Chapter 9

Conclusion and Future Scope of the Work
9.1 Conclusion

Polymer blends have attracted much importance in the recent years since new materials of technological importance can be prepared by simple blending of two or more polymers. Among the different types of polymer blends, thermoplastic elastomers from rubber/plastic blends have gained lot of interest as they combine the excellent processing characteristics of plastic with the performance of rubbers. Thermoplastic elastomers based on blends of isotactic polypropylene (iPP)/acrylonitrile-co-butadiene rubber (NBR) blends combine the oil resistant properties of nitrile rubber and processability and mechanical properties of polypropylene. In this thesis we have made systematic investigations on the morphology and properties of PP/NBR blends. Since these blends are incompatible and immiscible, the effects of compatibilisation and dynamic vulcanisation on morphology and properties were also studied.

Since the morphology is a determining factor in the final properties of polymer blends, a systematic investigation of the morphology and its effect on mechanical properties of PP/NBR blends were conducted. The processability characteristics analysed from the Brabender plastographs show that the viscosity of NBR/PP blends increases with increase in NBR content. Morphology of the blends indicates a two phase structure in which rubber phase is dispersed as domains in the continuous PP matrix at lower proportions of NBR and the size of the domains increases with increase in rubber content. At 70 wt % of NBR, it also forms the continuous phase resulting in a co-continuous morphology. The
mechanical properties of the blends are found to be strongly influenced by the blend ratio. The Young’s modulus, tensile strength and hardness of the blends were decreased with increase in NBR content. The tensile impact strength values decrease with NBR content up to 50 wt % and after that it shows an increase. In general, all the mechanical property-composition curves show a change in slope after 50 wt % NBR. This is associated with the change in morphology of the blends. A negative deviation from the additive line was observed for all the mechanical properties except hardness. Various composite models have been used to fit the experimental mechanical data. The tensile strength and Young’s modulus of the blends could be predicted by the Coran’s equation. The phenolic modified polypropylene and maleic modified polypropylene are found to act as compatibilisers in PP/NBR blend. With the increase in concentration of compatibilisers, the domain size of the dispersed NBR phase decreases, followed by a levelling off at higher concentrations which is an indication of interfacial saturation. The theories of Noolandi and Hong predict a linear decrease of interfacial tension with compatibiliser volume fraction for concentration less than CMC. Considering the fact that the interfacial tension is directly proportional to the domain size, it is demonstrated that the experimental data are in agreement with these theoretical predictions. The mechanical properties of the blend are also increased by the addition of compatibilisers followed by a levelling off at higher concentrations.

The dynamic vulcanisation of PP/NBR blends leads to fine and uniform distribution of rubber particles in the plastic matrix. The size of the dispersed rubber particles depend on the crosslinking systems used. Among the different vulcanising systems used, the sulphur system gives better properties for blends having high plastic content, while DCP system gives better properties for blends with high rubber content. The addition of fillers to PP/NBR blends has not much effect on the mechanical properties. It is observed that the addition of carbon black to PP/NBR blends adversely affects the properties.
The dynamic mechanical analysis of the blends is important as many of the polymeric materials usually undergo cyclic stresses during service. The analysis would also give an idea about the miscibility of the blend system. The effects of blend composition and compatibilisation on the dynamic mechanical properties were investigated in the temperature range -50 to +150°C. These investigations indicate that PP/NBR blends are incompatible as proved by the presence of two α-relaxation peaks corresponding to the Tgs of PP and NBR. As the concentration of rubber increases, the storage modulus of the system decreases, while the loss modulus and tan δ increase. The increase in loss modulus is more pronounced after 50 wt% of NBR in the blend. The change in viscoelastic properties with blend composition is correlated with the blend morphology. Various composite models have been used to fit the experimental viscoelastic data. Takayanagi’s model is found to fit the experimental values for 20% parallel coupling. The addition of phenolic modified polypropylene and maleic anhydride modified polypropylene is found to increase the storage modulus at lower temperature which indicates an increase in interfacial adhesion upon the addition of these compatibilisers. At higher concentration of these compatibilisers the storage modulus decreases due to interfacial saturation. Among the Vulcanised systems, the DCP system shows the highest modulus and sulphur system the lowest. The mixed system shows an intermediate behaviour.

