Chapter 10

Conclusion and Future Outlook
10.1 Conclusion

Polymer blends have gained much interest and of course have become a new branch of macromolecular science. The field of polymer blends is quite attractive due to the fact that already existing polymers can be used and thus the costly development of new polymers from new monomers can be avoided. Further blending is the most simplest and cheapest route of combining the properties of different polymeric materials.

Although blending looks very attractive, most of the polymer blends are immiscible and incompatible leading to heterophase polymer blends. This heterogeneity is an unfavourable one and this may lead to problems that reflect in the overall performance of the resultant material. The high interfacial tension and poor adhesion between the phases are responsible for the poor dispersion and lack of stability to gross phase segregation which are associated with incompatible blends.

There are different techniques to alleviate the above mentioned problems. Addition of a third component (block or graft copolymer) which is capable of having interaction with the blend components is a well-known method. Development of such a compatible blend system requires a thorough understanding of the copolymer behaviour at the blend interface.

The core point of the thesis consists of the interfacial activity of the compatibiliser (NR-g-PS) in incompatible natural rubber/polystyrene blends. The influence of the compatibiliser on the mechanical, rheological, morphological, thermal, and sorption characteristics of the blends were analysed.
The special features and different types of elastomer blend, problems and solutions of blend incompatibility, techniques of compatibilisation, basic features of compatibilisation, theoretical aspects of compatibilisation, etc. have been discussed in the introduction part of the thesis. In addition to this, earlier studies of compatibilisation of TPEs have been reviewed in detail. The details of the materials used and experimental techniques adopted in the present investigation are given in detail.

The morphology and mechanical properties of unvulcanised NR/PS blends have been analysed with special reference to the effect of blend ratio, processing conditions (solution casting vs. melt mixing) and vulcanising systems. In the case of melt mixed samples, the mixing torque increased with increase of rubber content. The increase in mixing torque with increase in rubber content is due to the higher viscosity of NR phase as compared to PS. The mixing temperature shows an initial and intermediate drop due to the introduction of the material and then it increases with mixing time. The dynamically cured samples show higher mixing torque compared to uncured samples. The morphology of the blends indicates a two-phase structure in which rubber phase is dispersed in the continuous PS matrix at its lower proportions and the reverse is the case at higher proportions of NR, i.e., phase inversion takes place. The nature of casting solvents on the morphology and properties has been studied. Domain size and polydispersity are highest for CHCl₃ casted samples and lowest for C₆H₆ casted samples. The CCl₄ casted samples take intermediate position. In spite of these, CCl₄ casted blends show inferior properties compared to CHCl₃ casted blends. This may be associated with the occlusion of the casting solvents due to their high boiling point (CCl₄, BP 77°C). The changes in morphology in different casting solvents are associated with the different levels of interactions of the blend components with the solvent. In the case of melt mixed samples the tensile and tear strength decrease with increase of rubber content whereas the impact strength increases with increase of rubber content. The same trend is observed in the case of solution casted blends. Although the domain size is smaller in melt mixed samples, the mechanical properties are inferior to solution casted samples. The mechanical and thermal degradation are the major reasons for
the inferior properties of melt mixed samples. The solution casted samples show variation in their properties depending upon the extent of interaction between the blend component and casting solvent. The experimental data was compared with different theoretical models like series, parallel, Coran’s, etc. It has been found that the experimental data are close to Halpin-Tsai model in the case of tear strength both at low and high rubber content. In the case of tensile strength at low rubber content the experimental data are close to parallel model and at high rubber content the data are close to the Coran’s model, in which \( n = 2 \). Dynamically cured samples show increase in mechanical properties compared to uncured samples. Among the varies dynamically crosslinked samples, peroxide system showed the minimum value of impact strength and sulphur system exhibited the maximum value and this could be related to the flexibility of crosslinks in different vulcanised systems. The dynamically cured samples showed very high modulus as compared to uncured samples. The behaviour of different vulcanising systems towards the mechanical properties could be related to the blend morphology, crosslink density and nature of crosslinks.

The compatibilising activity of NR-g-PS in heterogeneous NR/PS blends has been studied in detail. The graft copolymer (NR-g-PS) was characterised by both FTIR and H’NMR spectroscopy. Both the morphology and mechanical properties of NR/PS blends have been investigated. Concentration and molecular weight of the copolymer, composition of the blend, mode of addition of compatibiliser, homopolymer molecular weight and processing conditions were the controlling parameters on blend morphology. Copolymer addition reduces the domain size of the dispersed phase and finally gets levelled off at higher concentrations which is an indication of interfacial saturation. The experimental results were in agreement with the predictions of Noolandi and Hong. The area occupied by the compatibiliser molecule at the interface (\( \Sigma \)) has been estimated. As the molecular weight of the homopolymer decreases, the interfacial area occupied by the copolymer (\( \Sigma \)) increases, and hence more reduction in the domain size was observed. The \( \Sigma \) values were also influenced by the blend composition, mode of
addition and the nature of the casting solvents. By the selection of a suitable solvent having close solubility parameter to that of the homopolymers, the interaction of the compatibiliser with the interface could be enhanced. The mechanical property analysis are in agreement with the morphological changes. It was found that the tensile strength and modulus increase upon the addition of the compatibiliser and finally get levelled off at higher concentration. Attempts were made to deduce the conformation of the compatibiliser at the blend interface. Different models were discussed and found that the actual conformation is neither fully extended nor flat. A portion of the copolymer penetrates into the corresponding homopolymer and the rest of it remains at the interface.

