

Chapter@7

Conclusion and Future Work

Conclusion and Future Work:

Polyurethanes (PUs) are segmented polymeric material constituted by hard and soft domain and frequently used in common applications due to their processibility and better mechanical properties as well as biocompatible nature. This hard and soft domain is responsible for the superior property such as toughness and stiffness. Hard domain which is generating by the isocyanate moiety through the hydrogen bonding interaction between the urethane linkages provides the crystallinity to the material whereas soft domains create the amorphous zone in polymer. Depending upon the interaction between these hard and soft segment polymer may have lamellar or globular structure in their morphology. Properties of polymer may also tailored by incorporating the two dimensional graphene nanoparticle at different stage of polymerization or by adding the different functionalized graphene sheet. Self-assembly phenomena are also facilitated in presence of graphene or functionalized graphene which enhanced the physical property of polymer. Nanocomposites exhibit the sustained drug release as compared to the pure polyurethane as well as higher cellular growth for tissue engineering and are also in biocompatible nature. Hence, developed materials may have the potentials to use as a biomaterial for sustained drug released and in tissue engineering applications. The important conclusions of the present finding are summarized below:

- Aliphatic polyurethane with 30% hard segment has been synthesized by using the predetermined composition of poly-ol, diisocyanate and chain extender.
- Nanocomposites of polyurethanes have been synthesized by dispersion the two dimensional graphene sheet in early step of polymerization process.

- Decrease in the thermal stability was observed in nanocomposites as compared to pure polyurethane and this thermal stability further decrease as content of graphene were get increased in matrix.
- Depression in the melting temperature of soft and hard segment was observed in nanocomposites as compared to pure polyurethane.
- The Young's modulus gradually decrease with increasing the content of two dimensional graphene sheet whereas, toughness increased by increasing the graphene content up to a certain limit. Orientation of graphene sheet towards the applied force which suppressed the crack propagation process is the major factor for increasing the toughness to certain. At higher concentration agglomeration was occurred which caused the catastrophic effect leading to decrease in mechanical behavior of nanocomposites.
- The self-assembled network structure in aliphatic polyurethane and its different nanocomposites has been revealed through XRD, SANS, AFM and POM measurement. The cause of formation of self-assembled structure in pure polyurethane is the extensive hydrogen bonding interaction between the urethane moieties whereas in nanocomposite this interaction is minimized and interactions between graphene sheet and polymer chains get increased. The intermolecular distance (1.20→1.08nm) was decreased in nanocomposites as compared to pure aliphatic polyurethane suggesting the lesser number of polymer chains are required to form the self-assembled structure.
- Layer by layer molecular assembly starting from nano-scale (1.20nm) to micro-scale (5 μm) through the secondary forces like hydrogen bonding and

dipolar interaction has been established for the first time in polyurethane / graphene nanocomposites.

- Significant improvement in storage modulus was observed in nanocomposites as compared to pure polyurethane indicating the greater mechanical strength in melt condition. Furthermore, as the content of graphene get increased increase in storage modulus was observed due to the strong interaction to the filler causing the network structure due to the self assembly process transforming the nanocomposites into the greater melt strength.
- The splintering of the network structure and re-organization at higher frequency region in pure polymer and its nanocomposites has been also reported for the first time in melt condition. Furthermore, storage modulus at different temperature in varying frequency test also supports the breaking and reformation of the network structure. Magnitude of complex viscosity is also higher in nanocomposites as compared to pure polymer suggesting the networking structure due to the grater interaction.
- AFM topographs indicate the segmentization of soft and hard domains in polymer and its nanocomposites which is further elucidated by the SANS measurement by characteristic and correlation length to have known the compactness of these sheet structure at molecular level.
- Biodegradation of pure polyurethane and its nanocomposites has been studied in enzymatic media.
- Sustained drug release of the loaded drug was observed in nanocomposites as compared to pure polyurethane due to the barrier effect by the two

dimensional graphene sheets which hindered the diffusion of the loaded drug in medium. This becomes more prominent in nanocomposites having the greater content of graphene.