The investigation of melt rheology of these blends would help to optimise the processing conditions required for the production of the material. Hence the melt rheological behaviour of PP/NBR blends has been investigated over a wide range of shear rates and temperatures. The blends show pseudoplastic behaviour which is indicated by a decrease in viscosity with shear rate. The viscosity of these blends increases with increase in NBR concentration and shows a sharp change after 50 wt% of NBR. The variation in viscosity is correlated with the phase change of NBR from dispersed to continuous phase. The blends show negative deviation which indicated lack of interaction between the polar nitrile rubber and non-polar polypropylene.
Various theoretical models have been used to predict the experimental viscosity values. The viscosity values fit well with the values calculated using altered free volume model. The compatibilisation of these blends using phenolic modified polypropylene is found to increase the viscosity of the system, indicating an increase in interfacial interaction. The variation of viscosity is correlated with the phase morphology. As the compatibiliser concentration increases the size of the domain decreases with a levelling off at high concentration. The dynamic vulcanisation of PP/NBR blends leads to fine and uniform distribution of NBR particles and the size of the dispersed NBR particles varies in the order DCP < mixed < sulphur cured system. Among the dynamic vulcanised blends the sulphur cured system has the highest viscosity and DCP cured system has the lowest. In peroxide and mixed cured systems PP is degraded in presence of DCP. The die swell values of the blends have decreased on dynamic vulcanisation. The temperature dependence of viscosity was studied using Arrhenius equation. The compatibilised system show higher values of activation energy compared to uncompatibilised one. A shear rate-temperature superposition master curve has also been developed for polypropylene and 70/30 PP/NBR blend. The melt flow index of PP/NBR blend decreases with increase in rubber concentration. The MFI data have been correlated with capillary rheometer data. The effect of annealing on the morphology of uncompatibilised and compatibilised blends has been investigated. The domain size of NBR particles increased in the uncompatibilised system upon annealing the samples for one hour. Interestingly, the morphology of the compatibilised system is really stable.

The analysis of thermal stability of polymeric materials is necessary for the development of durable products. The thermal degradation of polypropylene/nitrile rubber blends was investigated using thermogravimetric method. The incorporation of nitrile rubber into polypropylene improved the thermal properties of polypropylene. The initial degradation temperature of polypropylene is increased on blending. Among the different blends compositions
the P50 blend shows the lowest degradation temperature. The thermal behaviour of various blend compositions was correlated with blend morphology. The weight loss corresponding to different temperatures is also decreased upon blending. The effect of compatibilisation of PP/NBR blend using phenolic modified polypropylene and maleic anhydride modified polypropylene on thermal degradation was also investigated. The compatibilisation increased the degradation temperature. The dynamic vulcanisation of the blends using sulphur, peroxide and mixed system consisting of sulphur and peroxide, improved the thermal stability. Among the three vulcanised systems, the mixed vulcanised system has the highest degradation temperature and sulphur cured system the lowest. The thermal behaviour of the three types of dynamic vulcanised blends is correlated with the crosslink density and type of crosslinks formed. The melting behaviour of binary PP/NBR blends was also investigated using differential scanning calorimetry. The melting temperature and heat of fusion values decreased upon the addition of NBR. The crystallinity of PP/NBR blends also decreases with increase in nitrile rubber concentration. The crystalline structure of PP/NBR blends was also investigated. The pure polypropylene and the blends showed α-monoclinic structure as evident from the presence of four reflections corresponding to the four planes. The compatibilisation of the blends did not affect the α-monoclinic crystalline structure of PP. The incorporation of nitrile rubber in to polypropylene increased the interplanar distance, which indicates the presence of rubber phase in intra spherulitic regions.

