to detect the number of layers present in graphene based materials.[74,114]

1.4.4. Other techniques

Differential Scanning Calorimetry (DSC): DSC is a very promising instrument to study the thermal properties of the polymeric materials. The glass transition temperature (T_g), melting temperature (T_m), crystallinity, kinetics of reaction, amount of endothermic or exothermic energy, etc. can be measured by DSC. Kalita and Karak reported that T_m was increased with the increase of functionalized-MWCNT content in the nanocomposites.[113]

Thermogravimetric Analysis (TGA): TGA is used to determine the thermal stability of polymer, nanomaterial and polymeric nanocomposites. The TGA thermogram is generally obtained by recording the change of weight of the sample with temperature due to decomposition, oxidation, or loss of volatiles (such as moisture). This technique is widely used to analyze degradation patterns, degradation mechanism and reaction kinetics, and determine organic and inorganic content of the sample.[62] Hu et al. reported that thermal stability of polystyrene enhanced from 270 to 350 °C upon incorporation of graphene.[16]

Vibrating sample magnetometeric study (VSM): VSM is usually used to measure magnetic properties such as saturation magnetization, initial magnetization and Curie temperature of magnetic materials like Fe_3O_4 nanoparticles. It is based upon the Faraday's law according to which an electromagnetic frequency is induced in a conductor by a time varying magnetic flux.

1.4.5. Testing methods

Mechanical test: Mechanical properties like tensile strength, modulus and elongation at break of HPU and its nanocomposites are measured by Universal Testing Machine (UTM). The tensile test is generally performed on rectangular film samples by using the standard test according to ASTM D 882.

Testing for shape memory behavior: Shape memory behavior of pristine HPU and its nanocomposites are evaluated by different testing methods as discussed below.

Stretching technique: In this technique, the polymeric film is heated above the transition temperature (T_s) and then stretched to twice of its original length (L_0). The stretched length is denoted as L_1. Immediately, the stretched samples are immersed into the low temperature (much below transition temperature) to fix the temporary shape for the specified period of time, and length is measured as L_2 after releasing the stretch. The cooled samples are triggered with different stimuli such as heat, light, microwave, electricity, etc. and the length obtained is denoted as L_3. The percentage of shape recovery and percentage of shape fixity are calculated by using the following equations.[66]

$$\text{Shape recovery (\%)} = \frac{(L_1-L_3)}{L_0} \times 100 \qquad \text{------------------ (1.1)}$$

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

Bending technique: In this technique, the polymer film is heated above T_s for the specified period of time similar to stretching technique and then the film is folded to a ring shape. The folded polymeric film is immediately immersed into the low temperature bath to fix the temporary shape. Then, it is triggered with different stimuli such as heat, light, microwave, electricity, etc.[29]

The shape recovery and shape fixity are two shape memory parameters calculated from the following equations:

$$\text{Shape recovery (\%)} = \frac{(90-\theta)}{90} \times 100 \qquad \text{------------------ (1.3)}$$

$$\text{Shape fixity (\%)} = \frac{\theta}{90} \times 100 \qquad \text{------------------ (1.4)}$$

where, θ in degree denotes the angle between the tangential line at the midpoint of the sample and the line connecting the midpoint and the end of the curved sample.

Besides these, cyclic thermo-mechanical test is also employed to determine the shape memory behavior of polymeric samples.

Self-healing test: In order to evaluate healing performance, the polymeric films are cut in transverse direction by a razor blade and the cracked films are healed by different stimuli. Healing efficiency is calculated as the ratio of tensile strength values of the nanocomposites before to after healing. The optimal healing time for each case is defined as the shortest time required to achieve the best healing efficiency under the given conditions. The healing efficiency is calculated using equation 1.5.[116]

$$\text{Healing effiency} = \frac{\text{T.S.}_{\text{before healed}}}{\text{T.S.}_{\text{after healed}}} \times 100 \qquad \text{------------------ (1.5)}$$

Antimicrobial test: Antimicrobial test of graphene based HPU nanocomposite is mainly performed by well diffusion method.[117] In this method, test microbes are spread on the surface of the Muller-Hinton agar or potato dextrose agar on Petri dishes. The dispersed nanocomposites are poured into 6 mm diameter wells on the solidified agar. In one well, a standard antibiotic is used as a positive control. Then the zone of inhibition diameter is measured using a zone scale after incubation for 24-48 h at 37 °C.