- For understanding the biocompatible nature of developed material cell viability, cell adhesion and fluorescence image experiments have been carried out showing the biocompatible nature.
- New nanocomposites were synthesized by using the amine modified graphene oxide using as a chain extender and dispersing the amine modified graphene in early stage of polymerization.
- Grafting of the prepolymer chain to the amine modified graphene is confirmed through the $^1\text{H-NMR}$ measurement.
- Enhancement in the thermal stability was observed in nanocomposites as compared to pure polyurethane and this improvement is more in nanocomposites having the amine modified graphene as a chain extender.
- Enhancement in the melting temperature of soft segment was observed in nanocomposites with respect to pure polymer indicating the graphene induced crystallization in soft segment in polymer chain.
- Modified graphene and polyurethane exhibits the grainy morphology indicating the crystalline in nature whereas, nanocomposites exhibit the cloth like morphology suggesting the amorphous nature.
- Decrease in the Young's modulus was observed in nanocomposite as compared to pure polyurethane indicating the lesser crystallinity in nanocomposites whereas, enhancement in the toughness was observed in nanocomposites as

compared to pure polyurethane due to orientation of amine modified graphene sheet towards the applied force which suppressed the crack propagation process. This enhancement is higher in nanocomposites having the modified graphene as a chain extender.

- Step by step modified graphene induced self-assembly from the nanometer scale to the micron level was investigated through X-ray diffraction (1.4nm), small angle neutron scattering (15nm), atomic force microscopy (212nm) and optical images (2.3 μ m) in the order of nanometer, tens of nanometer, hundreds of nanometer and micron size, respectively.

- Sustained drug release of the loaded drug was observed in nanocomposites as compared to pure polyurethane and this is more sustained in nanocomposites having the modified graphene as a chain extender. This is due to the hindrance created by the two dimensional graphene sheets as well as greater self-assembly which hindered the diffusion of the loaded drug in medium.

- For understanding the biocompatible nature of developed material cell viability, cell adhesion and fluorescence image experiments have been carried out showing higher biocompatible nature of the nanocomposites as compared to pure polymer.

- A series of nanocomposites was synthesized by using the diamine amine (ethyl, hexyl and dodecane diamine) modified graphene oxide using as a chain extender.

- Functionalization of graphene oxide is confirmed by FTIR, UV-visible, XRD and $^1\text{H-NMR}$ measurements.
- Grafting of the prepolymer chain to the diamine modified graphene is confirmed through the $^1\text{H-NMR}$ measurement.
- Nanocomposites were exhibited greater thermal stability as compared to pure polyurethane and this improvement is more in nanocomposites having the dodecane modified graphene as a chain extender.
- Enhancement in the melting temperature of soft segment was observed in nanocomposites with respect to pure polymer indicating the induced crystallization to the soft segments was occurred through the modified graphene.
- Diamine functionalized graphene and polyurethane exhibits the grainy morphology indicating the crystalline in nature whereas, nanocomposites exhibit the clothly like morphology suggesting the amorphous nature.
- Decrease in the Young's modulus was observed in nanocomposite as compared to pure polyurethane indicating the lesser crystallinity in nanocomposites as observed in XRD and SEM measurement whereas, enhancement in the toughness was observed in nanocomposites as compared to pure polyurethane due to orientation of amine modified graphene sheet towards the applied force which suppressed the crack propagation process. Furthermore, decrease in the toughness was observed in nanocomposites having the dodecane modified graphene.

- Layer by layer self-assembly phenomena which is responsible for the formation of strips structure in pure polyurethane and nanocomposites have been evaluated through XRD (1.41 nm), SANS (15nm), AFM (100-150 nm) and POM (~2.5 μ m) in sequence.
- Sustained drug release of the loaded drug was observed in nanocomposites as compared to pure polyurethane and this is more sustained in nanocomposites having the dodecane modified graphene as a chain extender. This is due to the hindrance created by the two dimensional graphene sheets as well as greater self-assembly which hindered the diffusion of the loaded drug in medium. Hence we can tune the release rate of the loaded drug by using the suitable length of modifier for functionalization of graphene oxide.
- Biocompatible nature of pure polyurethane and its nanocomposites were monitored by cell viability, cell adhesion, fluorescence image, Intracellular reactive oxygen (ROS) contents and Mitotracker analysis. These measurement elucidates the greater biocompatible nature of the nanocomposites as compared to pure polymer. Hence, developed material may have the potential for tissue engineering and control drug release applications.

Future Work:

In this thesis we have reported the synthesis and characterization of polyurethane nanocomposites using the two dimensional graphene / functionalized graphene. The effect of graphene / functionalized graphene on surface morphology, thermal,

mechanical, self-assembly and biological behavior of polyurethane has been studied in this report. However, there are some fields that could not be covered in this report. Some of those aspects are given below.

- Synthesis and characterization of P3HT-graphene nanocomposites for capacitor application.
- Surface modification of graphene oxide through the insertion of the Nitrogen atom in the ring of graphene sheet.
- Elucidate the effect of Nitrogen doped graphene on polyurethane properties.