Rheological properties of the blends have been investigated using a capillary rheometer and melt flow indexexer. Blends were prepared by both melt mixing and solution casting techniques. In both cases, the shear viscosity decreased with increase of shear stress indicating pseudoplastic nature. The viscosity of the system was found to increase with increase of rubber content. The solution casted blends showed higher viscosity compared to melt mixed samples. Mechanical degradation of both NR and PS at high temperature and shear must have contributed to the lower viscosity of melt blended samples as compared to solution casted samples. At lower shear rates, the viscosities of the blends are higher than those of the component polymers. However, at higher shear rates, the system exhibits a negative deviation. Thus the viscosity-composition curve of both solution and melt mixed blends showed that the viscosity of the blends are non additive functions of viscosities of NR and PS. The negative deviation in viscosity is associated with very poor physical and chemical interactions across the phase boundaries. Morphology analysis reveal that the particle size reduced significantly at high shear rate. The experimental viscosity values have been compared with theoretical predictions. Melt viscosity of the blends increases upon the addition of a few percent of the compatibiliser (NR-g-PS) followed by a decrease at higher loading. The increase in viscosity has been explained on the basis of the high interfacial
interaction between the blend components. The micelle formation is responsible for the decrease in viscosity at higher graft loading. The SEM analysis of the extrudate surface reveal that the domain size decreases with increase of copolymer loading, and finally gets levelled off at higher copolymer loading. Arrhenius plots and activation energy measurements gave information about the temperature dependence of different blend systems. Melt elastic parameters like die swell, principal normal stress differences, recoverable shear strain, etc. were calculated for both compatibilised and noncompatibilised blends. Melt flow index studies are in agreement with the capillary rheometer data. Master curves have been constructed using the MFI and rheometer data and this could be used to construct the rheograms of the NR/PS systems by simply knowing the MFI data.

The stress-relaxation behaviour of various NR/PS blends in tension has been studied as a function of the effect of strain level, ageing, composition and compatibiliser loading. The rate of relaxation was found to increases with strain level. It was observed that ageing produced interesting effects on the relaxation pattern. Aged samples follow a two-stage relaxation pattern. The rate of relaxation increases with temperature due to the degradation of the sample. The relaxation pattern of different blends depend upon the NR content and phase morphology. The compatibilised blends show a different pattern of relaxation compared to noncompatibilised blends. The compatibilised blends below CMC, followed a two-stage relaxation pattern whereas above CMC the blends showed a three-stage relaxation pattern which is associated with the micelle formation. The compatibilised blends indicated an increase in the rate of relaxation because of the presence of a broader interface and improved interfacial interaction.

The dynamic mechanical properties of NR/PS blends were analysed in detail. It was found that at all frequencies the tan δ values increase with increase in temperature up to the glass transition of NR and thereafter it levels off in the low temperature region ( -70 to 30°C). In the high temperature region it was found that at all frequencies the tan δ values increase with increase in temperature up to the
glass transition of polystyrene and thereafter the values decrease. The tan δ values were found to increase with increase of frequency. The storage modulus decreases with increase of temperature at all frequencies due to the decreasing stiffness of the samples. In all cases as expected, as the frequency increases, the Tg values due to the blend components shifts towards the high temperature region. In all cases, as the frequency increases, the storage modulus values increase and the variation is more pronounced in the transition region. Loss modulus value also increase with increase of frequency. At the low temperature region, the loss modulus values are higher at the low frequencies and lower at higher frequencies. However, in the high temperature region reverse is the case. As the frequency increases, E" peak temperature due to NR phase shifts towards the high temperature region. The damping behaviour increases as the NR content increases. The storage modulus of different NR/PS blends decreased with increase of NR content. The modulus values decrease with temperature and finally levels off at high temperature. In the case of blends with 1.5% compatibiliser, the tan δ values are higher compared to noncompatibilised blends at all frequencies. At low temperature region, addition of 3% compatibiliser decreases the damping behaviour of the blends due to its interfacial activity. But the trend is reversed in the high temperature region because the interfacial activity of the compatibiliser is weakened at high temperature. At higher compatibiliser loading, the tan δ values are increased, due to the formation of micelles which is highly undesirable. Addition of 3% compatibiliser enhances the modulus value. Different theoretical models such as series, parallel, Coran's, Halpin-Tsai, etc. were used to fit the experimental viscoelastic data. It was found that, up to 50 wt % NR, the experimental values are close to Halpin-Tsai model and beyond that the values are close to the Coran’s model.

