

PREFACE

Polymeric materials especially polyurethane has drawn the tremendous attention for various applications over a decade due to its easy processibility, better mechanical and thermal properties as well as eco-friendly in nature. Properties of polymeric materials can be improved by using the small amount of nanofiller. Recently carbon especially graphene nanofillers are frequently used to improve the properties of native polymer. Self-assembly phenomena due to the strong hydrogen bonding between the segmented zones of polyurethane which produced the material with superior strength and stiffness was also facilitated in presence of graphene nanofiller. This self-assembly phenomena can be altered by changing the nature of precursor molecules or surface modification of graphene. Sustained drug release as well as biocompatible nature of the developed material indicates the nanocomposites may have the potential to use as biomaterials.

Present work explores effect of graphene / modified graphene on various properties of pure polyurethane including self-assembly as well as biomedical applications. This thesis has been categorized in following outlines: Introduction, Experimental, Results and Discussions and Conclusions. The brief description of different chapters is given below:

Chapter 1: This chapter includes the general introduction describing the components, synthesis and applications of polyurethane. Brief description about the graphene, types of nanocomposites and synthesis technique of nanocomposites has been discussed. A brief recent review of the literature on polyurethane nanocomposites has been presented. Objectives of the work have been given at the end of this chapter.

Chapter 2: It contains the details of material and experimental process including synthesis of polyurethane, different surface functionalization of graphene oxide and synthesis of polyurethane nanocomposites using these graphene or functionalized graphene. Dispersion of graphene in polymer matrix was verified through transmission electron microscopy. Molecular level self-assembly from micrometer level to nanometer level was studied through Optical Microscopy, Atomic Force Microscopy, Small Angle Neutron Scattering and X-ray Diffraction techniques. Thermal properties of material have been studied through Thermogravimetric and Differential scanning calorimeter technique. Mechanical behavior in solid as well as in melt condition was studied through Universal testing machine and Rheometer respectively. Biocompatible nature of material was verified through cell viability, cell adhesion, fluorescence image, reactive oxygen species and mitotracker analysis over different cell lines.

Chapter 3: This chapter includes the effect of graphene on polyurethane in terms of self-assembly, mechanical, thermal, drug release and biocompatible properties. Crystallinity and thermal degradation was decreased with increasing graphene content in polymer matrix suggesting the inhibition nature of graphene. Molecular level self-assembly from nanostructure to microstructure through X-ray diffraction (1.2nm), small angle neutron scattering (SANS) (16nm), atomic force microscopy (500nm) and optical microscope (5 μ m). These self-assembly play an important role in improvement of mechanical property in solid as well as in melt condition. Decrease in the Young's modulus with increasing graphene while enhancement in the toughness was observed at certain content of graphene. Self-assembly phenomena also play significant role in drug release from

nanocomposites. Biocompatible nature of nanocomposites was verified on bone marrow derived mesenchymal stem cell lines (BMMSc).

Chapter 4: This chapter describes the comparative studies of two different nanocomposites (Physically mixed and chemically grafted nanocomposites) synthesized by amine modified graphene with respect to pure polyurethane. Chemically grafted nanocomposite exhibits the superior property over the physically mixed and pure polymer. Step by step self-assembly phenomena from molecular level to nanoscale level were facilitated in presence of modified graphene. Enhancement in thermal degradation temperature was observed in nanocomposites as compared to pure polyurethane and this was more significantly improved in chemically grafted nanocomposite. Sustained drug release was observed in nanocomposites as compared to pure polyurethane and this is more control in chemically grafted nanocomposites. Chemically grafted nanocomposites exhibits better biocompatible nature over the physically mixed and pure polyurethane.

Chapter 5: In this chapter polyurethane nanocomposites have been synthesized by using the different diamine functionalized graphene as a chain extender and evaluates the effect of different diamine modified graphene on polyurethane properties. Significant improvement in toughness has observed in nanocomposites as compared to pure polymer. Nanocomposites show the amorphous nature as with significant improve in thermal degradation temperature. Step by step self-assembly from nanostructure to microstructure through X-ray diffraction (1.4nm), small angle neutron scattering (SANS) (15nm), atomic

force microscopy (150nm) and optical microscope (2.5 μ m). Sustained drug release was observed in nanocomposite as compared to pure polymer and this sustains is more control in nanocomposite having bulkier diamine (dodecane diamine) as a chain extender. Biocompatibility of material has been verified through cell viability, cell adhesion, fluorescence image, mitotraker analysis and reactive oxygen species measurement on human breast cancer cells MDA-MB-231.

Chapter 6: This chapter includes the synthesis of polyurethane sulfonated graphene nanocomposites and evaluates the effect of sulfonated graphene on polyurethane properties. Grafting of prepolymer chain to modified graphene was confirmed through the ¹H-NMR and FTIR spectra. Homogenous dispersion was achieved in nanocomposites leading to significant improvement in properties of polyurethane through greater interaction. Self-assembly phenomena from molecular level to nanoscale level were facilitated in presence of modified graphene. Significance enhancement in corrosion inhibition efficiency was observed in nanocomposites suggesting the developed material may have the potential to use as corrosion inhibitor. Furthermore, nanocomposites exhibit the more biocompatible behavior even at higher concentration of modified graphene indicating the synthesized material may also used in tissue engineering arena.

Chapter 7: This chapter describes the main feature and observation, key finding and future work.

List of books and journals used in these studies has been given at the end of the thesis under the References heading.