Preface

Polymer nanocomposites are a segment of the growing interest in nanotechnology. Polymer layered silicate nanocomposites (PLSNC) are the foremost members of such nanocomposites. Geometrically two-dimensional reinforcement of PLSNC is expected due to the anisotropic platelet structures of the layered silicates with higher aspect ratio and surface area.

In the present investigation, unmodified and chemically modified poly (styrene-ethylene-co-butylene)-styrene [SEBS]-clay nanocomposites have been prepared and characterized.

The thesis is organized in **nine** chapters. **Chapter 1** provides the introduction to the present investigation with detailed literature survey in this field. At the end of this chapter, the scope and objectives of the thesis on block copolymeric nanocomposites based on unmodified and chemically modified SEBS and montmorillonite nanoclays have been discussed.

The base materials chosen for research, material sources, sample preparation, designation and experimental methods for characterization of neat SEBS block copolymer, nanoclays and the resulting nanocomposites by various characterizing tools have been detailed in the experimental section as **Chapter 2** of the thesis.

Preparation and properties of thermoplastic elastomer (TPE) - clay nanocomposites based on SEBS triblock copolymer using natural montmorillonite clay (MT) and organically modified clays (OMT) prepared by solution and direct melt intercalation processes have been studied in **Chapter 3**. Organically modified montmorillonite clay gives best mechanical and dynamic mechanical properties at 4 phr (parts per 100 parts of rubber) among 2, 4 and 8 phr loaded nanocomposites. The X-ray diffractograms indicate expansions of clay gallery with the incorporation of the amines in nanoclays. The bulk morphological studies by AFM and TEM reveal exfoliation in the case of OMT and agglomeration in the unmodified montmorillonite MT clay filled SEBS composites at 4 phr loading.

Comprehensive nanoscale surface morphological characterization of neat SEBS and its OMT and OC clay based nanocomposites by using AFM have been carried out in **Chapter 4**. The phase images show position and distribution of the brightest clay platelets in the well-ordered phase separated morphology consisting of bright nano-phasic domains corresponding to hard styrene block component (PS) and darker domains corresponding to softer rubbery ethylene-co-butylene block (PEB) lamella of the base matrix of the nanocomposite. The lamellar thickness of the soft phases is widened to 50-75 nm, where the layered clay silicates (40-54 nm in length and 4-17 nm in width) are embedded in the soft rubbery phase.

Atomic force microscopy (AFM) has also been used for surface roughness as well as quantitative investigation of surface forces measured at constituting blocks and clay regions of nanocomposite with OMT clay. These are discussed in **Chapter 5**. The roughness and power spectral density analysis of surface topography has provided an increment in random roughness (in the range of 0.5- 2.5 nm) of the nanocomposites. Large adhesive force of 25 nN and contact force of 260 nN in soft PEB segments and higher cantilever deflection of 210 nm in clay regions are observed for SEBS-clay nanocomposite from AFM force-distance analysis. Mapping of elastic modulus of the glassy and rubbery blocks and clay regions have been probed by employing Hertzian and JKR models from respective approaching and retracting force–distance curves.

In **Chapter 6,** functionalization of SEBS at the mid-block by means of chemical grafting by two polar moieties - acrylic acid (AA) and maleic anhydride (MA), and subsequent novel synthesis of nanocomposites based on hydrophilic montmorillonite clay (MT) at very low loadings and their characterization have been discussed. The nanocomposites derived from the grafted SEBS and hydrophilic MT clay have conferred dramatically better mechanical (40% improvements in tensile strength and modulus), dynamic mechanical and thermal properties (by 18°C for AA grafted and 45°C for MA grafted nanocomposites respectively) as compared to those of neat SEBS and its MT clay based nanocomposites. XRD, AFM and TEM studies reveal better interaction and dispersion of MT clays with grafted SEBS matrix. Thermodynamic calculations and interfacial tension measurements provide possible ways of favourable intercalation-exfoliation mechanism of maleated and acrylated SEBS–MT nanocomposites.

Synthesis of sulfonated SEBS (SSEBS) by reaction of acetyl sulfate with SEBS and subsequent preparation of SSESB- clay nanocomposites from hydrophilic MT and organically modified OMT at very low loading have been described in **Chapter 7**. Micro-phase separated morphology has been shifted from cylindrical-lamellar for neat SEBS to distorted one for sulphonated SEBS. On sulphonation (3 and 6 weight %) of SEBS, hydrophilic MT clay based nanocomposites exhibit better mechanical, dynamic mechanical and thermal properties and also controlled water – methanol mixture uptake and permeation and AC resistance. The resulting nanocomposites have potential as proton transfer membranes for fuel cell applications.

In **Chapter 8, t**he effect of nanoclay platelets on the lamella orders of SEBS and polar modified SEBS in the nanocomposites has been investigated by using small angle X-ray scattering (SAXS). The MDSC studies have shown that 2-4 wt% OMT loading assists increment in the lamellar orders of the neat SEBS owing to interaction in these hybrid systems supported by the positive shift in glass transition temperature by DSC. Polar modified SEBS samples show deviation of the corresponding ordering lengths and pattern, while their unmodified MT nanoclay based nanocomposites exhibit structural regeneration of ordering pattern and morphology due to nucleating effect of the added nanoclay.

Finally, in **Chapter 9**, the summary and conclusions of all the chapters have been provided.