SYNTHESIS AND COMPATIBILIZING EFFECT OF WELL DEFINED LINEAR AND BRANCHED COPOLYMERS IN HETEROGENEOUS POLYSTYRENE-RUBBER BLENDS

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ABSTRACT

This thesis presents results on the synthesis and characterization of linear diblock and star-branched copolymers of styrene and isoprene by anionic polymerization and their application as compatibilizers in heterogeneous poly(styrene)/rubber blends.

Linear diblock copolymers of styrene and isoprene with M_n in the range of 50,000 to 2.6×10^5 and with narrow polydispersities (<1.10) were synthesized over a wide range of composition. Star-branched copolymers of styrene and isoprene having different molecular architectures were also synthesized successfully. The chemical composition was established by ^{1}H NMR. The structure of copolymers was confirmed by FT-IR.

The consequence of adding a diblock copolymer poly(styrene)-b-poly(isoprene) (PS-b-PI) to an immiscible blend of poly(styrene) (PS)/natural rubber (NR) on properties, such as, morphology, particle size distribution, critical micelle concentration (CMC), thermal transition and mechanical properties of the blends were investigated. Scanning electron microscopy (SEM) showed that the block copolymer reduced the domain size of the dispersed phase in the blends. The compatibilizing effect was also investigated as a function of block copolymer molecular weight, composition and concentration. The effect of homopolymer molecular weight, processing conditions and mode of addition on the morphology of the dispersed phase were also investigated by optical microscopy and SEM. The compatibilizing effect of the diblock copolymer arises due to its presence at the interface of PS and NR phases. The respective block segments penetrate into the corresponding phases.

Compatibilizing ability of heteroarm star polymer composed of PS and PI diverged from DVB core was investigated. By using this copolymer as a compatibilizer of an immiscible PS/NR blend, a sharp reduction in particle size was observed. Mechanical properties of the compatibilized blends also improved indicating that the effective penetration of each arm of the heteroarm star into the blend component was operative. The influence of number of arms of star was also studied. In spite of

complex molecular architecture of heteroarm star, it appears to easily migrate to the blend interface.

Molecular architectural effect of compatibilizer was studied using star-block, heteroarm star and linear diblock of PS and PI copolymers as compatibilizer. It was found that heteroarm star polymer having higher number of PS and PI arms were the most efficient.

Dilute solution viscosity (DSV) measurement was used to study the miscibility of polymer blends. Using this approach, blends of PS with NR have been found to be immiscible. Chee's method was applied to determine ΔB and μ of polymer blend solution, where ΔB and $\mu \geq 0$ signifies miscibility and < 0 indicates phase separation. The influence of the nature of the solvent on the miscibility of polymer blend was also studied.

The compatibilizing effect of PS-b-PI in heterogeneous SAN (styrene-co-acrylonitrile) /NR blend was studied. It was found that with increasing amount of the block copolymer, the particle domain size decreased and leveled off at critical micelle concentration (CMC). The influence of block copolymer concentration on impact strength of the blends was also studied. In this approach using an A-b-C diblock copolymer to bridge the incompatibility gap between two polymers B and C have also proven to be valid when A and B is compatible.

A comparative evaluation of properties, such as particle size of the dispersed phase and impact strength of commercial ABS and HIPS with compatibilized SAN/NR and PS/NR blends, prepared in the laboratory were made

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SUMMARY AND CONCLUSIONS

Diblock copolymers have some unique characteristics for improving the compatibility of immiscible polymers, wherein, one block is identical or at least miscible with one blend component, and the second constituent block is identical to/or miscible with the second blend component. Depending on the molecular structure and properties diblock copolymers exhibit high interfacial activity and reinforce the interface. In this thesis, the synthesis and compatibilizing effect of diblock and star-branched copolymers in heterogeneous polystyrene/rubber blends have been examined.

Block copolymers (using sequential monomer addition) of styrene and isoprene were synthesized in the molecular weight range of 50,000-250,000 with controlled molecular weight, narrow polydispersity and a wide range of compositions using sec-BuLi as initiator in cyclohexane at 60 °C. Hydrocarbon solvent was used in order to obtain predominantly cis-l,4-poly(isoprene). Multiarm star-branched polymers contain a central core with linear polymer chains (arms) radiating outwards. Heteroarm star polymer, (A_nB_n), and star-block copolymer, $(AB)_n$, of styrene and isoprene with varying number of arms and chemical composition were synthesized by living anionic polymerization using sec-BuLi as initiator and DVB as coupling agent. The number of arms of star polymer was varied by changing the ratio of [DVB]/[BuLi]. Heteroarm star polymer was synthesized by a combination of arm-first and core-first methods whereas star-block copolymer was synthesized by arm-first method. SEC/MALLS technique was used to determine the absolute molecular weights of block and star-branched copolymers of styrene and isoprene. The chemical composition of the copolymers were determined by ^{1}H NMR.

