

# *Chapter@1*

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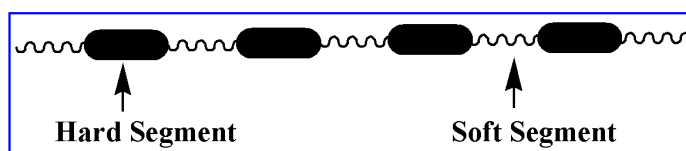
## *Introduction*

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## **1.1 Introduction:**

Segmented polyurethanes (PUs), one of the most versatile polymeric material that contains the urethane linkage in their chain composed of soft and hard segments and frequently used in several fields such as coatings, adhesives, foam, and flame retardants as well as in biomedical area like aortic grafts, heart valves, intra-aortic balloons, sustained drug / gene release and in ligament reconstructions etc [Zhou et al. (2011)]. It is the sixth most used polymeric material in 2011 with a global production of 17.5Mt [Rokick et al. (2015)]. Initially, it was synthesized by Prof. Otto Bayer, in 1937, a German chemist through the addition process [Krol et al. (2007)]. It was used as a replacement of rubber and coating material to protect from the mustard gas as well as corrosion during World War II. Polyurethanes are synthesized through polyols, diisocyanate and low molecular weight of chain extenders. Polyurethane performance properties can be modified either by changing the chemical nature, composition, selecting the appropriated raw materials used in synthesis process as well as incorporation of suitable filler in polymer matrix [Mishra et al. (2010)]. Generally, polyols have macroglycols of polyesters, polyethers, and polycarbonates with terminated dihydroxyl group. However, low molecular weight diols such as N-BOC-Serinol and pentaerythritols are also used in polyurethane synthesis [Cherng et al. (2013)]. These polyols are the responsible for generation of soft segments as well as the flexibility in polymer chains. Polyurethanes having the polyesters as diols exhibit hydrolytic degradation than polyethers based. Polyurethanes which are easily go for the degradation is term as the biodegradable PUs and mainly used in drug delivery and tissue repairing area whereas, degradation resistant polymer is term as bio-inert

polyurethanes and frequently used in making the artificial organs and medical devices due to its better mechanical properties, chemical stability and abrasion resistant in nature [Silva et al. (2010)]. Extension of the diisocyanate terminated prepolymer with low molecular weight chain extender moieties leads to generate the hard segment zones in polymer chains. These hard zones in polymer are responsible for the mechanical strength in PUs. Properties of the polymer are also governed by the nature of the chain extenders. Morphology of these segmented zones is influence through the specific interaction between soft- soft, soft-hard and hard-hard segments of polymer chain. Depending upon the interaction these zones may be cylindrical, spherical, globular etc [Yeh et al. (2003)].



**Figure 1.1:** Schematic representation of segmented polyurethanes (SPUs)

Moreover, depending upon the purity of chemical and method followed in polyurethane synthesis along with urethane functionality biurete groups, urea group, azaheterocyclic (isocyanurate) structure, oxazolidone structures as well as ionic moieties are also present in polymer chain which affects the polymeric properties [Krol et al. (2007)]. Self-assembly phenomena which are more common in dendritic and block copolymer also observed in aliphatic polyurethanes through interactions between the urethane moieties in polymer chain. This layer by layer self-assembled polymer show excellent mechanical, chemical, physical and biological behavior as compared to the conventional micelles [Riess et al. (2003); Discher et al. (1999)]. However, these self-assembly phenomena did not occurred

in aromatic polyurethane due to the presence of the bulky aromatic ring which hindered the interaction between the urethane moieties. Recently waterborne polyurethane (WPU) is frequently used in place of conventional polyurethane which contained the organic moieties as well as some free isocyanate monomer [Cao et al. (2007)]. WPU have high molecular weight, non toxic in nature as well as wide range in applicability however, mechanical properties, thermal stability and insolubility is lower than organic based polyurethane and it required to improved [Hsu et al. (2006)]. Improvement in properties of polyurethane can be achieved by adding the suitable nanofiller such as metal and its oxides [Arbatti et al. (2007)], clay [Lee et al. (2006)] and carbon in different forms [Wang et al. (2011)].

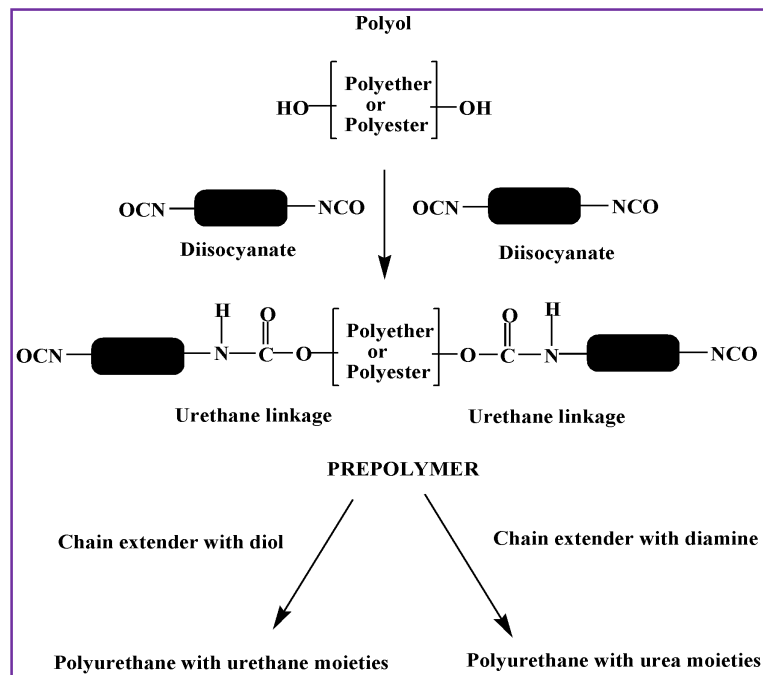
### **1.2 Synthesis of Polyurethanes (PUs):**

Both condensation polymerization and addition polymerization process is involved in polyurethane synthesis. Condensation polymerization process leads by eliminating the small molecules such as water or carbon dioxide molecules. However, no eliminations of such type of molecules are occurred during polyurethane polymerization. It is difficult to control the final molecular weight and molecular weight distribution of polymeric material in condensation process. There are two methods (one step and two step) are available for synthesis of polyurethanes.

One step polymerization process is easiest and rapid method for polyurethane synthesis. In this method desired isocyanates and polyols is mixed in melt condition in mold to allow the polymerization in inert medium. Synthesized polymers have

little cross linked network structure. Curing of polymer leads to generate the elastomeric nature in materials.

Two step polymerization processes is most common method for synthesis of polyurethane and given in (Figure 1.2), in which low molecular weight of diisocyanate terminated prepolymer is formed through the reaction of polyols and diisocyanates followed by the addition of the chain extender molecules to form the high molecular weight polymeric materials. This process is preferred for synthesis of materials over to one step synthesis due to the easy control the chemical and physical properties of the material as well as process ability etc [Ortel et al. (1993)].



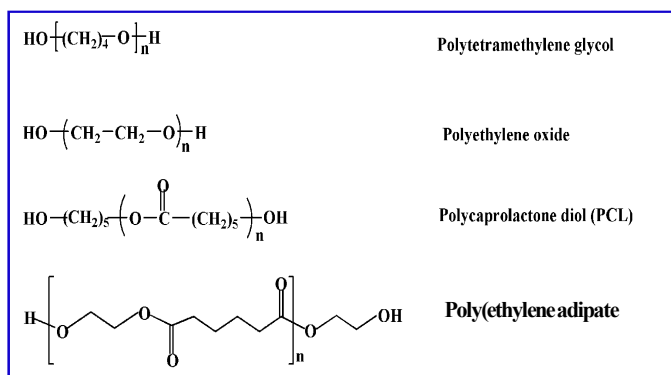
**Figure 1.2:** Two step polyurethane synthesis process: Formation of prepolymer through reaction between polyol and diisocyanate followed by chain extension step.

### 1.3 Components of Polyurethanes (PUs):

Polyurethanes can be synthesized through polyols, diisocyanate and chain extender. Chain extender may be diol or diamine in nature. Properties of polymer can be tuned by changing the chemical nature and composition of these components [Versteegen et al. (2005); Koerner et al. (2004); Velankar et al. (2004)]. Concise descriptions of polyurethane components are given below:

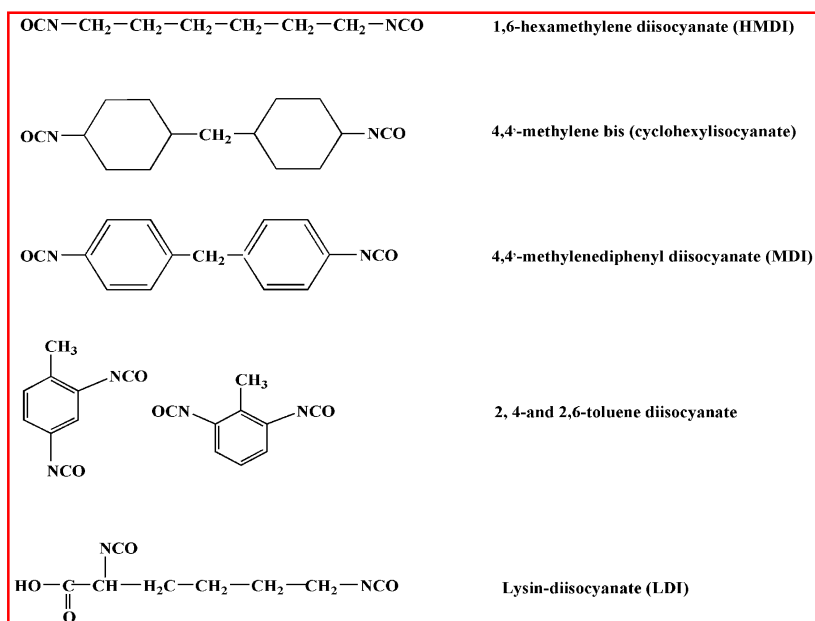
#### 1.3.1 Polyols:

Commonly polyols are macroglycols of polyether, polycarbonates and polyester with di-hydroxy terminated moieties. Polyether polyols are synthesized through the reaction between epoxide and compounds containing active hydrogen whereas, polyester based polyols are prepared by polycondensation process between hydroxyl compounds and carboxylic acids. Molecular weights of most commonly used polyols are in range of 400-5000. Nature of polyols plays an important role in determining the properties of obtained polyurethane. For example PUs made by polyethylene oxide (PEO) as polyols exhibits water sensitivity whereas, polypropylene oxide based PUs show the lesser water sensitive behavior [Cherng et al. (2013)]. Some commonly used polyols are given below:

