

1 Introduction

1.1 General Consideration

The subject of phase behavior of polymer melts, polymer mixtures (or blends) and polymer interfaces [1, 2, 3, 4, 5, 6, 7] has attracted a great deal of attention because of intriguing physical properties and an essential role in polymer technology. The practical importance arises from the many **industrial applications** of these materials and scientific importance arises from the **complex behavior** they display, a molecular description of which is a challenging problem in statistical mechanics. Therefore, the study of phase behavior of polymer blends or alloys is very important for the design of new multiphase materials as well as to understand their complex behavior.

Polymers do not mix at a molecular level at equilibrium under a wide variety of circumstances because any slight incompatibility of monomers in enthalpic interactions and/or entropic packing effect is amplified by the number of monomers in the macromolecule and cannot be balanced by the entropy of mixing. If such a pair of polymers are dispersed mechanically, there will be domains of one polymer in the other. In such a situation, one is interested to know the nature of the interface between the two coexisting phases and determination of the interfacial energy. The morphology of the mixture will be greatly influenced by the interfacial energy [8], which will control the domain size, while the microscopic structure of this interface will determine the degree of adhesion between the phases. Thus the mechanical properties of the whole mixture will be largely controlled by properties of these interfaces. Further, interfacial properties of polymers play important role in kinetics of the phase separation. Moreover, one may be interested to know at what condition the two components mix. An important feature of polymeric interfaces is that they are often characterized by structure and correlations on scales significantly larger than the monomer size [5], resulting in a degree of universality of interfacial properties. Correlations between interfacial and bulk properties are present on various length scales. The mechanical stability of the alloy depends upon the local interfacial structure - the interfacial width, the conformation of polymers, enrichment of chain ends or the solvent at the interface.

Polymer interfaces play an important role in polymer technology of polymers including adhesives, blends, resists and coatings. Polymeric materials provide an exceptionally varied class of interfacial systems. Polymers can have interfaces with air or solid sub-

strates (external interfaces or surfaces), but also can form internal interfaces, for example the interface between two incompatible homopolymers. The material properties of polymers depend sensitively on the structure and the properties of the interfaces between different phases. Therefore, key to applications of polymeric materials is the ability to control surface or interfacial properties. In polymer blends or filled polymer composites, for example, interfacial tension and adhesion are primary factors in establishing microstructure, strength, and mechanical properties.

Polymer blends are generally “structurally asymmetric” corresponding to species-dependent local intramolecular features such as monomer shape, branch content, and persistence length [9, 10] or aspect ratio. Such asymmetries are expected to have a major impact on blend thermodynamics and phase diagrams, and can give rise to non-Flory-Huggins miscibility behavior. The nonideal free energy of such mixtures involves an excess entropic part due to athermal (packing) correlations induced by the structural asymmetries, and also an enthalpic part [11]. The Flory-Huggins like theories [12] describe the dependence of the phase transition on the molecular weights of the two polymers, the composition of the blend, and the interaction parameter χ [12, 13]. Differences in the chemical structure may lead also to different spatial extension of the chemical repeat units corresponding to different persistence length [9, 10], i.e. the stiffness disparities. Such stiffness disparities may occur even in chemically very similar materials e.g., different polyolefins [14]. The phase behavior and the surface properties [15] of Polyolefins [16, 17] with varying microstructure has recently attracted considerable interest. The mixtures are often modeled [11, 16, 18, 19] as blends of flexible and semiflexible polymers. Helfand and Sapse [20] extended the self-consistent field theory to Gaussian chains with different statistical segment lengths. For infinitely long chains, in the strong segregation limit, they have obtained analytical expressions for interfacial width ‘ w ’ and the interfacial tension ‘ σ ’. Both increase upon increasing the statistical segment length of one component, keeping χ and other components unaltered, see the chapter 2. Similarly, Fredrickson and Liu [21] have obtained an expression of free energy for a mixture of a flexible and semiflexible polymers based on two order parameters, the detailed is described in chapter 2. Morse and Fredrickson [22] have studied polymer interfaces using the self-consistent field theory. They have obtained analytic expressions for interfacial width and interfacial tension both of which decrease with the increase in rigidity of the semiflexible polymers. They considered a symmetric system of semiflexible polymers.

