1. INTRODUCTION

1.1 Significance of Block Copolymers

Polymeric materials offer a wide range of application relevant properties. Therefore, these materials find growing applications in various fields of everyday life. Since their ultimate properties are determined by their chemical microstructures, control of chemical structure (macromolecular designing) is the first step of creating materials of desired properties profile. In practice, different properties are simultaneously desirable, e.g. a combination of stiffness and drawability, or strength and toughness etc. A technological way of achieving these combinations is the heterogenisation of existing polymers. Polymer blends represent this strategy of designing polymeric materials [1-3].

Blending may often lead to the deterioration of the mechanical properties due to insufficient phase adhesion resulting from the incompatibility of the blend components; hence these blends need compatibilisation. One of the strategy being practiced for about 50 years to get rid of this problem is to join the desired polymer chains with a primary covalent bond which has given rise to today’s fascinating world of block copolymers [2-4].

All block copolymers belong to a broad category of condensed matter sometimes referred collectively as soft materials, which, in contrast to crystalline solids, are characterised by fluid-like disorder on the molecular scale and a high degree of order at longer length scales. Combining the incompatible polymer chains in a single macromolecule leads to intra-molecular phase separation whereby the problem of inadequate phase adhesion will be eliminated. This, in turn, leads to the formation of highly ordered self-assembled “crystalline-like” phase separated structures in melt as well as solid state whose periodicity lies in the range of radius of gyration \( R_g \) of the constituent molecules. The nature and size of these structures can be controlled by various methods including interfacial and architectural modification [4].

The block copolymers find application in diverse fields: as thermoplastic elastomers, pressure sensitive adhesives, impact modifiers, compatibilisers etc. In solutions, their surfactant properties are exploited in foams, oil additives, solubilisers, thickeners and dispersion agents. The block copolymers may have potential applications in medicines, nanotemplating and nanotechnology [2]. An annual growth rate of 9-10% of thermoplastic elastomers (compared to 2-4% growth rate of other polymers) in the last 20 years reflects the significance of these materials in polymer market [5].

Recently, synthesis of several block copolymer architectures including ABC triblock copolymers has triggered the discovery of novel morphologies and opened new potential of controlling mechanical properties [2]. Especially, the block copolymers with complex molecular characteristics are being paid special attention.
1.2 Aims and Overview of Thesis

Styrene/butadiene block copolymers find applications as thermoplastic elastomers, moulding products, toughness modifiers and films. They are, generally, not used commercially as pure materials but compounded with other polymers, fillers etc. to achieve the particular requirements for each end-use. In many applications, mechanical properties are of prime interest. In spite of a detailed knowledge of phase behaviour of simple linear block copolymers, correlation between their morphology, mechanical properties and micromechanical mechanisms, very important for technical applications, is not well understood. Hence, it is of prime importance from materials scientific stand point that this correlation is intensively investigated.

The primary goal of this work is to investigate experimentally correlations between phase behaviour, morphology and micromechanical deformation behaviour of block copolymers (and blends) as a function of their molecular architecture.

The work is limited to amorphous styrene/butadiene block copolymers in a narrow composition range ($\Phi_{\text{styrene}} \sim 0.70$) with an special emphasis on few selected asymmetric architectures. Detailed discussion of morphology development in a wide composition range and their synthetic and rheological aspects are outside the scope of this thesis. The thesis has been organised in the following way:

A short review of thermodynamics, morphology and deformation behaviour of amorphous block copolymers is given in chapter 2. Chapter 3 deals with experimental techniques and general methods of synthesising block copolymers of the types used in this study. Experimental results are discussed in chapters 4, 5 and 6. A brief summary of the research works and future perspective are given in chapter 7.

First, influence of block copolymer architecture on microphase morphology and ultimate mechanical properties of styrene/butadiene block copolymers, which is the main issue of this work, is discussed in chapter 4. For this purpose, phase behaviour, morphology, mechanical properties and micromechanical deformation mechanisms of linear and star shaped block copolymers having different interfacial structures are comparatively analysed.

Styrene/butadiene block copolymers are often used in combination with polystyrene homopolymer (hPS) which find applications in injection moulded parts, food packaging films and beakers for soft and warm drinks. In such applications, a balance between transparency and toughness lies in the centre of interest. Hence, another objective is to study the morphology and micromechanical as well as mechanical behaviour of binary star block copolymer/hPS blends in chapter 5.
Finally, binary block copolymer blends offer new possibilities of tailoring mechanical properties. Despite a few works on phase behaviour and morphology of block copolymer blends, no systematic works about their mechanical behaviour are reported. Structure-property correlations of binary block copolymer blends (star block and triblock) shall be discussed in chapter 6 especially using several concepts of elastic-plastic fracture mechanics.

1.3 Sample Preparation and Investigation Methods

Block copolymers samples synthesised via living anionic polymerisation and provided by the BASF were prepared by different methods: solution casting, extrusion, injection and compression moulding. Polystyrene homopolymers used to blend with selected block copolymers were synthesised by radical polymerisation.

Electron microscopy (TEM, SEM and HVEM) and scanning force microscopy (SFM) were used as principal experimental tools. Mechanical properties are characterised by tensile and impact testing. Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were employed to determine the glass transition temperature and gain insight into the phase behaviour of the materials. Samples were prepared by solution casting and common processing techniques (injection moulding, press moulding and extrusion).