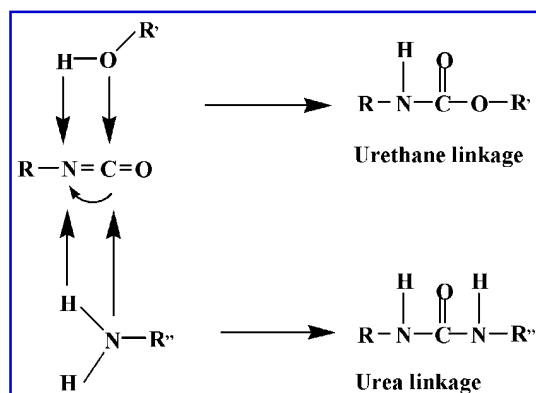


### 1.3.2 Isocyanates

Isocyanates are the important and very reactive component of polyurethane polymer. Isocyanates quickly react with compounds containing active hydrogen such as alcohols or amines and give the polymer having the urethane or urea moieties respectively. However, an isocyanate unit also reacts to another isocyanate and gives dimer or trimer through nucleophilic process or self-condensation reaction [Levchik, et al. (2004)]. Aromatic isocyanates are more reactive than aliphatic one due to presence of electron withdrawing benzene ring which creates the more electrophilic environment at isocyanate carbon for nucleophilic reaction. Reaction between primary as well as secondary alcohols with isocyanates are governs rapidly at elevated temperature (50-100°C) and no need of catalyst is required however catalyst such as dibutyltin dilaurate (DBTDL) is required in case of tertiary alcohols and phenols due to slow reaction process [Luo et al. (1997)]. Structures of some commonly used isocyanates are given below:



Aromatic isocyanate gives the better mechanical and thermal properties as compared to aliphatic one. Chemistry of formation of urethane and urea linkage is given below:



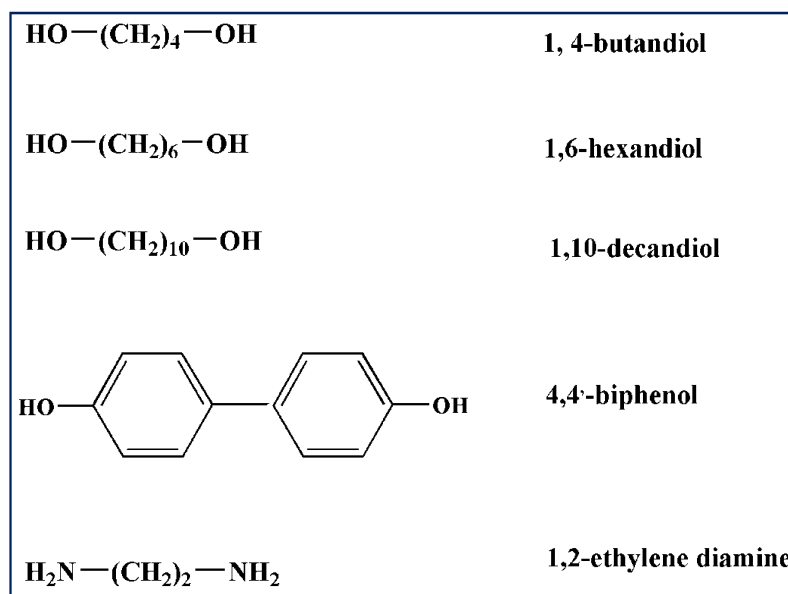
**Figure 1.3:** Urethane and urea formation

### 1.3.3 Chain extenders:

Polymer obtained after reaction of polyols with diisocyanates exhibits the poor mechanical properties as well as in low molecular weight. To enhance the mechanical behavior, molecular weight and hydrogen bond density in materials chain extenders are used. These are low molecular weight compounds containing hydroxyl or amine functionality in their chain [Cherng et al. (2013)]. Chain extenders play an important role in determining the polymer morphology and gives polymer with different microphase separation between the two (Hard segment made by urethane moieties with chain extender and soft segment from polyols) thermodynamically incompatible segments [Ping et al. (2007); Cao et al. (2007)]. Aliphatic chain extenders provide softness to the materials as compared to aromatic chain extenders. However, these chain extenders may also act as cross



linking or branching agents in presence of higher functionality. Superior strength is obtained in case of cyclic chain extenders as compared to linear chain extenders. Diamine chain extenders are very reactive in nature and quickly react to diisocyanate terminated prepolymer and produced urea linkage polymeric materials. Structure of some commonly used chain extenders are given below:



Catalyst plays a critical role in polyurethane polymerization. Generally organometallic based such as dibutyltin dilaurate is frequently used in polyurethane synthesis. However, tertiary amine is also used as a catalyst in polyurethane synthesis.

#### **1.4 Applications of Polyurethane (PU):**

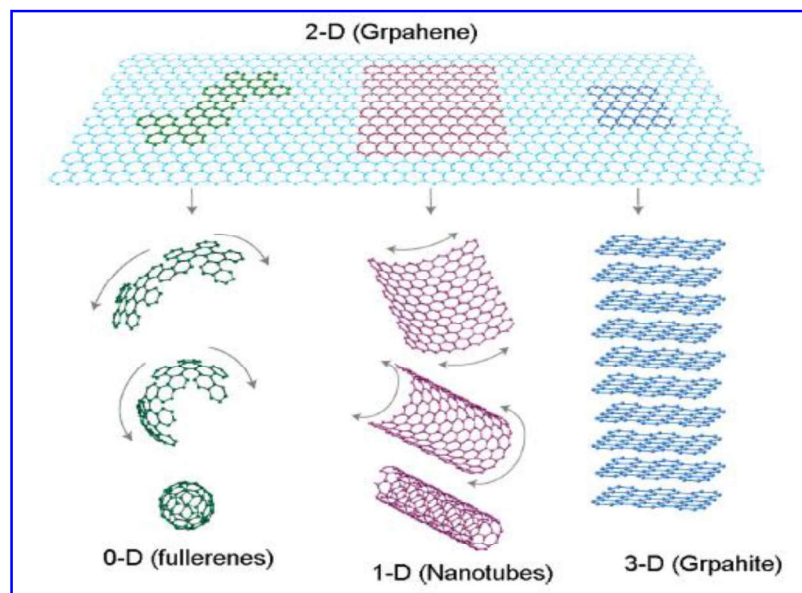
Polyurethanes are most versatile polymeric materials having a wide range of applications. Important applications of polyurethanes are given below:

- Leading utilization of polyurethanes is done as foaming material. Both flexible as well as rigid types of foam are made by polyurethane. Flexible foam is used in furniture's, automobiles and packaging. However, rigid foam is extensively used in thermal insulation and structural applications.
- Polyurethanes are used as adhesive materials for production of variety of wood products such as decorative cladding panels etc. It is also used as coating materials to protect the corrosion.
- Currently, polyurethanes are extensively used in production of show sole, automobiles sheets, tennis grips, door frames, window headers and other various applications due to its stable and durable nature.
- Polyurethanes are also used in textile industry.
- Due to the biocompatible nature of polyurethane, it can be used in biomedical arena in form of artificial heart valve, pace maker and catheters etc.
- It can also used in delivery of drugs, proteins and nucleic acids.
- High performance composites of polyurethanes made by carbon reinforcement are being frequently used in aerospace applications.

## 1.5 Graphene:

Graphene, is two dimensional single layer of carbon atom with  $sp^2$  hybridized hexagonally arranged structure discovered by Andre Geim and co-worker in 2004 at University of Manchester [Geim et al. (2007)]. Graphene contains both sigma ( $\sigma_{C-C}$ ) and pi ( $\pi$ ) bond in their structure. In graphene one of the strongest  $\sigma_{C-C}$  is present in plane whereas  $\pi$  bond orients toward the out-of-plane which make a delocalized electronic structure that is responsible for mobility of the electrons [Huang et al. (2011)]. Graphene has extraordinary electronic [Novoselov et al. (2004)], thermal [Balandin et al. (2008)], optical [Rao et al. (2009)], as well as mechanical properties [Latil et al. (2006)]. Andre Geim and co-worker were awarded by Nobel Prize in 2010 for discovery this extraordinary material. Graphene has high specific surface area ( $\sim 2630 \text{ m}^2/\text{g}$ ), thermal conductivity ( $\sim 5000 \text{ W/m/K}$ ), superior electronic conductivity ( $2 \times 10^5 \text{ cm}^2/\text{V/s}$ ) and superior mechanical properties (Younge's modulus  $\sim 1100 \text{ GPa}$ ) [Shen et al. (2012)]. There are several methods such as micromechanical exfoliation [Novoselov et al. (2004)] chemical vapor deposition [Kim et al. (2009); Li et al. (2009)] and epitaxial growth [Sutter et al. (2008); Emtsev et al. (2009)] are available which is frequently utilized in preparation of graphene with high quality for various applications. Besides these, chemical synthesis of graphene from graphite, graphene oxide or other graphite derivatives provides an alternate route for graphene synthesis with new functionality and processibility [Park et al. (2009)]. However, graphene oxide was discovered much earlier by Professor B. C. Brodie from the University of Oxford in 1859. He was taken the mixture of graphite and fuming nitric acid ( $\text{HNO}_3$ ) in presence of potassium chlorate ( $\text{KClO}_3$ ) and heated up to  $60^\circ\text{C}$  for three

to four days. Obtained material was washed and re-oxidised in above condition for four repetitions. After this a light yellow solid material was obtained and dried at 100°C. They found that obtained material is dispersible in pure or alkaline water, but not in acidic medium and describes the material as “graphic acid” with C: H: O composition of 61.04: 1.85: 37.11 and molecular formula of  $C_{2.19}H_{0.80}O_{1.00}$  [Brodie et al. (1859)]. In (1898) Staudenmaier improved the Brodie's oxidation method with addition of concentrated sulphuric acid ( $H_2SO_4$ ) to increase the acidity of the medium and addition of potassium chlorate ( $KClO_3$ ) was done in multiple steps [Staudenmaier et al. (1898)]. This method is practically better than the Brodie's oxidation method because it does not require the repetitions process. After few decades later, in (1937) Hofmann was used non-fuming nitric acid in placed of fuming nitric for synthesis of graphene oxide [Hofmann et al. (1937)]. In 1958, Hummers and Offeman was developed a new efficient method for synthesis of graphene oxide by using the potassium permagnate ( $KMnO_4$ ) and sodium nitrate ( $NaNO_3$ ) [Hummers et al. (1958) ]. Here no used of corrosive fuming nitric acid is required and more widely used for synthesis of graphene oxide. However, production of the toxic gas such as  $NO_2$ ,  $N_2O_4$ , and explosive  $ClO_2$  (in Staudenmaier-Hofmann) restrict it. Currently, a very efficient and safe method was developed by Tour group for synthesis of graphene oxide by utilizing the potassium permagnate ( $KMnO_4$ ), concentrated sulphuric acid ( $H_2SO_4$ ) and phosphoric acid ( $H_3PO_4$ ). The basic advantage of this method is that it gives the more oxidized graphene oxide without evolutions of any toxic gases [Marcano et al. (2010)]. Different allotropic form of carbon material is given in (Figure 1.4).



