

List of Figures

	Page No.
1.1 Schematic representation of segmented polyurethanes (SPUs)	2
1.2 Two step polyurethane synthesis process: Formation of prepolymer through reaction between polyol and diisocyanate followed by chain extension step.	4
1.3 Urethane and urea formation.	7
1.4 Different form of carbon allotrope.	12
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 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.	14
1.6 Non covalent interaction between (a) Pyrene butanoic acid succidimidyl ester (PBASE) and graphene sheet through π - π stacking interaction 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.	16
1.7 Transmission electron micrographs of TPU with 3 wt% of reduced graphene in melt-blended, solvent mixing and in-situ polymerization.	21
1.8 XRD patterns of (i) GO, (ii) HPU, (iii) HPU-GO 0.5, (iv) HPU-GO 1 and (v) HPU-GO 2 and (b') XRD patterns of TPU and its indicated nanocomposites where number indicates the weight% of functionalized graphene in polyurethane matrix.	22
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).	24

1.10	AFM image of (a) pure polyurethane (50 μ m \times 50 μ m), and nanocomposites (b) 2wt% of MWCNTs and (c) 2wt% of graphene. (Image is taken after the crystallization).	26
1.11	DSC thermograms of polyurethane and its indicated nanocomposites.	28
1.12	TGA thermograms of polyurethane and its nanocomposites.	29
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.	31
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).	32
1.15	The oxygen transmission rate for PET films coated with different types of samples.	34
1.16	Electrical conductivity of PU/rGO composites as a function of graphene content.	35
1.17	The release profile of dexamethasone loaded drug on GO at different pH values.	38
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 24h).	40
1.19	(a) Percentage hemolysis of RBCs incubated with different concentration (2, 5 and 10 μ g/ml) of graphene oxide and amine modified graphene oxide and (b) RBCs suspension were exposed to varying concentration (2, 5 and 10 μ g/ml) of graphene oxide and amine modified graphene oxide for 3h followed by centrifugation.	41
3.1	Bright field transmission micrograph of indicated PU nanocomposite (4 wt% graphene).	65

3.2	Bright field transmission electron micrographs of nanocomposites (4 wt% graphene) in polymer solution, showing the stacking nature of graphene in polymer matrix.	66
3.3	(a) X-ray diffraction patterns of PU and its indicated nanocomposites. Vertical lines indicate the peak position with interplanar spacing; (b) Small angle neutron scattering patterns; I (q) vs q (wave vector) plot of PU and its indicated nanocomposites. Inset figure shows the Debye-Bueche fitting for the calculation of correlation length, (ξ); (c) AFM images of PU and its indicated nanocomposites ($5\mu\text{m} \times 5\mu\text{m}$) obtained through tapping mode (d) Polarizing optical images of PU and its indicated nanocomposites.	69
3.4	(a, a') FTIR spectra of PU and its indicated nanocomposites showing peak position shifted in nanocomposites as compared to pure PU; (b) UV-visible spectra of PU and its indicated nanocomposites exhibiting absorption peaks; (c) DSC thermograms of PU and its indicated nanocomposites showing heat of fusion; (d) Plot of heat of fusion and melting temperature vs. percentage graphene content.	72
3.5	Wide-angle X-ray diffraction of PU and its indicated nanocomposites, showing the reduced in the intensity of polymer nanocomposites as compared to pure PU and the intensity further reduced when the content of graphene is increased.	73
3.6	Mechanical properties of PU and its indicated nanocomposites in solid and liquid state (a) Stress-strain curves of pure PU and its nanocomposites; (b) Comparison of modulus (MPa) and toughness (MJm^{-3}) values of PU and its nanocomposites as indicated in the bar graph; (c) storage modulus and (d) complex viscosity of pure PU and its nanocomposites as a function of frequency.	76
3.7	Melt state mechanical behavior of pure PU and its indicated nanocomposites. (a) Storage modulus and (b) complex viscosity of pure PU and its indicated nanocomposites as a function of Frequency at 190°C , showing the enhancement in melt state mechanical property of nanocomposites as compared to pure PU.	77
3.8	Degradation behavior of PU and its indicated nanocomposites in nitrogen atmosphere.	78
3.9	Enzymatic degradation of pure PU and its indicated nanocomposite; (a) through <i>lipase</i> and (b) <i>protease</i> .	79