Fredrickson, Liu and Bates [18], and Liu and Fredrickson [23] have shown that a small positive contribution to the Flory-Huggins parameter χ arises due to the stiffness disparity of the chains. Similar results have been reported, by Singh and Schweizer [11] using the polymer reference interaction site model (PRISM), by Freed and Dudowicz [24] using the lattice cluster theories and by Mueller [25] in the Monte Carlo simulations. As the back folding of the chains becomes less probable with increasing stiffness and the number of intermolecular contacts increases the Flory-Huggins parameter χ increases and reflects so the increase of the repulsive interaction between different types of monomers. Worm like chain model [26] has been also used to study the stiffness

disparity of the polymer blends.

Freed and Pesci [27] have obtained an entropic contribution to χ_{eff} that arises from differences in monomer shape using lattice cluster expansion [28]. Weinhold and coworkers [19] have estimated excess entropic contribution to the free energy of mixing of polymer blends of different stiffnesses. Mueller has studied [29, 30] the phase behavior of polymer mixture of flexible and semiflexible polymers by computer simulation for very low stiffness disparity. This author has shown that the critical temperature, at which two component phase separate, increases with the increase in stiffness of semiflexible components in flexible-semiflexible polymer blend.

Gauger and Pakula [31] have investigated a mixture of flexible and very stiff chains in the canonical ensemble and used the subblock method to analyze their simulation data. Due to the stiffness and the excluded volume constraints, they found evidences for a separation into a pure phase of stiff chains and a phase of mixed composition. Further Yethiraj and coworkers [32] have investigated an athermal mixture of flexible and stiff chains in the vicinity of hard walls. Their finding is an entropy-driven surface segregation of the stiffer chains at melt like densities, because the stiffer species packs more efficiently at the hard walls. For the general review of liquid-crystalline order in polymer systems the reader is referred to an article by Holyst and Oswald [33].

It is well-known that when there is a large difference in flexibility, such as in a blend of rods and coils, the system will phase separate for entropic reasons alone [34]. Liquid-crystal polymers and their mixtures are studied both because of their practical utility and due to fundamental interest [35, 36]. In the case of mixtures one wants to know how the location of various phases, isotropic and nematic, and their transitions depend on the properties of the two components, their rigidities, polymerization indices, interaction etc. An approach to this problem requires a model for the liquid crystal polymers. New high-performance materials which contain blends of small molecule liquid crystals or liquid-crystalline polymers with flexible polymers are typically multidomain composites. Since liquid crystals and liquid-crystalline polymers are quite stiff they mix poorly with flexible polymers [21, 37]. In spite of the fact that interfacial tension plays an important role to determine mechanical strength, adhesion and toughness of a polymer blend (as described above), relatively little is understood about the role of backbone stiffness in determining interfacial tension.

Most notably, Mueller and Werner [38] have studied the effect of the stiffness disparity in the interfacial properties of the well segregated phases by using the Monte Carlo simulations and compared their data with self-consistent field theory. They have used the bond fluctuation model (BFM) [39]. Due to limitations of this lattice based approach their work is restricted to rather small bending rigidities of the semiflexible components. In their study the stiffest chain exceeds the stiffness of the flexible one only by a factor of 1.5. Such a low stiffness disparity does not cover the whole range of the semiflexible chains whose flexibility lies between completely flexible chain and stiff rod.

As mentioned above polymer blends are structurally asymmetric. Bates and Fredrickson [16] have calculated excess free energy of mixing in polymer blend in which two different types of monomers differ in volume. Sakurai *et al.* [40] have studied the effect of segment size asymmetry on the scattering function. They used small-angled neutron scattering techniques to study the effect of segment size asymmetry in the structure factor. They have studied the phase diagram and obtained upper critical solution temperature behavior. Pesci and Freed [41] have provided the theoretical description of the computation of the corrections to the F-H approximation, heats of mixing for lattice models of flexible polymer blends where the monomers may cover several lattice sites and therefore have different sizes and shapes.