**Figure 1.4:** Different form of carbon allotrope [Liu et al. (2013)].

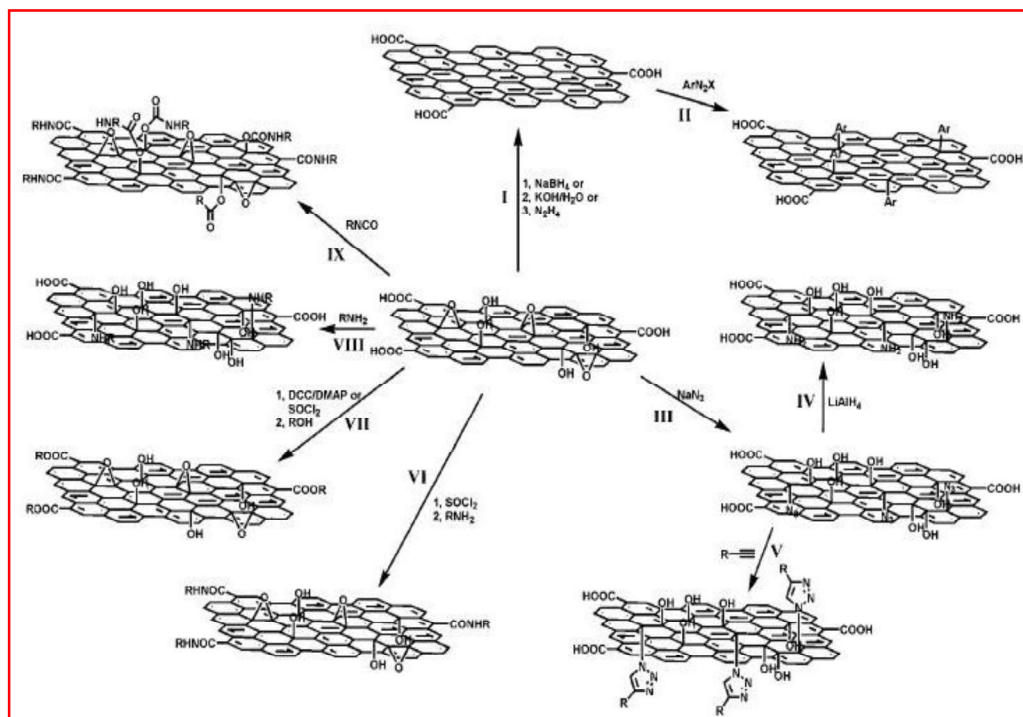
### 1.6 Functionalization of graphene and its associated chemistry:

Since pure graphene is hydrophobic in nature and it has limited solubility in common solvents [Li et al. (2008)]. Solubility nature can be modified through surface functionalization of graphene. This functionalization may be covalent C-C coupling reaction or non-covalent  $\pi$ - $\pi$  stacking in nature. Functionalization of graphene through various moieties improved the properties of graphene by forming the donor-acceptor system.

#### 1.6.1 Covalent functionalization:

Presence of several functional group such as hydroxyl (-OH), carboxylic (-COOH) and epoxy (-COC) in graphene oxide sheet arise a lot of possibilities for surface functionalization. Covalent surface functionalization of graphene oxide through various chemical reagents are given in (Figure 1.5). However presence of these oxygenated moieties disrupts the  $\pi$  conjugation which makes it in insulating nature. Moreover, graphene oxide exhibits the fluorescent properties because of

defect cause by oxidation process. Acylation is the most common approach to modified the surface at the carboxylic (-COOH) group. Graphene oxide is also modified with polyethylene glycol (PEG) for delivery of water insoluble anticancerous SN38 drug with high efficiency [Sun et al. (2008)]. Carboxylic group of graphene oxide can modified with taking the appropriate isocyanate moieties or through esterification process. Modification is also facilitated through the ring opening reaction at the epoxide centre in sheet through the suitable nucleophile [Yang et al. (2009); Wang et al. (2008)]. Amine modified graphene sheet can synthesized by the reaction of graphene oxide sheet through sodium azide followed by the reduction process. Reduction of graphene oxide is done by several reagents such as hydrazine ( $\text{NH}_2\text{NH}_2$ ), sodium borohydride ( $\text{NaBH}_4$ ) etc. to obtained the conducting graphene [Loh et al. (2010)].



**Figure 1.5:** Schematic representation of covalent modification of graphene oxide through various reagents (I) Reduction of graphene oxide into graphene through various reducing agents, (II) Surface modification of reduced graphene through diazonium reaction, (III) Modification of graphene oxide through sodium azide, (IV) Reduction of azide functionalized graphene oxide with  $\text{LiAlH}_4$  to obtained amine functionalized graphene, (V) Functionalization of azide functionalized graphene oxide through click chemistry, (VI) Modification of graphene oxide through acylation reaction, (VII) Surface functionalization of graphene oxide through esterification reaction, (VIII) Nucleophilic ring opening reaction at epoxide moieties through amine terminated molecule, (IX) Formation of amides or carbamates esters through reaction of isocyanate groups. [Loh et al. (2010)].

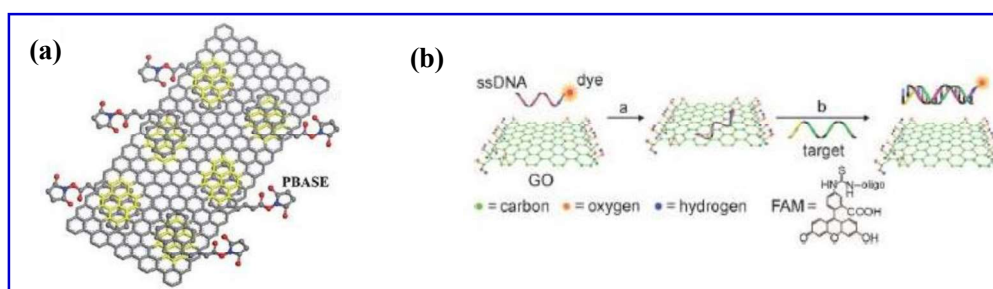
**1.6.2 Non-covalent functionalization:**

Van der Waals forces and  $\pi$ - $\pi$  stacking interaction is the key factor for non-covalent modification of graphene oxide [Xu et al. (2008); Wang et al. (2009)]. The major advantages this kind of functionalization is that it does not disrupt the  $\pi$  conjugation of graphene sheet as compared to covalent functionalization where defect is created during the modification. Both graphene oxide as well as graphene undergo the  $\pi$ - $\pi$  stacking and form different polymer nanocomposites as a result of this interaction. Mostly aromatic derivatives have the strong tendency to form the nanocomposites with graphene sheet through  $\pi$ - $\pi$  stacking interaction which also provides the stability to graphene in aqueous solution [Xu et al. (2008)]. Pyrene butanoic acid succidimide ester (PBASE) can easily absorb on graphene surface through  $\pi$ - $\pi$  stacking interaction and gives stable nanocomposites. Su et al. (2009) were prepared the pyrene-1-sulfonic acid sodium salt (PyS) / graphene and disodium salt of 3,4,9,10- perylenetetracarboxylic diimide bisbenzenesulfonic acid (PDI) / graphene composite through  $\pi$ - $\pi$  stacking interaction and observed their conductivity behavior. PDI-based composites exhibit the superior conductivity (13.9 S/cm) as compared to reduced graphene (3.0 S/cm). Whereas, approximately 30% decreased in conductivity was observed in PyS / graphene composites (1.9 S/cm). However, improvement in overall power conversion efficiency (PCE) (0.78 $\rightarrow$ 1.12%) was observed by using PyS / graphene composites as anodes in solar cells as compared to reduced graphene [Su et al. (2009)].

Lu et al. (2009) were show  $\pi$ - $\pi$  stacking interaction and fluorescence quenching effect of graphene oxide with nucleobases (single stand DNA) and aromatic dye. Non-covalent interaction between GO and base in presence of dye is



given in (Figure 1.6). Graphene oxide strongly binds the nucleobases and quenched the fluorescence property of aromatic dye. In presence of complementary target nucleobase, disturbing in the interaction between graphene oxide and dye-labeled DNA was occurred and due to this interaction releasing of dye-labeled DNA was occurred from graphene oxide which causes the restoration of aromatic dye fluorescence [Lu et al. (2009)].



**Figure 1.6:** Non covalent interaction between (a) Pyrene butanoic acid succidymidyl ester (PBASE) and graphene sheet through  $\pi$ - $\pi$  stacking interaction [Xu et al. (2008)] and (b) schematic representation of the target induced fluorescence change of aromatic dye labeled ssDNA with graphene oxide. Here FAM is the fluorescein-based fluorescent dye. [Lu et al. (2009)].

### 1.7 Nanocomposites:

Nanocomposites or nanohybrids are new category of material that contains two or more synthesized materials at least one dimension of material is in the nanometer scale. Nanocomposites are synthesized by dispersing the filler in suitable matrix. There are various types of fillers such as metal and its oxides [Arbatti et al. (2007)], layered silicates (nanoclay) [Lee et al. (2006)] and carbon in different form likes carbon fullerenes, carbon nanotubes (CNTs), graphene [Wang et al. (2011)] and layered double hydroxides (LDH) [Wang et al. (2012)] are frequently used in nanocomposites fields. Depending upon their structure

carbon allotropes term as fullerenes (0-D), carbon nanotubes / nanoribbons (1-D), graphene (2-D) and graphite (3-D). Graphene has higher surface area which provides the better platform for greater interaction between matrix and filler leading to improvement of various properties. Nanocomposites exhibit superior structural, mechanical, and thermal properties as compared to pure polymer. Depending upon the dispersion nature of graphene and interaction nanocomposites can be flocculated, intercalated and exfoliated in nature.