1.5. Property

Many properties of pristine polymer are significantly improved by the formation of nanocomposites with GO/RGO or their nanohybrids. Also, the presence of RGO and its nanohybrid in polymer matrix generally offers a few new interesting properties. Thus, some important properties of graphene based polymer nanocomposites are discussed in this section.

1.5.1. Mechanical

Pristine graphene is known as the stiffest material of the world with elastic modulus almost 1 TPa.[118] Despite of several structural defects in RGO compared to pristine graphene, it also possesses high elastic modulus of 0.25 TPa.[118,119] Therefore, incorporation of graphene based nanomaterials such as GO, RGO and RGO based nanohybrid in polymer matrix effectively improves the mechanical properties of the pristine polymer system. Tensile modulus, tensile strength and toughness of PU are dramatically enhanced after incorporation of small amount of such graphene based materials. But improvement of tensile modulus is more promising in case of elastomeric thermoplastic materials of PU and HPU.[120] This is due to greater stiffness difference between reinforcing agent and matrix. Kim and co-workers compared the stiffening performance of different types of functionalized graphene. They dispersed the nanomaterials in elastomeric PU via different blending routes.[121] Among the different RGO nanocomposites, solvent processed (directly cast from the solution) nanocomposites exhibited higher stiffness than melt processed ones. The lower modulus of melt processed nanocomposites is due to re-aggregation of RGO sheets under extensional flow during melt compounding. Wu et al. also incorporated hyperbranched aromatic polyamide functionalized RGO in the PU matrix and found that the mechanical properties such as tensile modulus and tensile strength were tremendously improved upon incorporation of functionalized RGO.[36] However, generally elongation at break of PU decreased slightly with the addition of graphene based materials.[36] Xiang et al. reported that mechanical properties of PU improved after incorporation of hexadecyl-functionalized RGO.[122] The effect of hydroxyl modified MWCNT and graphene on PU was investigated by Swain and co-workers.[123] They found that PU/MWCNT nanocomposite demonstrated higher tensile strength compared to the PU/graphene nanocomposite in the same filler content. Yadav et al. also found mechanical properties of HPU was greatly enhanced after incorporation of 3 wt% MWCNT.[124] Except the graphene or carbon based nanomaterial, a few other nanomaterials are also used to improve the mechanical properties of pristine PU. Mahapatra and co-workers found that incorporation of small amount of polyhedral oligosilsesquioxane (POSS) in the HPU matrix effectively improved the mechanical properties.[125]

1.5.2. Thermal

Thermal properties of polymeric materials are vital for their service life and high temperature stability. Various thermal techniques such as TGA, DSC, differential thermal analysis (DTA), etc. are available for the studies of thermal properties of PU, nanomaterials and nanocomposites. Their thermal stabilities are determined by using TGA. Numerous studies have been carried out which reported that thermal stability of PU increased after incorporation of RGO and RGO based nanohybrid.[126] Decomposition of RGO based PU nanocomposites is significantly slower than neat PU, which is owing to restricted chain mobility of PU near RGO surface.[127] During combustion, nanomaterial produces a blocked network of char layers which hinders the transport of the decomposition products. Even GO, which is thermally unstable itself, can improve the overall thermal stability of the resulted nanocomposite compared to the pristine polymer.[126] Wang et al. reported that the temperature for 5% weight loss of PU increased by about 40 °C after incorporation of 2 wt% modified RGO.[34] Incorporation of functionalized MWCNT also effectively improves the thermal stability of HPU.[120]

Whereas, DSC is also a valuable tool to investigate the thermal transition behaviors and determination of T_g and T_m of HPU and its graphene based nanocomposites. After incorporation of RGO or RGO based nanohybrid in HPU matrix, T_g and T_m are generally shifted to higher temperature due to the increased toughness and rigidity of the nanocomposites as compared to the pristine PU.[127,128] Scognamillo et al. reported that T_g of PU increased in the presence of very low amounts of graphene.[129] Sun et al. reported that T_g of HPU was significantly increased from 91.9°C to 99.7°C after incorporation of MWCNT. [130] Presence of MWCNT acts as nucleating agent and aids to crystalline the polymer chains. Kalita and Karak also witnessed similar observations that T_g of HPU significantly improved from 39.1 °C to 46.2 °C, after adding of 2 wt% of functionalized MWCNT in HPU matrix.[113]