Computer simulation has become a major tool in polymer science, complementing both analytical theory and experiment. The physics of polymer blends possess universality [1, 4, 42, 43]. Further in polymer blends the global material properties and local interfacial properties are closely related. These properties of polymer blends make them particularly suited for computer simulation [42]. The computer simulation can simultaneously provide a detailed microscopic picture of the interfacial structure, and information on the thermodynamics of the interfaces. Comparing to experiment, simulation provides a test of the microscopic model which has been used and comparing to theories, they serve as a test of the theory within a well-defined microscopic model. Moreover, they may provide structural information which may not yet be accessible experimentally or theoretically. They can thus contribute substantially towards a deeper understanding of the connections between the microscopic parameters, the microscopic structure and the macroscopic properties of a material [4]. For example, the Flory-Huggins theory [12] is not free of uncontrollable approximations (see chapter 2). To test the reliability of the theory, one needs to compare theory and experiments. However, comparing theory with experiments is not sufficient because in most cases, the agreement is not good, but one cannot tell whether the discrepancies are due to inadequacies of the model used in the theory or due to inaccuracies of the approximations. Since the simulation can be performed on exactly the same model which the analytical theory considers (but avoiding the uncontrolled mathematical approximations of the later), the simulations provide “benchmarks” against which these theories can be reliably tested. Such a test of Flory-Huggins theory is carried out by Deutsch and Binder [44, 45]. True symmetrical monodisperse polymer mixtures hardly exist, and the temperature range over which $T_c(N)$ can be studied is limited by the glass transition temperature from below and by chemical instability of the chains from the above. Simulations are free of such limitations, of course, and can test such theories much more stringently than the experiment.

In the present work also the phase behavior and interface properties of polymer blends of different stiffnesses will be studied by using computer simulations. Further, the interface properties of polymers with different monomer sizes which is referred as ‘monomer size disparity’ will be discussed. The main goal of the present work is to test

existing mean field theories (dealing with the asymmetric polymer interfaces) using the computer simulations. Further, the development of off-lattice model [46, 47] to study the unsymmetric polymer-polymer interfaces is also one of the main aims of the present work. All the interface properties which characterize the interface for the stiffness disparity system and monomer size disparity systems are studied. The critical value of Flory-Huggins parameter, χ , is estimated by the simulation data for the systems of low stiffness disparity.

1.2 Scope of the Present Work

This section is devoted to the scope of the present work. First part of the chapter 2 deals with a general review of analytical theories which are used to study phase behaviors of polymer blends and polymer-polymer interfaces. The second part of the chapter 2 is devoted to discuss computer simulation methodology to study phase behavior and interface properties of polymers.

The chapter 3 deals with different systems of study, model and technical details. Three different systems of polymers namely, flexible-semiflexible system, flexible-stiff rod system and polymers with different monomer sizes i.e., monomer size disparity have been studied. The models which are used to study the interfaces of flexible-semiflexible, flexible-stiff rod and system with monomer size disparity have been discussed. The techniques to determine the interfacial tension by using virial theorem and capillary wave spectrum are also presented.

In chapter 4 results will be presented and discussed. All the interface properties which characterize interfaces namely, interfacial tension, monomer density profiles, interfacial width, chain orientation near the interface, distribution of chain ends and center of mass of chains have been studied for flexible-semiflexible polymers and system with monomer size disparity. Studying interfacial properties at weak segregation limit (by reducing Flory-Huggins parameter), the critical value of χ below which the two types of polymers mix, have been estimated for flexible-semiflexible polymer systems. The simulation data have been compared with the mean field data.

The chapter 5 deals with our findings and conclusions. Further we briefly discuss about an outlook on the future work.