### **1.8 Preparation of nanocomposites:**

There are various methods available which is used in nanocomposites synthesis. Their advantage and drawbacks are given below:

#### **1.8.1 Melt blending method:**

This method required equipment like extruder which generates high shear rate at elevated temperature. Filler is incorporated in molten polymer and shear it with higher rate. No additional solvent is required in this method which is the major advantage of this method. However, fine dispersion may not be achieved and only small concentration can be used [Moniruzzaman et al. (2006)]. Degradation of polymer chain may be occurred at high shear rate at higher temperature.

#### **1.8.2 Solution casting method:**

This is most common method for composites preparation. Dispersion of filler is done in suitable solvent through mechanical stirring or sonication followed by the dissolution of polymer in same solvent. Then dispersed filler is mixed with

polymer solution at suitable temperature. Composite films are obtained by casting the mixture.

### **1.8.3 In-situ method:**

In-situ method provides the uniform dispersion of filler in polymer matrix. Here, fillers are dispersed in low viscous monomer, generally in presence of solvent followed by incorporation of chain extender or hardener for polymerization at suitable temperature. Significant improvements in the properties are occurred due to the homogenous dispersion are achieved which facilitates the greater interaction.

### **1.8.4 Latex technique:**

This technique is more suitable for those polymers which have the capacity to form emulsion or prepared through emulsion polymerization technique. Surfactant is used for stabilization of aqueous dispersion of filler followed by the incorporation of these dispersed filler into polymer latex. Nanocomposite is obtained after freeze-drying the mixture followed by melt processing. No requirement of organic solvent, easy processibility and better dispersion of filler in viscous medium is advantage of this method [Grossiord et al. (2006)].

## **1.9 Types of Nanocomposites:**

Depending upon the interaction between the polymer matrixes with incorporated nanofiller and processing technique naocomposites may have three kinds of the morphology. These are as follows:

### **1.9.1 Flocculated nanocomposites:**

This kind of nanocomposites is formed when very less polymer chains are inserting inside the gallery of the nanofiller. Moreover, due to the more interaction at edge on increase in its lateral dimension is observed as compared to pure nanofiller. No significant improvements in the properties of nanocomposites are achieved as compared to native polymer.

### **1.9.2 Intercalated nanocomposites:**

Intercalated nanocomposite is formed when the polymer chains are inserted in a regular fashion between the galleries of the nanofillers. However, nanofiller are still maintained their stacks patterns even after the intercalation of polymer chains due to secondary interaction between filler. An intercalated nanocomposite is generally obtained through dispersion of the nanofiller in polymer matrix at the last step of the polymerization process. Moderate improvements in the properties of nanocomposites were observed as compared to pure polymer.

### **1.9.3 Exfoliated nanocomposites:**

In exfoliated nanocomposite stacking pattern of filler is disappeared into individual layer by the inserting of the polymeric chain in their intergallery space. This type of nanocomposite is formed by incorporating the filler in early step of in-situ polymerization process. Due to the better dispersion and interaction of filler into polymer matrix significant improvement in properties of nanocomposites is observed as compared to other kinds (flocculated and intercalated) of nanocomposites.

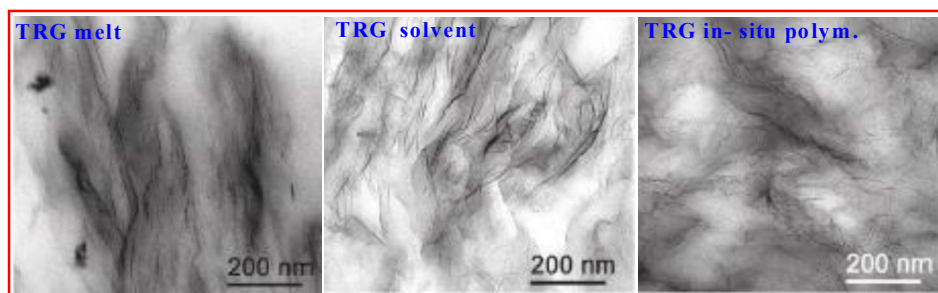
## **1.10 Literature review:**

### **1.10.1 Dispersion and structure:**

Properties of polymer are highly influence by the dispersion nature of filler in matrix. Dispersion of filler in polymer matrix is observed through transition electron microscope (TEM). TEM image of polyurethane / graphene nanocomposites is given in (Figure 1.7). Kim et al. (2010) were synthesized the polyurethane / graphene nanocomposites through different (melt compounding, solvent blending and in-situ polymerization) process and observed the dispersion nature of graphene in polyurethane matrix. More stacked type distribution of thermally reduced graphene was observed in melt compounding process as compared to other processing techniques. Better dispersion was achieved in solvent blending and in-situ polymerization technique. However, nanocomposites obtained through solvent blending process exhibits more better dispersion as compared to in-situ polymerization where graphene was added after the formation of viscous prepolymer which restrict the homogenous distribution [Kim et al. (2010)].

Homogenous dispersion of graphene in polyurethane matrix was achieved through in-situ polymerization process. Wang et al. (2011) were prepared the polyurethane / graphene nanocomposites using 4,4'-Diphenylmethane diisocyanate (MDI) and poly(tetramethylene glycol) (PTMG, molecular weight: 2000). Nanocomposites exhibit the fine dispersion of graphene and as the content of graphene increased some stacked structure is also obtained. However, dimension of these stacked structures are still in nanometer range. Fine dispersion leads to improvement in various properties of polymer such thermal, structure and

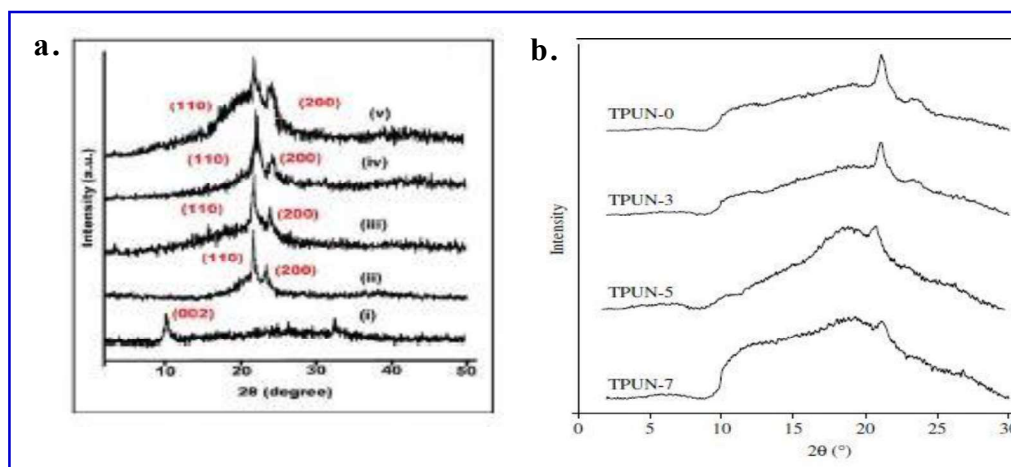
mechanical through greater interaction between polymer matrix and graphene which have high surface area [Wang et al. (2011)].



**Figure 1.7:** Transmission electron micrographs of TPU with 3 wt% of reduced graphene in melt-blended, solvent mixing and in-situ polymerization [Kim et al. (2010)].

Dispersion of nanofillers into polymer matrix and their interfacial interaction affect the properties of polymeric material. Thakur et al. (2013) has synthesized castor oil-modified hyperbranched polyurethane (HPU) / graphene oxide (GO) nanocomposites having graphene oxide in different weight ratio. XRD pattern of polyurethane and its nanocomposites is given in (Figure 1.8). Graphene oxide exhibits two diffraction peaks at  $9.84^{\circ}$  and  $43^{\circ}$  for the (002) and (001) planes respectively in X-ray diffraction measurement [Geim et al. (2007)]. Pure polyurethane and nanocomposites exhibit two diffraction peaks at  $21.1^{\circ}$  ((110) plane  $d$  spacing =  $4.19\text{\AA}$ ) and  $23.4^{\circ}$  (200)  $d$  spacing =  $3.81\text{\AA}$ ) which are originated polycaprolactone moieties [Karak et al. (2009)]. Enhancement in the intensity of these diffraction peaks is observed in nanocomposites due to strong nucleating effect of graphene oxide and higher interfacial interaction. Shifting of these peaks towards higher angle in nanocomposites as compared to pure polymer indicates formation of more crystalline structure is occurred [Thakur et al. (2013)].

Lowering in the intensity of these peaks  $21.1^{\circ}$  and  $23.3^{\circ}$  is also observed in polyurethane / graphene nanocomposites. Pure polymer exhibits sharp peak at  $23.3^{\circ}$  whereas intensity of these peak get suppressed in nanocomposites indicating the inhibition in crystallinity is occurred in presence of graphene in polymer matrix [Nguyen et al. (2009)]. Yu et al. (2012) was prepared polyurethane / graphene nanocomposite by using the modified graphene oxide with 4, 4' - Diphenylmethane diisocyanate (MDI) and hydroxyethyl acrylate and cured with UV-light. Pure polymer exhibits a broad X-ray diffraction peak at  $19.4^{\circ}$  indicating the amorphous nature of polymer matrix. No significant change in X-ray diffraction peak is observed in nanocomposites [Yu et al. (2012)].