1.5.3. Electrical

Presence of graphene sheet can offer percolated pathways for electron transfer in nanocomposite, which makes the nanocomposite electrically conductive. Similar results can be attained with other carbon reinforcing agents such as conductive carbon black, CNT, carbon nanofibers, and expanded graphite.[120] However, graphene allows the transition from insulator polymer to conductor at significantly lower loading, compared to CNT. Kim and co-workers reported that incorporation of 0.5 wt% of RGO produced electrically conductive PU nanocomposite.[121] Among the RGO based nanocomposites, conductivity of *in situ* and solvent-processed nanocomposites is higher than melt-processed ones at the same filler volume fraction. Yousefi et al. reported that PU/RGO nanocomposites showed good electrical conductivity with a very low percolation threshold of 0.078 vol%.[131] The electrical conductivity of the graphene based HPU nanocomposites shows a significant anisotropy with high RGO contents due to the special formation of conductive networks along the in-plane direction. Wu et al. found that PU nanocomposite exhibited high permittivity and low dielectric loss after incorporation of hyperbranched polyamide functionalized RGO.[36] Swain et al. also reported that the percolation threshold was much higher in PU/functionalized RGO nanocomposite compared to PU/functionalized MWCNT nanocomposite.[123] Zhao and co-workers prepared PU nanocomposite by incorporating HPU-grafted MWCNT which exhibited high electrical conductivity.[132] Mahapatra et al. reported that HPU/SWCNT nanocomposite demonstrated tunable dielectric permittivity.[133] They found that the tunability was more prominent with SWCNT amount in HPU. Seveyrat and co-workers investigated the effect of different carbon based nanomaterials (MWCNT, graphene, carbon black) on the dielectric properties of PU and they found that the percolation thresholds mainly depend on the size and shape of the carbon based nanomaterials.[134]

1.5.4. Gas barrier

The incorporation of GO/RGO can significantly decrease the gas permeation through the nanocomposite compared to the pristine HPU.[121,135] A percolating network of GO/RGO layers forms due to high aspect ratio of GO/RGO, which can provide a ‘tortuous path’ to inhibit molecular diffusion through the matrix. Rate of diffusion of a penetrating molecule mainly depends on the degree of dispersion of GO/RGO in the PU matrix.[126] Kim and co-workers reported the improved gas barrier property of RGO based PU nanocomposite. They compared gas permeation through PU membranes filled with different types of graphitic reinforcements.[121] They also found that PU nanocomposite with isocyanate terminated GO exhibited better N_2 gas barrier property. Further, RGO decreased permeability of PU more than organically modified montmorillonite layers at same loading percentage. Also, the study showed that solvent processed nanocomposite exhibited better gas barrier properties than the melt processed one, due to better dispersion of RGO in PU matrix.[120] Xiang et al. found that N_2 gas diffusivity of PU was declined by 3 orders of magnitude after incorporation of only 0.5 wt% hexadecyl-functionalized RGO.[122]

1.5.5. Catalytic

Semiconductor nanomaterials like TiO_2, ZnO, SnO_2, etc. are widely used as photocatalysts.[136-138] These materials generate electron/hole (e^-/h^+) pairs after excitation by the light. These e^-/h^+ pairs react with H_2O and O_2, and generated reactive oxygen species like $^{\cdot}OH$ and $^{\cdot}O_2^-$ which take part in the catalytic reactions.[137] However, requirement of ultraviolet (UV) light to activate such photocatalysts significantly restricts their practical applications as content of UV light in the solar spectrum is very less (about 2-3 %).[136] In this regard, RGO based semiconductor nanohybrid such as RGO-TiO_2 and RGO-ZnO nanohybrid showed remarkably enhanced photocatalytic performance under visible light.[136,138] However, the use of these bare nanomaterials causes difficulties in reuse of the photocatalyst as well as agglomeration generally occurs. Thus, polymer nanocomposites are largely used as heterogeneous catalysts for this purpose. Karak et al. reported that sunflower oil based HPU/Ag nanocomposite exhibited good catalytic activity in the reduction of 4-nitro phenol to 4-amino phenol.[139]