Cole-Cole plots of compatibilised and non-compatibilised blends showed the heterogeneous nature of the system. However, the compatibilised system shows a tendency to form a homogeneous phase. The time-temperature superposition master curve was constructed via the shifting procedure based on the principle of
time-temperature correspondence. Thus it was enabled to have a complete modulus-time behaviour at a constant temperature.

Thermogravimetric analysis and differential scanning calorimetric analysis were carried out to study the thermal behaviour of NR/PS blends. The effects of blend composition and compatibiliser loading on the thermal behaviour of blends were analysed. It was found that blending improved the thermal properties of the blends. The weight loss of the blends was found to be lower than that of the blend components. The addition of compatibiliser influenced the thermal behaviour. The weight loss of the blends at various temperatures was found to be decreased upon the addition of the compatibiliser. Further, the initial decomposition temperature was raised upon the addition of the compatibiliser. DSC studies indicated the existence of two glass transitions for the non-compatibilised and compatibilised blends. Even with the addition of technological compatibiliser (NR-g-PS) the NR/PS blends are thermodynamically incompatible.

Diffusion and transport of three solvents namely, petrol, mineral turpentine and diesel through dynamically crosslinked NR/PS blends were analysed in Chapter 9. Three vulcanising systems namely, sulphur, mixed and DCP have an important role in the sorption phenomena. Sulphur system shows the highest solvent uptake and the DCP system the minimum. The mixed system occupies the intermediate position. This has been explained based on the flexibility of the crosslinked networks. As the penetrant size increases, the solvent uptake decreases. Solvent uptake is maximum for petrol and minimum for diesel. Mineral turpentine occupies the intermediate position. The value of molar mass between the crosslinks ($M_c$) was estimated for different blend systems and found that it varies in the same order as that of $Q_\infty$, i.e., sulphur > mixed > DCP. As the temperature increases, the equilibrium sorption increases in all the cases. The Arrhenius parameters were computed. The Van’t Hoff’s relationship was used to estimate the entropy, enthalpy and free energy of sorption. Rubber-solvent interaction parameter was estimated. Effect of blend composition on sorption
behaviour was studied and found that the 50/50 NR/PS blend shows the maximum solvent uptake.

10.2 Future outlook

10.2.1 Influence of block copolymer on compatibilisation

In the present investigation, we have carried out the technological compatibilisation of the immiscible natural rubber/polystyrene blends via non-reactive compatibilisation technique, i.e., by the addition of natural rubber-graft-polystyrene. It is well known that the block copolymers are more effective than graft copolymers as far as the interfacial activity is concerned. It is possible to prepare the block copolymer of NR and PS and its interfacial activity could be studied in detail. However, expensive anionic polymerisation technique should be used for the copolymer synthesis. The influence of segmental mass ratio, molecular weight, etc. on the morphology and properties is worth probing.

10.2.2 Interfacial tension measurement

It is expected that the copolymer addition will reduce the interfacial tension in an immiscible blend. The action of a compatibiliser in an immiscible blend can be well followed by the measurement of interfacial tension across the phase boundary with and without the copolymer using highly specialised pendant drop apparatus. This can be followed with the help of a video digital image processing technique. Other techniques such as breaking thread method and embedded fibre retraction technique can also be used for the interfacial tension measurements.

10.2.3 Interfacial thickness measurements

Addition of copolymer to an immiscible blend leads to an increase in the interfacial thickness by the localisation of the copolymer at the blend interface. The techniques of ellipsometry has been used by several researchers to measure the interfacial thickness between two polymer layers. The same can be adopted in this
The measurements can be carried out using an automated ellipsometer with a series of bilayer specimens. Small angle X-ray scattering (SAXS) and neutron scattering (SANS) measurements can also be used to estimate the interfacial thickness with and without the addition of the copolymer.

10.2.4 Location of the copolymer

The copolymer may locate at the blend interface or may present in the bulk. In the second case it may exists either as the dispersed phase or as the continuous one. In some cases, it may exist both at the interface and at the bulk. In all these cases, the location of the copolymer is important. There are several methods which can be successful utilised to locate the copolymer. These include fluorescence spectroscopy, fluorescence microscopy and transmission electron microscopy.

10.2.5 Fabrication of useful products

The use of NR/PS blends for applications such as automobile body parts, dashboards, bumpers, aircraft mouldings, etc. is worth attempting.