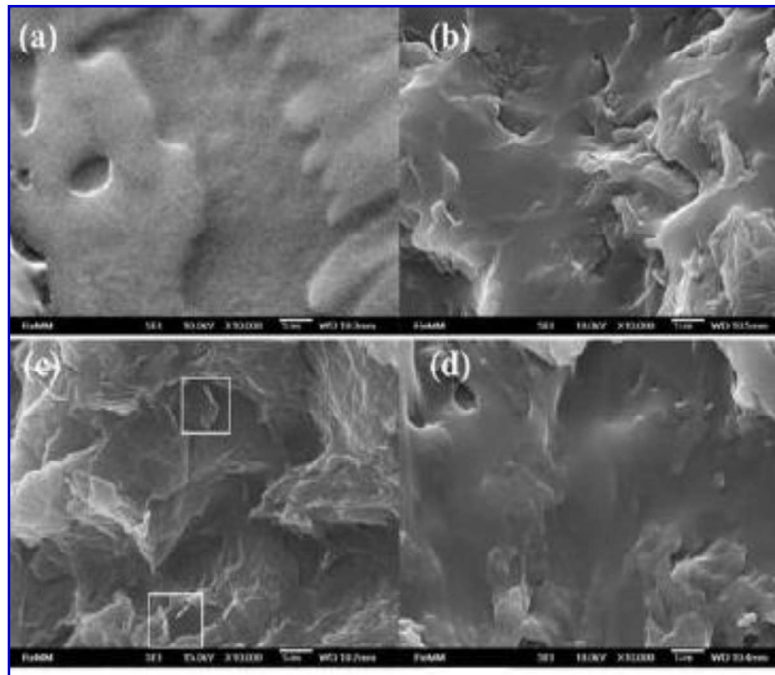
**Figure 1.8:** XRD patterns of (i) GO, (ii) HPU, (iii) HPU-GO 0.5, (iv) HPU-GO 1 and (v) HPU-GO 2 [Thakur et al. (2013)] and (b') XRD patterns of TPU and its indicated nanocomposites where number indicates the weight% of functionalized graphene in polyurethane matrix [Nguyen et al. (2009)].

**1.10.2 Morphology:**

Surface morphology of polyurethanes is highly influenced by the modification nature and content of graphene as well as the interface interaction of nanofiller to the polymer matrix [Zhang et al. (2014)]. Surface morphology of the cryogenically fractured polyurethane /functionalized graphene (TPU/FGS) has been given in (Figure 1.9). Fractured surface of pure polyurethane exhibits the smooth morphology whereas nanocomposites show the rough surface in SEM image. As the content of graphene was increased projection of functionalized graphene sheet oriented toward outside from the matrix indicating the weak interfacial interaction between the graphene sheet and polymer matrix [Choi et al. (2011)]. Ding, et al. (2012) has synthesized the waterborne polyurethane (WPU) graphene nanocomposites and examines the effect of the graphene on surface morphology of polyurethane. Pure polyurethane show the smooth surface morphology whereas, nanocomposites with lower contents of graphene (1 and 2wt %) show the scattered island morphology whereas, as the content of graphene get increased (4wt %) network structure is observed in nanocomposites [Ding et al. (2012)]. Comparative studies of surface morphology of polyurethane / functionalized graphene and polyurethane / graphene nanocomposites were done by Yadav et al. (2013) through SEM measurement. Functionalization of graphene oxide was done by 4-aminophenethyl alcohol through diazotization and coupling reaction. Nanocomposites having graphene in polymer matrix show the outside projection of graphene sheets from fracture surface indicating the weak interaction between matrix and graphene sheet whereas, dense and inside projected morphology is observed in nanocomposites having the functionalized graphene indicating the



strong interaction between polymer matrix and functionalized graphene sheet. However, some aggregation was observed in nanocomposites having graphene content of 2wt % [Yadav et al. (2013)].



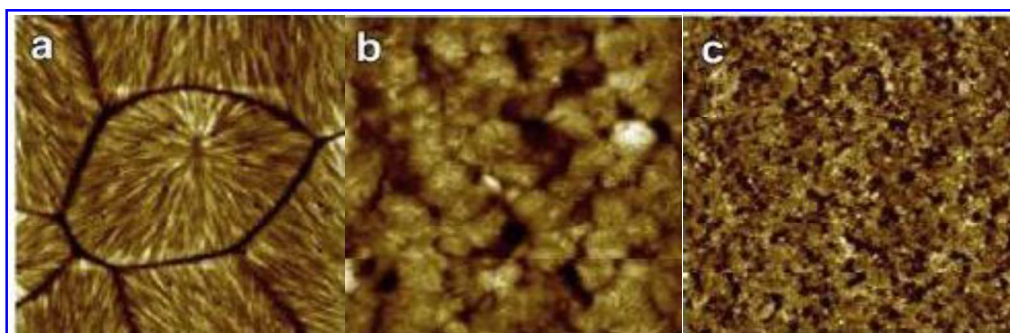
**Figure 1.9:** SEM images of cryogenically fractured TPU/FGS nanocomposites: (a) TPU, (b) 1.0G1, (c) 3.0G1, and (d) 3.0G2 (here numerical value prior to G indicates the wt.% of graphene and before G indicates the different oxygen content nature of graphene oxide) [Choi et al. (2011)].

Yan et al. (2012) synthesized the rigid polyurethane foam (RPUF) using the graphene nanofiller and compared the nucleating effect of graphene with same weight content of carbon nanotubes (CNTs). Pure polyurethane foam exhibits the cell diameter of  $165 \mu\text{m}$  with cell density of  $3.6 \times 10^5 \text{ cells cm}^{-3}$ . Decrease in the cell diameter ( $145 \mu\text{m}$ ) and increase in cell density ( $5.3 \times 10^5 \text{ cells cm}^{-3}$ ) was observed in addition of 0.3 wt % of two dimensional graphene in polymer matrix whereas with same weight loading of carbon nanotubes (CNTs) gives the cells

with diameter of  $161 \mu\text{m}$  and  $3.8 \times 10^5 \text{ cells cm}^{-3}$  cell density. This result indicates that graphene shows a moderate heterogeneous nucleating affect in foaming process whereas this effect is negligible in CNTs [Yan et al. (2012)].

Bian et al. (2013) were synthesized polyurethane graphene nanocomposites in varying content of microwave exfoliated graphene oxide (MEGO) through melt compounding method followed by the injection molding and study its effect on surface morphology of polyurethane through AFM. Nanocomposites having the lower content of exfoliated graphene exhibit the sheet thickness approximately 40 nm in cross-section measurement, whereas pure microwave exfoliated graphene oxide (MEGO) show the sheet thickness of approximately 50nm. This is due to the shearing force during melt compounding. Moreover, at higher graphene content (8 wt %.) agglomeration was clearly observed in AFM measurement with sheet thickness of approximately 70 nm which is higher than the pure graphene oxide sheet as well as the nanocomposites having the low content of graphene. This is due to the restacking of the exfoliated graphene oxide sheet at higher concentration leading to the decrease its properties especially mechanical behavior [Bian et al. (2013)]. Effect of dispersed graphene on surface morphology of polyurethane was studies by Krol et al. (2015) through Atomic Force Measurement (AFM) technique. No significance change in surface roughness was observed in nanocomposites as compared to pure polyurethane. Surface irregularity in materials did not exceed the several ten of nanometers range. Appearance of the scattered dense structure in nanocomposites is due to graphene sheets with dimension of about  $1\mu\text{m}$ . Hard segments of polyurethane give the granular types of morphology in AFM measurement [Krol et al. (2015)]. Landa et

al. (2014) was synthesized the polyurethane nanocomposites using multiwall carbon nanotubes (MWCNTs) and graphene as a filler and evaluated its effect on the surface morphology of polyurethane through AFM measurement. AFM image of pure polyurethane and its nanocomposites is given in (Figure 1.10). It was observed that pure polyurethane exhibits the spherulites morphology whereas spherical structure is observed in nanocomposites. This is probably due to the reduction of the crystal size by the nucleating affect of the nanofiller. This nucleating affect is more prone in composite having the carbon nanotubes as filler [Landa et al. (2014)].



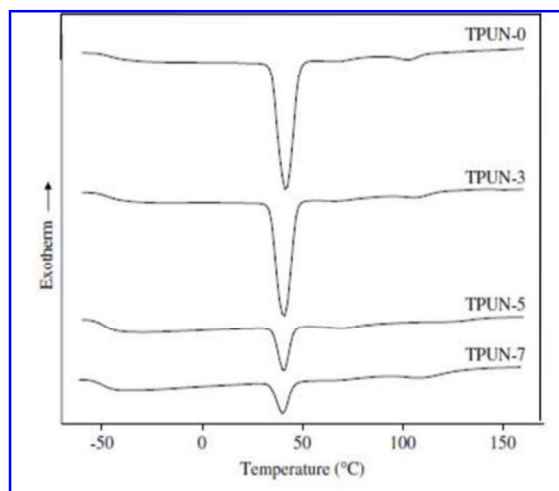
**Figure 1.10:** AFM image of (a) pure polyurethane ( $50\mu\text{m}\times 50\mu\text{m}$ ), and nanocomposites (b) 2 wt% of MWCNTs and (c) 2 wt% of graphene. (Image is taken after the crystallization) [Landa et al. (2014)].

### **1.10.3 Thermal behavior:**

Melting behavior of polymer is highly influence by the dispersion nature and contents of nanofiller in matrix. Lee et al. (2009) were synthesized polyurethane / graphene nanocomposite using two different types of diols (polycaprolactone and polytetramethyle glycol) in presence of isophorone diisocyanate (IPDI).