1.5.6. Flame retardancy

The flame retardant polymer nanocomposites are those which retard or inhibit heating, degradation or decomposition, ignition of flammable gases and combustion with heat generation during burning process. Special element such as halogens, phosphorus, metal, etc. containing PU generally exhibited flame retardancy.[62] Again, the formation of PU nanocomposites with clay, silica, CNT, carbon nanofiber, RGO, etc. increases the flame retardancy behavior of pristine PU.[140] These nanomaterials are collapsed or formed non-flammable char during the burning process and thus, reduce the heat release rate. The char also prevents the fire spreading by holding the structural integrity of PU.

1.5.7. Antimicrobial activity

Pristine PU generally does not exhibit antimicrobial activity. However, PU nanocomposite with metal or metal oxide nanoparticles like, Ag, Cu, CuO, TiO_2, ZnO, etc. showed excellent antimicrobial activity.[141,142] The presence nanomaterial in the nanocomposite strongly interacts with the cell surface of the microorganisms. The antimicrobial PU nanocomposites are basically used in advanced surface coatings for inhibiting microbial growth. Formation of PU nanocomposites offers stability to the active nanomaterials by uniform dispersion and strong interactions which aid in long time utility of the material by slow releasing rate. Jena and co-workers reported that HPU/ZnO nanocomposites demonstrated good antibacterial as well as antifungal activity. They found that the antimicrobial activity was enhanced with increasing ZnO concentration in HPU and effect was more profound in case of *Escherichia coli*.[143] Yadav et al. also reported that HPU/MWCNT nanocomposite showed good antimicrobial activity against *E. coli*. The bacterial growth was inhibited to 50% within 21 h in case of the nanocomposite with 3 wt% of MWCNT.[124] Liu et al. investigated the antibacterial activity of different type graphene based materials (graphite, graphite oxide, GO and RGO) against *E. coli*.[144] GO exhibited the highest antibacterial activity under similar concentration and incubation conditions. Chen et al. also found that GO showed good antimicrobial activity against different bacterial phytopathogens and fungal conidia.[145] After incorporation of GO in polylactic acid-PU, the nanocomposite showed good antibacterial activity against the gram-positive bacterium, *Staphylococcus aureus* and the gram-negative one, *E.coli*.[146]

1.5.8. Shape memory properties

Shape fixity, shape recovery and recovery time are the important parameters that are used to describe shape-memory effects of a polymeric material.

Shape fixity: Shape fixity is the extent of a temporary shape being fixed for a shape memory polymer. It is similar to strain fixity and shape retention. The shape fixity is thus equal to the percentage of the ratio of fixed deformation to total deformation.

Shape recovery: Shape recovery is defined as the ability of a polymeric material to memorize the original shape from a temporary deformed shape. The shape recovery is therefore the percentage of ratio of deformation recovered by the specimen to the deformation taken place to the specimen.

Recovery rate: This parameter describes the speed i.e. the rate of recovery from a fixed temporary shape to its original shape during the recovery process of polymeric material under the application of an appropriate stimulus. It can also be said as the speed of recovery process or shape recovery speed.

M. ferrea L. seed oil and sunflower oil based HPU exhibited good shape memory effect.[29,147] Kalita et al. reported that *M. ferrea* L. seed oil based HPU demonstrated good solvent induced shape memory behavior.[56] Again, Jana et al. reported that the enhancement of shape memory properties of PU nanocomposites reinforced with poly(ε-caprolactone)-grafted CNT.[148] Sahoo et al. reported that CNT based PU nanocomposites exhibited good shape recovery (90-95%) under the actuation of an electric field.[149] Lee and Yu fabricated a PU/SWCNT nanocomposite which demonstrated good elctroactive shape memory effect.[150] They found that nanocomposite with 4 wt% SWCNT showed good electroactive shape recovery (88%) within 90 s upon triggering of 30 V and 0.1 amp electrical power. Yadav et al. prepared PU/functionalized RGO nanocomposite via *in situ* polymerization and demonstrated a good improvement of shape recovery, to the extent of 96%.[127]

1.6. Applications

Graphene based polymer nanocomposites are already explored for a range of applications as surface coating, self-healing, shape memory materials, and biomaterial, etc. (**Figure 1.5**).