3.10	Standard curve of Tetracycline Hydrochloride standard stock solution (1mg/ml) drawn after taking absorbance using UV-visible spectrometer at 360 nm in the concentration range of 1-100 µg/ml.	80
3.11	(a) Sustained drug release profile of pure PU and indicated nanocomposites and (b) Korsmeyer-Peppas fitting in pure PU and its indicated nanocomposites.	82
3.12	Biological studies on pure PU and its indicated nanocomposites. (a) BMMSCs cell viability of pure PU and its nanocomposites with time interval of 1 and 5days; (b) Fluorescence microscopic image of cell cultured on PU and its indicated nanocomposites after 1 day of cell proliferation; (c) BMMSCs cell adhesion on PU and its indicated nanocomposites in terms of optical density. The absorption value was taken at 570 nm.	85
4.1	¹ H-NMR spectra of the pure PU and its indicated nanocomposites.	92
4.2	(a) Bright filed transmission electron microscope image of indicated; nanocomposites; (b) FTIR spectra of amine modified graphene oxide with graphene oxide and graphite flake and (c) UV-visible spectra amine modified graphene oxide, graphene oxide and graphite.	93
4.3	FTIR spectra of pure PU and its indicated nanocomposites in –N-H frequency range.	94
4.4	(a) FTIR Spectra of the pure PU and its indicated nanocomposites. (b) UV-visible spectra of the modified graphene with physically and chemically tagged nanocomposites. (uv-visible spectra of pure PU Inset) and (c) PL spectra of pure PU and its indicated nanocomposites with modified graphene.	96
4.5	(a) XRD pattern of the pure PU and its indicated nanocomposites. (XRD of modified graphene inset) (b) DSC thermograph of pure polyurethane and its nanocomposites.	98
4.6	(a) TGA curve of the pure polymer and its nanocomposites and (b) SEM image of modified graphene with physically and chemically tagged nanocomposites.	99
4.7	Mechanical behavior of the polymer and its nanocomposites. (a) Stress-stain curve of the polymer and its nanocomposites. (b) Toughness of the pure polymer and its indicated nanocomposites and (c) Modulus of pure	101

polyurethane and its nanocomposites in bar diagram.

- 4.8** (a) XRD pattern of pure PU and its indicated nanocomposites (inset XRD pattern of amine modified graphene). (b) Small- angle neutron scattering patterns of the pure PU and its nanocomposites (inset Debye-Bueche fitting for calculation of the correlation length (ξ)). (c) AFM image of the polymer and its nanocomposites ($1\mu\text{m}\times 1\mu\text{m}$) and (d) Optical image of the pure PU and its indicated nanocomposites. (Scale bar $20\mu\text{m}$). **104**
- 4.9** Enzymatic degradation of the pure polymer and its indicated nanocomposites through lipase (*Pseudomonas cepacia*). **106**
- 4.10** Standard curve of Dexamethasone standard stock solution (1mg/ml) drawn after taking absorbance using UV-visible spectrometer at 242 nm in the concentration range of 5-100 $\mu\text{g/ml}$. **107**
- 4.11** (a) Sustained drug release profile of indicated PU and its nanocomposites. (b) Korsmeyer- Peppas model for mechanism of drug release in PU and its indicated nanocomposites. **109**
- 4.12** Biological studies on pure PU and its indicated nanocomposites. (a) HeLa cell viability of pure PU and its nanocomposites with time interval of 1, 3 and 5 days; (b) Fluorescence microscopic image of cell cultured on PU and its indicated nanocomposites after 1 day of cell proliferation and (c) HeLa cell adhesion on PU and its indicated nanocomposites. **112**
- 5.1** (a) FITR spectra of graphene oxide and diamine modified graphene oxide. (b) UV-visible spectra of graphene oxide and various diamine functionalized graphene oxide in solid state. **118**
- 5.2** (a) X-ray diffraction pattern of graphene oxide and diamine functionalized graphene oxide and (b) Proton NMR spectra of graphene oxide and ethylene diamine modified graphene oxide. **119**
- 5.3** ^1H -NMR spectra of pure PU and indicated nanocomposites with modified graphene. **120**
- 5.4** (a) Transmission electron micrographs of the indicated PU nanocomposites, (b) FTIR spectra of the pure PU and its indicated nanocomposites and (c) UV-vis spectrum of pure polymer and its indicated nanocomposites. **122**
- 5.5** (a) SEM image of hexyl diamine modified graphene oxide, pure polyurethane and indicated nanocomposites and (b) XRD pattern of pure **123**

PU and its indicated nanocomposites.