Nanocomposites were prepared through polycaprolactone as a diol is term as WPUCL (waterborne polyurethane with polycaprolactone diol) and polytetramethylene glycol based composites is WPUMG (waterborne polyurethane with polytetramethylene glycol). Number indicates contain of graphene in polyurethane matrix. Nanocomposites show two melting temperature in lower region associated with the soft segment of polymer. An enhancement in heat of fusion ( $\Delta H_m$ ) is observed in nanocomposites as compared to pure polyurethane indicating induced crystallization in nanocomposites in soft segment of polyurethane chains. However, decrease in heat of fusion ( $\Delta H_m$ ) of hard segment is observed as the content of graphene increased in polymer matrix indicating the suppression in crystallinity of hard segments was occurred in presence of graphene [Lee et al. (2009)]. Change in the melting behaviour of polyurethane / graphene nanocomposites were observed when hexamethylene diisocyanates (HMDI) is used in place of isophorone diisocyanate (IPDI). DSC thermograms of polyurethane / graphene nanocomposites are given in (Figure 1.11). Pure polyurethane exhibits the two melting temperature and a glass transition temperature ( $T_g$ ). Endothermic peak in lower temperature region is originated by the soft segments of polymer whereas hard segments appeared at higher temperature region. Decrease in heat of fusion of soft segments ( $\Delta H_{ms}$ ) is observed as the content of graphene get increased indicating the inhibition in the crystallinity of soft segment was occurred in presence of graphene. Inhibition in crystallinity of soft segment through graphene is responsible for decreasing the glass transition temperature ( $T_g$ ). No significant change in heat of fusion of hard segments ( $\Delta H_{mh}$ ) is observed in nanocomposites as compared to pure polymer

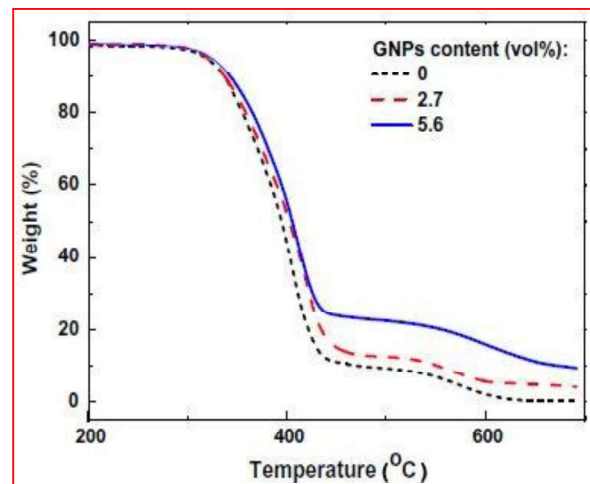
suggesting the dispersion graphene is predominantly occurred in soft segment zones of polymer. Enhancement in melting behaviour of hard segments at higher content of graphene as compared to pure polyurethane is due to the inhibition in mobility of hard segments at melt condition in presence of graphene [Nguyen et al. (2009)].



**Figure 1.11:** DSC thermograms of polyurethane and its indicated nanocomposites [Nguyen et al. (2009)].

Degradation behavior of polymeric material is highly depending upon the content of nanofiller as well as the distribution nature. TGA thermogram of pure polyurethane and its nanocomposites is given in (Figure 1.12). Pure polymer and nanocomposites exhibit the more than one degradation temperature. The first stage degradation is occurred in range of  $\sim 300$  to  $450^{\circ}\text{C}$  for hard segment of polymer chain. Second stage degradation is occurred in range of  $500$  -  $700^{\circ}\text{C}$ . At higher temperature region soft segment of the polymeric chain such as C-O and C-C moieties are degrades indicating the hard segment of polymer chain is more susceptible towards the thermal degradation than soft segment. TGA thermogram of TPU/GNS nanocomposites clearly indicates the enhancement in thermal

stability is occurred as compared to pure polyurethane due to the barrier effect of the two dimensional graphene sheets in matrix which inhibits the escape of volatile degradation product and char foramation [Quan et al. (2009); Kaur et al. (2015)]. However, one stage of degradation in polyurethane and its graphene nanocomposite is also observed by the cross-linking of hard and soft segments to each other [Nawaj et al. (2012); Hsiao et al. (2013)]. Decrease in the thermal stability in nanocomposites is also observed after certain content of graphene in matrix due to the agglomeration of graphene sheet [Luo et al. (2016)].



**Figure 1.12:** TGA thermograms of polyurethane and its nanocomposites [Quan et al. (2009)].

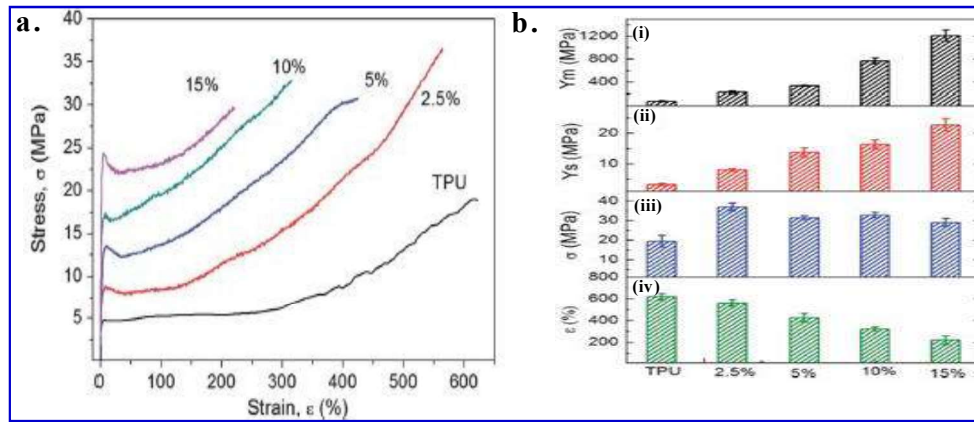
#### 1.10.4 Mechanical behavior:

Incorporation of nanofiller into polymer matrix leads to improvement in the physical performance of composite materials due to the homogeneous dispersion as well as strong interfacial interaction. Improvement in the mechanical properties is observed in nanocomposites as compared to pure polyurethane. Nanocomposites having the 4wt % of graphene oxide exhibits ~7 times greater Young's modulus

as compared to pure polyurethane. This enhancement is due to the better interaction between polymer matrix and graphene oxide which facilitates the load transfer from polymer to filler. Approximately ~50% enhancement in toughness was observed in nanocomposites having 1wt % of graphene oxide in polymer matrix. This is due to the orientation of graphene oxide sheets towards the applied force and suppresses the crack propagation process [Cai et al. (2012)]. Enhancement in the mechanical properties of polyurethane in presence of reduced graphene oxide is also reported by the Yousefi et al. (2013). This enhancement is due the well dispersed and high degree of orientation of reduced graphene oxide towards the applied force which facilitated the load transfer from polymer matrix to graphene sheet. Approximately 21folds and 9-folds increase in tensile modulus and strength was occurred in nanocomposites as compared to pure polymer at 3 wt% of reduced graphene oxide respectively [Yousefi et al. (2013)].

Stress-Strain curve of pure polymer and nanocomposites is given in (Figure 1.13). Nanocomposites having the hyperbranched aromatic polyamide functionalized graphene in polymer matrix show the superior mechanical properties as compared to pure polymer. This enhancement is due to the uniform dispersion of hyperbranched aromatic polyamide functionalized graphene sheet in thermoplastic polyurethane (TPU) matrix and good compatibility with polymer matrix through hydrogen bonds which facilitated the load transfer efficiency from polymer matrix to graphene sheets. Addition of 2.5 wt% of functionalized graphene in polyurethane matrix significance enhancement in tensile strength (18MPa →37 MPa) was occurred as compared to pure polymer. However, slightly

decrease in strain at break (610% to 560%) was observed in nanocomposites as compared to pure polymer [Wu et al. (2012)].

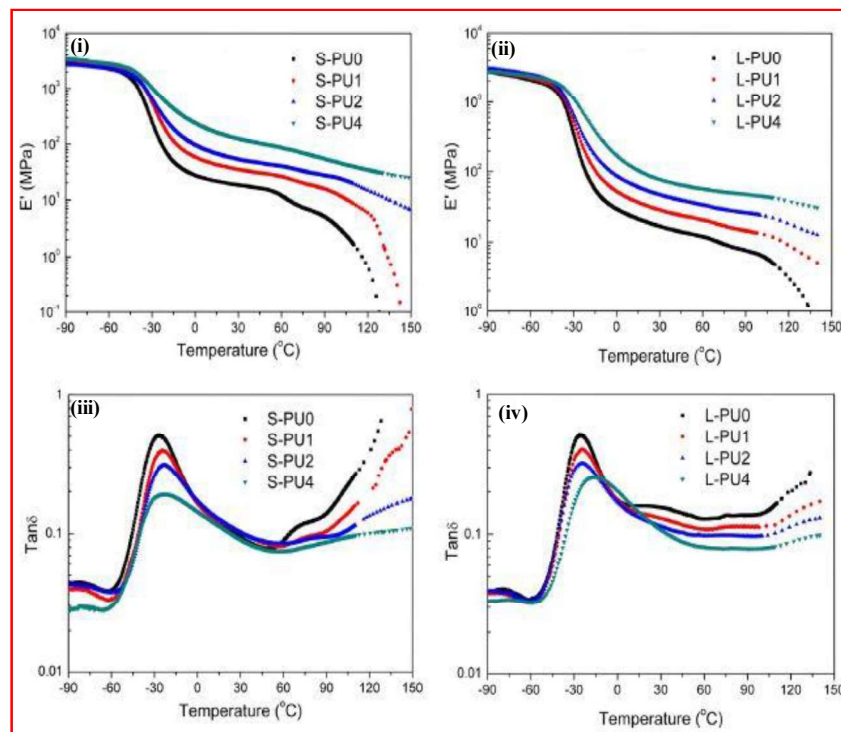


**Figure 1.13:** Mechanical behavior of polyurethane and its nanocomposites **(a)** Stress-strain curve of pure TPU and its nanocomposites and **(b)** bar diagram of mechanical behavior of TPU composites as a function of polyamide functionalized graphene **(i)** Young's modulus **(ii)** tensile yield strength **(iii)** ultimate tensile strength and **(iv)** strain at break [Wu et al. (2012)].

Storage modulus of polyurethane is highly affected by the length of hard segment as well as nature of nanofillers. Pokharel et al. (2015) was synthesized polyurethane graphene nanocomposites with varying length of hard segments. Mechanical behavior of pure polyurethane with small and large hard segment and its nanocomposite in melt condition is given in (Figure 1.14). Nanocomposites exhibit higher storage modulus as compared to pure polymer and this enhancement is 6.9 fold higher in nanocomposite containing 4 wt% of graphene oxide. However, it was observed that polymer having larger length of hard segments show lesser storage modulus than short segments due to lesser interaction between graphene oxide and hard segment by different polymerization process. Shifting in transition peak of damping factor ( $\tan\delta$ ) towards higher temperature region in nanocomposites indicate the restriction in movement is



occurred in polymer chain in presence of graphene oxide through the greater interaction [Pokharel et al. (2015)]. Wang et al. (2013) were synthesized the functionalized graphene polyurethane nanocomposites and evaluates the effect of functionalized graphene on polyurethane properties. Graphene oxide was modified with 3-Methacryloxypropyl trimethoxysilane (MPTES). Enhancement in the storage modulus is observed in nanocomposites as compared to pure polyurethane due to the homogenous dispersion of functionalized graphene which facilitates the higher interaction between polymer matrix and functionalized graphene. This interaction leads the shifting in transition peak of damping factor ( $\tan\delta$ ) towards the higher temperature region [Wang et al. (2013)].