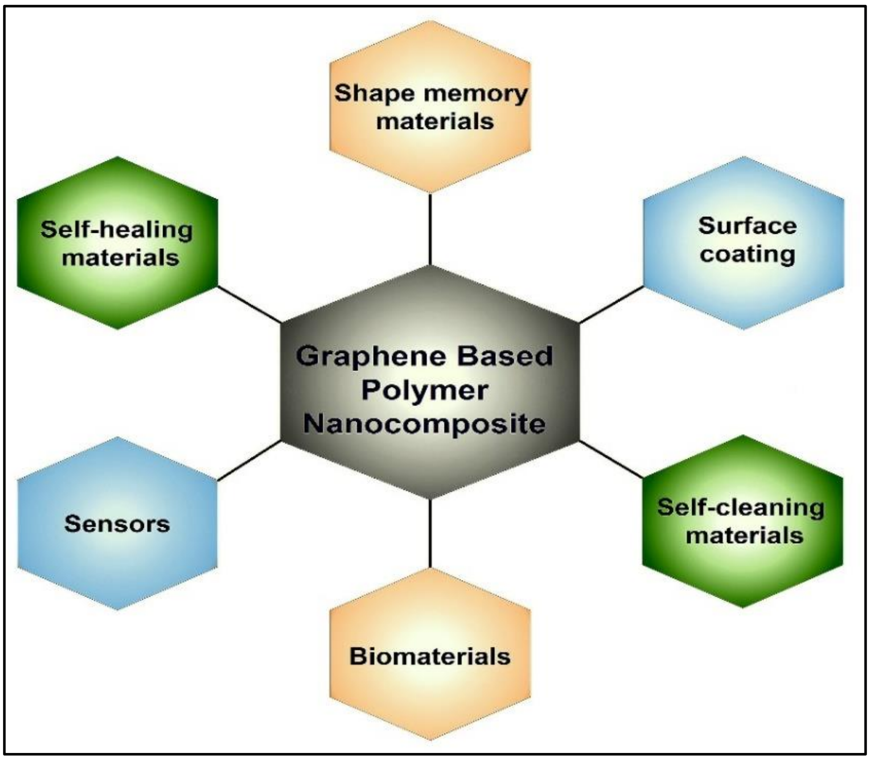


Figure 1.5 Prospective applications of graphene based polymer nanocomposite

1.6.1. Surface coating

Surface coating materials are used for the protection of a substrate from damages by the external factors and for the decoration purpose. PU coatings are widely used in different objects, like oil and gas pipeline, storage tanks, ships, bridges, and other facilities. These coatings have been effectively used due to their exceptional life and performance, resistance to aggressively corrosive environments, high abrasion resistance, strong adhesion, etc. Sabzi et al. prepared PU/TiO_2 nanocomposite which exhibited improved UV protection ability and provided clear coating.[151] Song and co-workers reported that incorporation of ZnO nanoparticles and ZnO nanowhiskers improved the reducing-friction and anti-wear abilities of the PU coatings.[152] They found that ZnO whiskers were superior as compared to ZnO nanoparticles in terms of the ability to decrease friction-coefficient and wear rate of the PU coating. Li et al. found that anticorrosion properties of PU was enhanced by the incorporation of titanate functionalized GO.[153]