The effect of addition of a small amount of PS-b-PI on the interfacial properties of PS and NR blends was studied. Compatibilization mechanism of PS-b-PI in compatibilized PS/NR blends was investigated by various techniques such as optical microscopy, SEM, mechanical properties etc. When a small amount of the diblock copolymer was added, more regular and finer dispersion was observed. An increase

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in tensile strength and Young's modulus observed upon addition of PS-b-PI was attributed due to enhanced interfacial adhesion between the phases. The concentration, composition, and molecular weight of the copolymer, composition of the blend, mode of addition of the compatibilizer, homopolymer molecular weight and processing conditions were the parameters that controlled the nature of blend morphology. The area occupied by the compatibilizer molecule at the interface (Σ) was estimated. The (Σ) values were influenced by the molecular weight of homopolymer, blend composition, mode of addition and the nature of the casting solvent. It was found that the conformation of the compatibilizer at the blend interface is neither fully extended nor flat. A portion of the copolymer penetrates into the corresponding homopolymer and the rest remains at the interface.

Heteroarm star polymers of styrene and isoprene (of the type A_nB_n) with larger number of arms can act as emulsifying agent of immiscible PS/NR blends. When the total number of arms (2n) increased from 12 to 34, the CMC value of 30/70 PS/NR blends decreased from 0.42 to 0.23. All the micrographs of the modified blends showed emulsion behavior, since a significant decrease in the microdomain size of the dispersed phase was evident. Reflecting this, the modulus, tensile strength and elongation at the break were improved. These results indicate that each arm of star polymer penetrates efficiently into the corresponding blend component, resulting in the increase of adhesion at the PS/NR blend interphase. Thus, with higher number of arms of the star polymer more effective binding of two components of blend was observed.

The compatibility of binary blends of PS and NR were analyzed by DSV. PS/NR blends are found to be incompatible from the results obtained for Chee's parameters ΔB and μ. The negative value of ΔB and μ is an indication of incompatibility of PS/NR blends in all compositions. The heat of mixing values (ΔH_m) and the interaction parameters (χ) of PS/NR blends further support the incompatibility of the blends. The 'intrinsic viscosities of transfer' approach gives a very good qualitative picture of the interaction among the polymers, and hence, the miscibility. Depending on the strength of the interaction, the magnitude of $\Delta[\eta]$ varies. The effects of PS-b-PI as an emulsifying agent on the interfacial properties of PS/NR blends were studied based on the phase separation behavior. The incompatibility causes the

phenomenon of phase separation of the polymer blend solutions. The block copolymer identical to the component homopolymers acts as the emulsifier which, locates at the interface and extends into the homopolymer phases with which it is compatible. The demixing behavior was found to be a function of diblock copolymer concentration, mode of mixing, nature of solvent and molecular weight of homo and block copolymers. The demixing behavior has been studied by noting the phase separation time and volume of the phase separated region. The addition of block copolymer decreased the demixing behavior of the blends.

PS-b-PI is also an effective compatibilizer for blends of SAN and NR. Addition of the diblock copolymer caused the size of dispersed particles to decrease. Furthermore, the size distribution also became narrower. With increasing concentration of PS-b-PI, the impact strength of the blends improved, reflecting better adhesion between two phases.

SYNOPSIS

The thesis titled **'Synthesis and compatibilizing effect of well defined linear and branched copolymers in heterogeneous polystyrene-rubber blends'** consists of **seven chapters and Chapter 8** provides a summary of results and conclusions.

Introduction

Blend of two or more polymers has been an effective and powerful technique to obtain a new polymeric materials with desirable properties [1,2]. However, most polymer blends are thermodynamically incompatible because of the positive enthalpy change of mixing and the lower entropy change of mixing resulting from the high molecular weight of the polymers. Incompatible polymer blends exhibit coarse morphology and, thus, poor mechanical properties. Therefore, compatibilization techniques have been widely used in order to improve the properties of immiscible polymer blends.

Compatibilization technique can be separated into two categories: physical compatibilization utilizing a pre-made copolymer as a compatibilizer[3-8] and chemical compatibilization with an in situ reactive compatibilizer[9]. In physical compatibilization, the morphology of a polymer blend is controlled with a copolymer concentration in the blend. It has been found that the molecular weight of the copolymer, the copolymer architecture and composition as well as the concentration of the copolymer at the interface are the key parameters that influence the blend morphology.

However, there are some limitations to using a pre-made copolymer as a compatibilizer[10-12]. As the molecular weight of the copolymer increases, less of the copolymer reaches the interface and the remainder stays in the bulk phase owing to the higher possibility of micelle formation of the copolymer. Similarly, if the concentration of the copolymer increases beyond CMC, it forms micelle at the interface causing an adverse effect on emulsifying efficiency.

One of the unresolved issue in polymer blends research is the effect of molecular architecture on the performance of copolymer compatibilizer. There have been few

experimental[13-17] or theoretical[18-19] reports on the study of compatibilizers possessing different molecular architecture, but with a constant molecular weight.