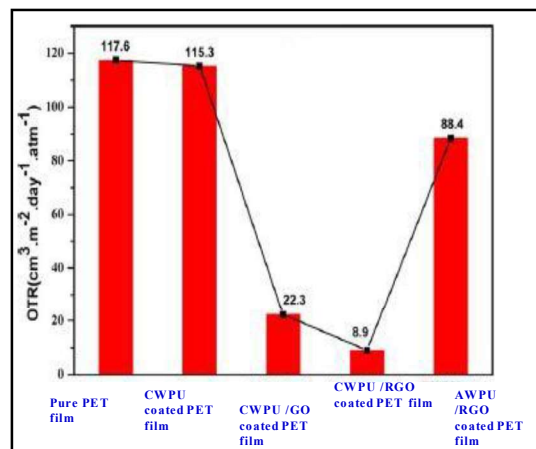
**Figure 1.14:** Mechanical behavior of pure polyurethane with small and large hard segment and its nanocomposite in melt condition. **(i and iii)** storage and loss modulus pure polymer with small hard segment and its nanocomposites and **(ii and iv)** storage and loss modulus of polymer with large hard segment and its indicated nanocomposites. (numerical value indicates the wt.% of graphene in matrix) [Pokharel et al. (2015)].

### **1.10.5 Gas barrier and Conductivity:**

Gas barrier behavior and conductivity of polymer is highly influence by the nature and content of the nanofiller in matrix. Gavgani et al. (2014) were synthesized polyurethane reduced graphene nanocomposites and monitor the effect of graphene for oxygen diffusion. Approximately 90% decrease in oxygen permeability was observed in nanocomposites having 2 wt% reduced graphene oxide as compared to pure polyurethane. This is due to exfoliated reduced graphene oxide creates the tortuous path in matrix which inhibits the molecular oxygen diffusion resulting the decrease in the permeability [Gavgani et al. (2014)]. Kim et al. (2010) were prepared polyurethane graphene nanocomposite through three (melt blending, solvent casting and in-situ polymerization) different routes and studies their comparative performances. Approximately 90% decrease in Nitrogen permeability was occurred in 3 wt% (1.6 vol%) of isocyanate modified graphene (Phenyl or Acetylphenyl isocyanate). This decrease in gas permeability is due to the presence of impermeable graphene sheets which restrict the flow of the gas through matrix. However, Nanocomposites were synthesized through melt blending and solvent casting show superior reduction in nitrogen gas permeability as compared to in-situ polymerization [Kim et al. (2010)].

Wu et al. (2016) were prepared cationic waterborne polyurethane graphene nanocomposites (CWPU/GO) through the latex polymerization process. Gas barrier behavior of pure polyurethane and its graphene nanocomposites is given in (Figure 1.15) in form of bar diagram. Pure cationic waterborne polyurethane and poly (ethylene terephthalate, PET) show the poor oxygen barrier property.

However, enhancement in gas barrier property is observed in CWPU/GO-coated PET film. The oxygen transmission rate (OTR) of CWPU coated PET film was  $115.3 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1}$  whereas, OTR of CWPU/GO coated PET film was  $22.3 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1}$ . This increase in gas barrier is due to presence of impermeable GO in polymer matrix which increase the path tortuosity and decrease the gas permeability. Furthermore nanocomposites having thermally reduced graphene in polymer matrix exhibits better barrier response as compared to nanocomposites were prepared through graphene oxide. The oxygen transmission rate (OTR) of CWPU/RGO-coated PET film was  $8.9 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1}$ . This difference in gas barrier is arising due to more defect nature of graphene oxide as compared to reduced graphene as well as fine dispersion of reduced graphene in polymer matrix [Wu et al. (2016)].

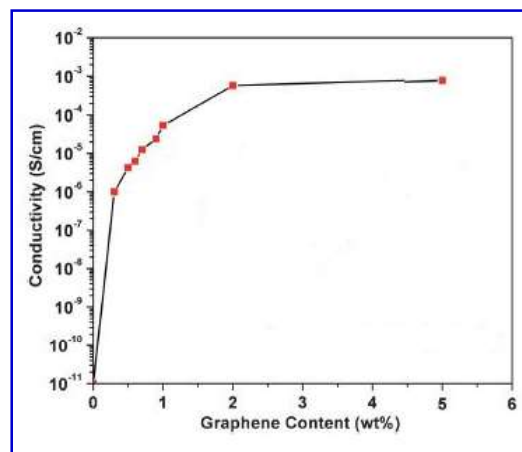


**Figure 1.15:** The oxygen transmission rate for PET films coated with different types of samples [Wu et al. (2016)].

Pure graphene has excellent electrical conducting property. Improvement in electrical conductivity was observed through incorporation of graphene sheets in the polymer matrix. Pure CWPU and CWPU/GO were showed the electrical conductivity in range of  $5.66 \text{ E-11 S/m}$  and  $5.76 \text{ E-13 S/m}$  respectively indicating

the insulating nature of materials. However, CWPU/RGO nanocomposites exhibit electrical conductivity in range of 0.28 S/m. This difference in electrical behavior was due to defect nature of graphene oxide which lost its conducting property whereas reduced graphene oxide has a conducting network structure [Wu et al. (2016)].

Yousefi et al. (2012) synthesized reduced graphene oxide polyurethane nanocomposites and evaluated the effect of reduced graphene on the conductivity of polyurethane. Electrical conductivity of polyurethane–reduced graphene oxide as a function of graphene content is given in (Figure 1.16). Nanocomposite having 0.5 wt% reduced graphene exhibited 7 times higher conductivity as compared to pure polyurethane ( $\sim 10^{-11}$  S/cm). This is due to the homogeneous dispersion of conducting graphene in the polymer matrix, which facilitates the conductivity. A steady increase in conductivity was observed by increasing the content of reduced graphene. Furthermore, after a certain concentration of reduced graphene, no enhancement in the conductivity occurred due to the saturation of graphene in the matrix [Yousefi et al. (2012)].



**Figure 1.16:** Electrical conductivity of PU/rGO composites as a function of graphene content [Yousefi et al. (2012)].

### **1.10.6 Biological studies:**

For biological application developed material should be in biocompatible nature, not cause any immune response as well as supports to the growing cells. Several polymers such as chitosan [Li et al. (2012)], Polylactide acid (PLA) [Montjovent et al. (2008)], Polycaprolactone (PCL) [Mondrinos et al. (2006)], Poly(lactic-co-glycolic acid) (PLGA) [Buschmann et al. (2012)] and Polyurethane (PU) [Hofmann et al. (2008)] are frequently used in biological field. Out of these polyurethanes are extensively used in medical applications due to its biocompatibility and flexible nature [Mi et al. (2013)]. However, very few reports are available to use of polyurethane graphene nanocomposites in biological arena. Various nanomaterials such as single / multiwall carbon nanotubes and graphene with superior physical and chemical properties are extensively used in biomedical applications for drug delivery system [Kim et al. (2008)], imaging probe [Kim et al. (2009)], diagnostic device [Xia et al. (2008)], biosensor [Yang et al. (2010)], biochip [Chen et al. (2009)] and implantable medical devices [Liu et al. (2007)]. Surface wettability, stiffness, dimensions, chemical composition and topographical properties of materials can affect the cell adhesion and cell growth [Ryoo et al. (2010)].

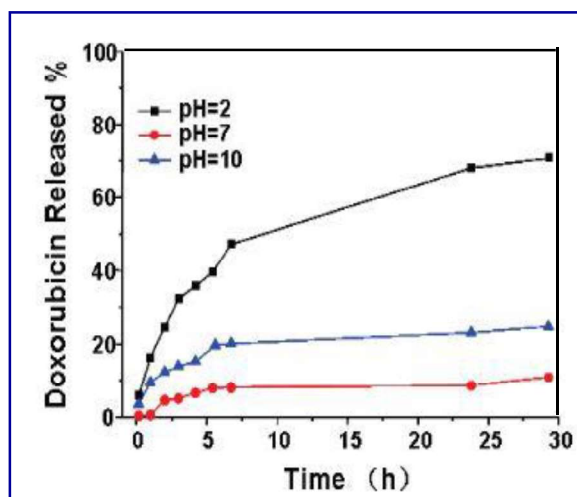
Nayak et al. (2011) were observed the effect of graphene on human mesenchymal stem cells (hMSCs) in term of cell viability, morphology and differentiation. They were observed that cell growth is not hampered in presence of graphene. Cell morphology was also not influence by graphene and cells were maintained their normal shape indicating the biocompatible nature. Graphene also induced the osteogenic differentiation of the stem stems. Presence of

immunofluorescent stain (OCN for Osteocalcin) only in graphene coated surface in osteogenic medium clearly indicates the differentiation of stem cells. This result is also supported by the measurement of calcium deposition through Alizarin red stain. Calcium deposition is occurred through the formation of bone nodule. Surface coated with graphene exhibits the higher extent of calcium deposition in absence of growth factor (BMP-2) indicating the differentiating nature of graphene. Whereas stem cells were growth on normal medium did not show any calcium deposition within the 15 days of time frame of experiment [Nayak et al. (2011)]. Since graphene oxide have various functional groups such as hydroxyl (-OH), carboxylic (-COOH) and epoxy's (-COC) and higher surface area which facilitates the conjugation with various system via chemically or physically adsorption. Liu et al. (2008) were modified loaded water insoluble anticancerous drug (SN38) through physically adsorption ( $\pi$ -  $\pi$  stacking) onto amine modified graphene oxide and evaluates its efficiency on HCT-116 cells. Efficiency of loaded drug was much higher as compared to other water soluble anticancerous drug Camptothecin (CPT) even in lower concentration range [Liu et al. (2008)].

#### **1.10.6.1 Drug Delivery:**

Graphene oxide or its derivatives is frequently used in drug delivery area due to its high surface area and functionality which facilitates the adsorption of different kinds of drug. Yang et al. (2008) were synthesized the Graphene Oxide-doxorubicin hydrochloride (GO-DXR) nanocomposites and studies the release of loaded drug at different pH. Release of the loaded drug is given in (Figure 1.17). Strong  $\pi$ -  $\pi$  stacking interaction and hydrogen bonding between graphene oxide

and drug is the key factor for the loading of doxorubicin hydrochloride. Slow release was observed in neutral condition (pH=7) and only 11% of loaded drug was released through the nanocomposites after 30h. This is due to the strong hydrogen bonding interaction at neutral pH between drug and graphene oxide surface resulting the insufficient release. However, 25% and 71% release of loaded drug was observed through nanocomposites at pH 10 and 2 after 30h respectively. Partial dissociation of the hydrogen bonding interaction at acidic and basic pH is responsible for enhancement in release rate from nanocomposites. The release amount of loaded drug in acidic medium was much higher as compared to basic medium [Yang et al. (2008)].