1.6.2. Shape memory materials

Vegetable oil-based HPU and its nanocomposites showed excellent shape memory behavior.[29,66] Shape memory polymers (SMPs) are used in different fields of applications such as aerospace engineering, textile engineering, packaging, self-peeling reversible adhesives, etc. SMP is also used in biological and medicinal fields, especially for biomedical devices, which help in minimally invasive surgery. Jung et al. fabricated PU nanocomposite with a small amount (0.1 wt%) of graphene, which exhibited good shape memory effect.[154] Liang et al. prepared three different PU nanocomposites with isocyanate-graphene, sulfonated-graphene, and RGO. PU nanocomposites with 1 wt% sulfonated-graphene exhibit repeatable infrared-triggered actuation performance of lifting a 21.6 g weight up to 3.1 cm with 0.21 N of force.[33] Feng et al. also prepared PU nanocomposites with sulfonated RGO/sulfonated CNT nanohybrid which showed good IR absorption. PU nanocomposites with nanohybrid (sulfonated RGO: sulfonated CNT =3:1) showed the maximum IR-actuated stress recovery of lifting a 107.6 g weight up 4.7 cm in 18 s. The stress recovery delivered a high energy density of 0.63 J/g and shape recovery force up to 1.2 MPa.[155] Kalita and Karak reported that HPU/Fe_3O_4-MWCNT nanocomposite exhibited good shape recovery under the application of microwave energy and the shape recovery speed increased with the Fe_3O_4-MWCNT content in the nanocomposites.[156] Ali et al. prepared palm oil based HPU/clay nanocomposite which also demonstrated good shape memory behavior.[157]

1.6.3. Sensor

The polymer nanocomposites are widely used in sensor technology for sensing of gas, humidity, toxic chemicals, pressure, etc. The sensing responses of graphene based polymer nanocomposite are generally categorized into two main classes. Firstly, the nanocomposites exhibit noticeable changes in electrical conductivity based on the remarkable electronic property of graphene, and polymers functioned as supporting components here. Secondly, the nanocomposites respond to the external stimuli and demonstrate variations in color or shape. Graphene is also used as an absorbent of the visible/near-infrared light or thermal conductor. Graphene can also function as energy exchanger in many actuators due to the extraordinary optical, electrical, and thermal properties. For instance, Yao et al. fabricated PU/RGO nanocomposite for a piezoresistive sensor with ultra-high-pressure sensitivity (0.26 kPa^{-1}). That can sense also in very low pressure range (<2 kPa) and minimum detectable pressure is 9 Pa.[158] Nayak and co-workers reported that PU-titania nanocomposites exhibited excellent piezoelectric behavior with tunable dielectric properties.[159] PU based different sensors were fabricated which can effectively sense the pressure, presence of CO_2 gas, etc.[160,161] Goldman invented a capacitive biofeedback sensor by using PU which can be placed within a patient's shoe, boot, ankle, brace, crutch, hand grip, wheelchair, etc.[162]

1.6.4. Self-healing material

Self-healing materials, a class of smart materials, exhibited an ability to repair their damages which are encountered by mechanical stress during service period. Such recovery can take place autonomously or activate by a specific stimulus (e.g. heat, radiation). These materials are expected to provide the safety and durability to the polymer without external repair or the high costs of active monitoring. Different PU based self-healing materials are reported in the literature. Ghosh and Urban developed PU networks that showed good self-healing effect upon exposure to UV light.[163] The fabricated PU contains of an oxetane-substituted chitosan precursor. Upon mechanical damage, four-member oxetane rings open to create two reactive ends. During UV light exposure, chitosan chain scission takes place, which crosslinks with the reactive oxetane ends to repair the damage. Huang et al. prepared PU/few-layered graphene nanocomposite which demonstrated repeatedly healing by various stimuli such as IR light, electricity, and electromagnetic wave with healing efficiencies higher than 98%.[164] Henry fabricated a PU based corrosion resistant self-healing coating which showed promising resistance to acid as well as salt water, and exhibited good adhesion properties to different substrates.[165]

1.6.5. Self-cleaning materials

Self-cleaning is a desired property which makes the dream of a contamination-free surface into reality. Commonly, low surface energy and surface microstructure are the most vital facets for a self-cleaning surface. This is generally known as the superhydrophobic surface. Wu et al. fabricated PU which contained a perfluoropolyether segments to achieve such self-cleaning effect.[166] Zhang and co-workers reported PU foam which demonstrated super-repellency towards corrosive liquids, oil and it also showed good oil/water separation properties.[167] PU/photocatalyst nanocomposite also exhibited good self-cleaning properties by degrading the contaminants. In this regards, Charpentier et al. reported that PU/TiO_2 nanocomposite showed good photoinduced self-cleaning and antimicrobial properties.[168] Jena et al. fabricated PU/ZnO nanocomposite which exhibited the hydrophobic characteristic, which increased with increasing ZnO nanoparticle concentration.[143]