Objectives of the present investigation

a. The present study has been undertaken with a view to synthesize linear diblock copolymer of styrene and isoprene via anionic polymerization over a wide range of composition and molecular weights and to explore their applications as an emulsifying agent in heterogeneous PS/NR blends.

b. Another objective of the work is to synthesize heteroarm star polymer, (A_nB_n) and star-block copolymer, $(AB)_n$, of styrene and isoprene with varying number of arms and chemical compositions by living anionic polymerization using s-BuLi as initiator and DVB as coupling agent. The number of arms of star polymer is varied by changing the ratio of [DVB]/[BuLi]. Heteroarm star was synthesized by a combined method of arm-first and core-first method, whereas, star-block copolymer was synthesized by arm-first method.

c. Compatibilizing ability of heteroarm star polymers of styrene and isoprene segments diverged from DVB core was investigated. The influence of number of arms of star was also studied.

d. The effect of molecular architecture of compatibilizer was studied using star-block, heteroarm star and linear diblock of PS and PI copolymer having similar molecular weights and composition as compatibilizer in heterogeneous blends.

e. Dilute solution viscosity (DSV) and phase separation techniques were used to predict polymer-polymer compatibility.

f. Compatibilizing effect of PS-b-PI in heterogeneous SAN/NR blends was studied. Blend morphology was studied by optical microscopy and scanning electron microscopy. Mechanical property of compatibilized and uncompatibilized blends was studied.

g. The properties of commercial polymer (HIPS and ABS) and compatibilized blends of PS/NR and SAN/NR were examined.

Chapter 1. *Concept and mechanism of compatibilization*

This chapter provides a detailed survey of the literature related to the understanding of the concept of compatibilization and its mechanism of action. Both theoretical and experimental aspects have been described in this chapter. **Chapter 2.** *Objectives of*

the present investigation

This chapter covers the scope and objective of the present investigation.

Chapter 3. *Synthesis and characterization of linear and branched polymers via living anionic polymerization technique*

This chapter contains information regarding the sources of materials used, general purification methods for reagents, methods for preparation and estimation of initiators, techniques for synthesis of linear and branched polymers and their general characterization techniques.

Chapter 4. *Compatibilizing effect of poly(styrene)-b-poly(isoprene) copolymers in heterogeneous polystyrene/natural rubber blends*

This chapter deals with the compatibility of PS/NR, which can be improved by the addition of diblock copolymer of styrene and cis-polyisoprene. The compatibilizing effect is investigated as a function of block copolymer molecular weight, composition and concentration. The effect of homopolymer molecular weight, processing conditions and modes of addition on the morphology of the dispersed phase have been investigated by means of optical and scanning electron microscopy. The addition of the block copolymer improves the mechanical properties of the blend. An attempt has been made to correlate the mechanical property with the morphology of the blends and to understand the conformation of the block copolymer at the blend interface.

Chapter 5. *Heteroarm star polymers as emulsifying agent and influence of molecular architecture of compatibilizer in polymer blends*

This chapter deals with the compatibilizing ability of heteroarm star polymer composed of PS and PI diverged from DVB core. By using this copolymer as a compatibilizer of an immiscible PS/NR blends, a sharp reduction in particle size is observed. Mechanical property of the compatibilized blends also improves indicating the effective penetration of each arm of the heteroarm star into the blend component is operative. The influence of number of arms of star is also studied. Inspite of the complex molecular architecture of the heteroarm star, it can easily migrate to the blend interface.

Effect of molecular architecture of compatibilizer is studied using star-block, heteroarm star and linear diblock of PS and PI copolymers as compatibilizer. It is found that heteroarm star polymer is the most efficient one compared to other two

having similar molecular weight and chemical compositions. Heteroarm star

copolymers having higher number of PS and PI arms are found to be the most efficient compatibilizers.

Chapter 6. *Compatibility studies on solution of polymer blends (polystyrene/natural rubber) by viscometric and phase separation technique*

Dilute solution viscosity (DSV) measurement and phase separation technique has been used to predict polymer-polymer compatibility. Chee's method is applied to determine ΔB and μ of polymer blend solution, where ΔB and $\mu \geq 0$ signifies miscibility and < 0 indicates phase separation. The influence of the nature of the solvent on the miscibility of polymer blend is also studied.

Chapter 7. *Compatibilizing effect ofPS-b-PI in heterogeneous SAN/NR blends*

This chapter deals with the investigation of compatibilizing effect of PS-b-PI in heterogeneous SAN/NR blends. The morphologies and the properties of blends have been modified by the addition of PS-b-PI. The morphology has been studied as a function of copolymer concentration. A sharp decrease in the dispersed domain size is observed by the addition of a few per cent of the copolymer followed by leveling off at higher concentrations. This chapter also deals with a comparative evaluation of properties of a few commercial blends (HIPS, ABS) with compatibilized blends developed in the present study. Comparison of particle size and impact strength of commercial HIPS and compatibilized blend of PS/NR/PS-b-PI having similar composition of HIPS is studied.

Comparison of particle size and impact strength of commercial ABS and compatibilized blend of SAN/NR/PS-b-PI having similar composition of ABS has been examined.

Chapter 8. *Summary and conclusions*

This chapter summarizes the results and describes the salient conclusions of the work reported in this thesis. Scope for the further work is also discussed,

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