**Figure 1.17:** The release profile of dexamethasone loaded drug on GO at different pH values [Yang et al. (2008)].

Feng et al. (2011) were used the polyethyleneimine (PEI) modified graphene oxide (PEI-GO) for the delivery of gene. Plasmid DNA adsorbed to the modified surface of graphene oxide through electrostatic interaction. They were observed that transfection efficiency was higher in PEI-GO system as compared to pure

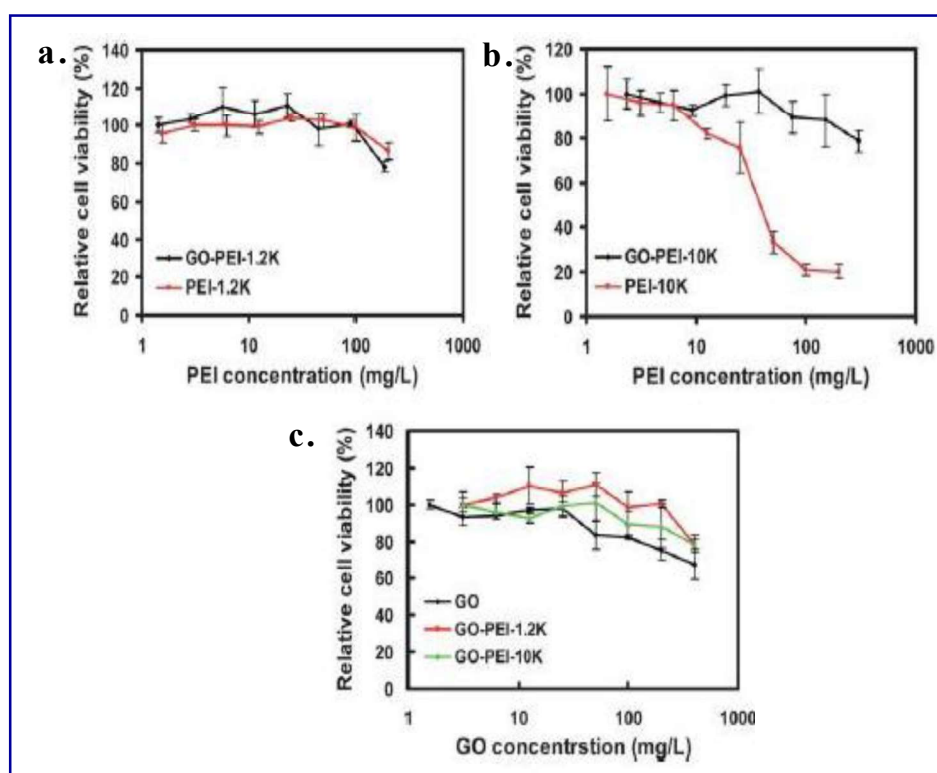
polyethyleneimine (PEI). It was also observed that grafting of polyethyleneimine (PEI) to graphene oxide surface not only reduced the cytotoxicity of the cationic polymer but also enhanced the transfection efficiency.

#### **1.10.6.2 Cytotoxicity:**

In vitro cytotoxicity of different PEI-GO complex was evaluated in compared to pure PEI on HeLa cells line and given in (Figure 1.18). Significant reduced in toxicity was observed in PEI-GO complex as compared to pure PEI indicating the more biocompatible nature. Moreover, variation in molecular weight of PEI also did not increase the cytotoxicity of graphene oxide. PEI-GO complex exhibit the higher cell viability as compared to pure graphene oxide due to the improved stability of PEI-GO in physiological condition [Feng et al. (2011)]. Akhavan et al. were used graphene oxide nanosheet and evaluates its effect on Gram-positive and Gram-negative bacteria. More damage in Gram-negative (*Escherichia coli*) bacteria was observed as compared to Gram-positive (*Staphylococcus aureus*) indicating the antibacterial behavior of graphene oxide. However, reduced graphene oxide sheet exhibits more antibacterial property than the graphene oxide. This is due to better charge transfer from the rGO surface during the surface interaction [Akhavan et al. (2010)]. Zhang et al. (2011) were prepared the graphene oxide via modified Hummers method and evaluate the distribution and biocompatibility nature of graphene oxide in mice using the radiotracer method. It was observed that graphene oxide was mostly deposited in lung and retained there for a long time. Graphene oxide show no toxic effect at low concentration (1mg/kg body weight) and show good biocompatible with red blood cells for 14 days



indicating the promising material for targeted drug delivery especially for lung for a short time period. However, at higher concentration (10mg/kg) several pathological changes were observed such as pulmonary edema, granuloma formation and inflammation due to the high accumulation and long time retention nature of graphene oxide [Zhang et al. (2011)]. This adverse effect of graphene oxide to lung is minimized by using the unoxidized graphene dispersed with block copolymer Pluronic [Duch et al. (2011)].

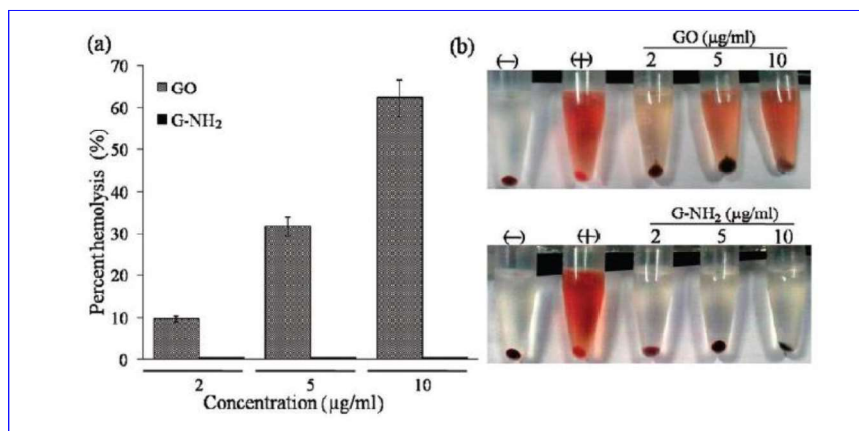


**Figure 1.18:** In vitro cell toxicity assay: Cell viability data of by MTT assay on HeLa cells line incubated with a different concentrations of GO-PEI-1.2k and PEI-1.2k (a), GO-PEI-10k and PEI-10k (b), as well as GO and two GO-PEI complexes (c) (incubation time was 24 h) [Feng et al. (2011)].

### 1.10.6.3 Hemocompatibility:

Surface chemistry also plays an important role in biological properties of nanomaterial. Singh et al. (2012) were synthesized the amine modified graphene

oxide and evaluates its effect on red blood corpuscles (RBCs) integrity (Figure 1.19). They were observed that pure graphene oxide nanoparticle exhibits the significant hemolysis (10%) at low concentration (2 $\mu\text{g}/\text{ml}$ ) which further increased  $\sim 62\%$  at 10 $\mu\text{g}/\text{ml}$  concentration. However, no significant hemolysis was observed in presence amine modified graphene oxide at higher concentration 10 $\mu\text{g}/\text{ml}$  suggesting that amine modified graphene is highly hemocompatible nanomaterial [Singh et al. (2012)]. Zhang et al. (2011) were prepared the covalently conjugated graphene oxide-dextran (GO-DEX) system and determined the biocompatibility by radiotracer technique. GO-DEX exhibits the significant improved stability in physiological condition. In-vivo studies in reticuloendothelial (RES) such as liver and spleen show no toxic effect in mice indicating the GO-DEX a fascinating material for various biological applications [Zhang et al. (2011)].



**Figure 1.19:** (a) Percentage hemolysis of RBCs incubated with different concentration (2, 5 and 10 $\mu\text{g}/\text{ml}$ ) of graphene oxide and amine modified graphene oxide and (b) RBCs suspension were exposed to varying concentration (2, 5 and 10 $\mu\text{g}/\text{ml}$ ) of graphene oxide and amine modified graphene oxide for 3h followed by centrifugation [Singh et al. (2012)].

### **1.10.7 Lackuna in polyurethane graphene nanocomposites:**

Graphene polymer nanocomposites exhibit the superior thermal and mechanical properties as compared to native polymer. A lot of work on polyurethane graphene nanocomposites has been done and emphasized their various applications. However, no report in literature is available in some points. These points are as follows.

- Self-assembly phenomena in polyurethane are not reported in presence of graphene or its derivatives.
- Drug delivery through polyurethane graphene nanocomposites is not reported. However there are several reports available in which graphene or functionalized graphene act as a drug carrier.
- Cellular behavior in polyurethane graphene nanocomposites is also not available.
- Inhibition of corrosion in presence of sulfonated graphene oxide is not reported.

### **1.10.8 Objectives of Work:**

Due to easy in synthesis, modification and biocompatible nature polyurethane has drawn the tremendous attention in polymer fields. Modification of polyurethanes is done by changing the chemical nature or composition of materials used in synthesis or by incorporation of the appropriate fillers in polymer matrix. Now a day graphene or its derivatives is frequently used in nanocomposites arena due to its unique properties. Properties of nanocomposites are highly affected by the dispersion nature of incorporated graphene in polymer matrix. To achieve the better dispersion in organic matrix some modification in graphene sheets (chemically or physically) are required. Chemical modification is done through covalent interaction where physical is obtained through the  $\pi$ -  $\pi$  stacking interaction.

Objectives of proposed work are given below:

- Synthesis of polyurethane graphene nanocomposites and evaluates the effect of graphene on polyurethane properties in terms of structural, mechanical and thermal properties as well as self-assembly phenomena and biocompatible nature of polyurethane.
- Amine modification of graphene oxide and studies the effect of this modified graphene on various properties of polyurethane such as structural, thermal, mechanical, self- assembly, drug delivery and biocompatible nature.
- Modification of graphene oxide through various diamine moieties such as ethylene, hexyl and dodecyl diamine and evaluates its effect on

polyurethane properties in terms of structure, thermal, mechanical, self-assembly, drug delivery and cellular response.

- Sulphonation of graphene oxide and evaluates the effect of sulfonated graphene on various properties of polyurethane such as structural, self-assembly, cellular response and corrosion activities.