1.6.6. Biomaterials

PU and its nanocomposites are widely used in the field of biomedical science such as tissue engineering, wound dressing, drug delivery, catheter and stent. Three dimensional biodegradable and biocompatible scaffold is the most important component in the tissue engineering. Scaffold generally helps to grow the tissue in the wounded area and hence the original shape as well as function restored in the tissue. Vegetable oil-based HPU and its nanocomposites are used as scaffold materials due to their good biodegradable and biocompatible properties.[69] HPU/functionalized MWCNT nanocomposite is a potential biomimetic scaffold for bone tissue engineering.[169] On the other hand, Fe_3O_4 decorated MWCNT nanohybrid/HPU nanocomposite showed its potentiality as an antibacterial wound healing material with controlled drug release efficiency.[170] Jing et al. fabricated a PU/GO nanocomposite based scaffold which showed good potential for tissue engineering applications.[171] The reported nanocomposite showed good biocompatibility and no such noticeable toxicity was found for GO. The same group also investigated the biocompatibility of PU/GO nanocomposite in mouse fibroblast (3T3) and human umbilical vein endothelial cells. They observed that cell viabilities for both types of cells were the highest at a 0.5 wt% GO and the nanocomposite showed a good potential to use as scaffold material.[172]

Miscellaneous

Graphene based polymer nanocomposites are used as electrostatic discharge (ESD) materials and shielding materials for electromagnetic interference (EMI) too. This is due to intrinsic high conductivity and aspect ratio of graphene which enable to attain the percolation threshold at very low loading. Also, graphene based polymer nanocomposites are used as supercapacitors, antistatic materials, etc. depending on the loading amount of graphene.

1.7. Scopes and objectives of the present investigation

From the discussions presented in the previous sections, it is noticed that a lot of works have been carried out on renewable or non-renewable resource based PU as well as their nanocomposites. But graphene based HPU nanocomposite is not explored sufficiently, especially vegetable oil-based HPU nanocomposites are rare in the domain. As, graphene is a wonderful material of this era with various outstanding and unique properties, it may provide some exceptional attributes to the resultant nanocomposite. Therefore, excellence of graphene together with vegetable oil-based HPU is yet to explore comprehensively. Again, mechanical, electrical and thermal properties of graphene based PU nanocomposite are mainly studied in literature. But different others applications such as shape memory behavior, self-healing and self-cleaning ability are not yet addressed fully. Thus, it opens a new area of research to use graphene based HPU nanocomposites as shape memory, self-healing and self-cleaning polymeric materials.

In this perspective, the main objectives of the present investigation are made as follows,

i) To synthesize, characterize and evaluate the properties of hyperbranched polyurethane.
ii) To prepare reduced graphene oxide from graphite by a simple greener route.
iii) To characterize the prepared graphene based nanomaterials using different analytical, spectroscopic and microscopic techniques.
iv) To prepare and characterize the graphene based nanohybrids with sulfur, iron oxide, etc.
v) To prepare and characterize the nanocomposites of hyperbranched polyurethane with graphene based nanomaterials and nanohybrids.
vi) To evaluate the performance of the prepared nanocomposites for their possible potential applications.

1.8. Plans of research

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

i) A thorough literature survey on the field of hyperbranched polyurethane, graphene based nanomaterials and their nanocomposites will be conducted.

ii) Hyperbranched polyurethane using multifunctional moieties with the other conventional reactants will be synthesized and characterized by using different analytical, spectroscopic and microscopic techniques such as FTIR, NMR, TGA, DSC, etc.

iii) Graphene based nanomaterial will be prepared from graphene oxide through a simple and greener reductive technique.

iv) Graphene based nanohybrids with sulfur, iron oxide, etc. will be prepared and characterized by using different analytical and spectroscopic techniques such as FTIR, XRD, TEM, TGA, etc.

v) Hyperbranched polyurethane nanocomposites will be prepared by the conventional technique as reported in literature using graphene based nanomaterials and nanohybrids.

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

vii) The performance characteristics of the polyurethane nanocomposites will be investigated by determination of tensile strength, modulus, elongation at break, impact resistance, scratch hardness, etc.

viii) The prepared nanocomposites will be utilized for their possible potential applications.

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