- 5.6 (a)** TGA thermograms of the pure PU and its indicated nanocomposites and **(b)** DSC thermograms of PU and indicated nanocomposites. **125**
- 5.7** Mechanical response of the PU and its indicated nanocomposites. **(a)** stress- strain curve of pure PU and its indicated nanocomposites **(b and c)** toughness and modulus values of pure PU and its indicated nanocomposites in the bar graph respectively. **126**
- 5.8 (a)**X-ray diffraction patterns of the pure PU and its indicated nanocomposites. **(b)** SANS patterns of the PU and its indicated nanocomposites **(c)** AFM image of PU and its indicated nanocomposites (1 $\mu\text{m}\times$ 1 μm) and **(d)** POM image of pure PU and its indicated nanocomposites. (Scale bar 20 μm .) **129**
- 5.9** Ornstein- Zernike fitting for calculation of correlation length (ξ). **129**
- 5.10** Standard curve of Dexamethasone standard stock solution (1mg/ml) drawn after taking absorbance using UV-visible spectrometer at 242 nm in the concentration range of 5-100 $\mu\text{g/ml}$. **130**
- 5.11 (a)** Sustained drug release profile of pure PU and its indicated nanocomposites. **(b)** Korsmeyer- Peppas model for mechanism of drug release in PU and its indicated nanocomposites. **132**
- 5.12** Biological behavior of pure PU and its indicated nanocomposites **(a)** Cell viability of pure PU and its indicated nanocomposites with time interval of 1, 3 and 5 days **(b)** Fluorescence microscopic image of PU and its indicated nanocomposites after 1day of cell proliferation (Mag: 20 \times) and **(c)** Cell adhesion on pure PU and its indicated nanocomposites after 1day. **135**
- 5.13 (a)** Formation of the ROS in MDA-MB-231 cells in presence of pure PU and its indicated nanocomposites after 24 h of incubation. **(b)** Mitotracker staining with DAPI of MDA-MB-231 cells on PU and its indicated nanocomposites. **137**
- 6.1 (a)** FTIR and **(b)** UV-visible spectra of graphene oxide and modified graphene oxide. **142**
- 6.2 (a)** XRD and **(b)** $^1\text{H-NMR}$ spectra of graphene oxide and modified graphene oxide. **143**
- 6.3** $^1\text{H-NMR}$ spectra of pure polyurethane and indicated nanocomposites. **144**

6.4	(a) Bright field Transmission electron micrographs of indicated nanocomposites, (b) FTIR and (c) UV-visible spectra of pure polyurethane and its indicated nanocomposites.	146
6.5	(a) SEM image modified graphene, pure PU and indicated nanocomposites, (b) XRD pattern of pure PU and indicated nanocomposites.	147
6.6	(a) X-ray diffraction patterns of PU and its indicated nanocomposites. Vertical lines indicate the peak position with interplanar spacing; (b) Small angle neutron scattering patterns; I (q) vs q (wave vector) plot of PU and its indicated nanocomposites. Inset figure shows the Ornstein-Zernike fitting for the calculation of correlation length, (ξ); (c) AFM images of PU and its indicated nanocomposites ($1\mu\text{m} \times 1\mu\text{m}$) obtained through tapping mode (d) Optical images of PU and its indicated nanocomposites. (Scale bar $20\mu\text{m}$).	150
6.7	Corrosion inhibition efficiency of modified graphene, pure PU and indicated nanocomposite	152
6.8	Biological behavior of pure PU and its indicated nanocomposites (a) Cell viability of pure PU and its indicated nanocomposites with time interval of 1, 3 and 5 days (b) Fluorescence microscopic image of PU and its indicated nanocomposites after 1day of cell proliferation (Mag: 20 \times) and (c) Cell adhesion on pure PU and its indicated nanocomposites after 1day and (d) Integrated Modulation Contrast (IMC) image of HeLa cell cultured on pure polyurethane and its nanocomposites after 24h (Mag: 40 \times)	154