The dielectric properties of PP/NBR blends were also studied to explore the possibility of using these blends as insulating materials. The dielectric properties such as volume resistivity, dielectric constant and tan δ of PP/NBR blends were measured over a wide range of frequencies. The dielectric constant of the pure components and blends decrease with increase of frequency. The variation in dielectric constant is in three stages due to the relaxations in interfacial and orientation polarisation. With the increase of NBR content in the blend, the
dielectric constant increases and shows a sharp change after 50 wt % of loading. The sharp change above 50 wt % NBR is correlated with the morphology of the blend. The experimental dielectric constant values were compared with theoretical models. It is found that the experimental data fit well with the data obtained from Maxwell-Wagner-Sillers equation. The effects of various fillers such as HAF black, silane treated silica and cork on dielectric properties were also investigated. The incorporation of fillers into PP/NBR blends affected the dielectric properties. The dielectric constant increases upon the addition of carbon black and the increase is more pronounced in 30/70 PP/NBR blend. The change is correlated with the formation of network of carbon black particles in the continuous NBR phase at 70 wt % of NBR. In silane treated silica filled blends, the dielectric constant increases up to 20 wt % loading while at 30 wt % loading the ε’ value decreases and in cork filled blends the ε’ value increases by the addition of 10 wt % of cork, while further increase in loading decreases the ε’ values. The increase in ε’ value upon the addition of fillers was correlated with the presence of polar groups in the filler and to the interfacial polarisation. The loss factor increased upon the addition of carbon black and silica while the addition of cork decreased the ε” values. The dynamic vulcanisation leads to an increase in ε’ values. Among the different vulcanising systems used, the sulphur system shows the lowest value and DCP vulcanised system the highest. The mixed system shows an intermediate value. The dissipation factor and loss factor values also increased upon vulcanisation.

The investigation of the transport properties of these blends in various aromatic solvents was carried out to get an idea about the barrier properties of these materials. The mechanism of transport is close to Fickian in PP/NBR blends. As the concentration of NBR increases, in the blend, the equilibrium uptake values and diffusion and permeation coefficients increase. The variation in transport parameters was correlated with morphology of the system. The equilibrium uptake values show a sharp increase after 50 wt % of NBR which is due to the phase
inversion of NBR from dispersed to continuous phase. The experimental permeation coefficients were compared with various theoretical predictions. Maxwell and Robeson's models have been used to predict the experimental permeation coefficients. The effect of nature of crosslinking on transport behaviour was studied. Among the three vulcanising systems used [sulphur, DCP and mixed (S+DCP) systems], the sulphur system shows the highest uptake and DCP the lowest and mixed system shows intermediate behaviour. The difference in the behaviour is correlated with the type of crosslinks formed and crosslinking density. The diffusion and permeation coefficients and $Q_\infty$ values decrease with increase in molar volume of solvents. The effect of different types of fillers on transport properties was also investigated. In the filled blends, the uptake values follow the order cork > silica > carbon black. The activation energy for diffusion and permeation was calculated and are found to decrease with increase in rubber content. Comparison of the crosslink density values with phantom and affine network models indicates that in PP/NBR blends, the network structure can be modelled by affine theory. The experimental and theoretical diffusion curves are in good agreement for the blend systems.

9.2 Future scope of the work

9.2.1 Crystallisation kinetics

The properties of rubber/plastic blends depend on the crystalline structure of plastic matrix. Hence a detailed investigation can be carried out on crystallisation kinetics and crystalline structure of PP/NBR blends. The spherulitic growth rate, spherulite structure and nucleation can be investigated using phase contrast optical microscopy and differential scanning calorimetry.
9.2.2 **Barrier property measurements**

The barrier properties of these blends can be studied to extend its application for the separation of various gases and liquids. The vapour permeation, pervaporation and gas separation studies can be carried out for this purpose.

9.2.3 **Interfacial characterisation**

In the present investigation we have seen that the compatibilisation of PP/NBR blends improved the properties. The investigation of interfacial tension and interfacial thickness in uncompatibilised and compatibilised blends can be studied using various modern techniques. The ellipsometry technique can be used to estimate the interfacial thickness in polymer blends. The small angle X-ray scattering (SAXS) and neutron scattering (SANS) can also be used to study the interfacial thickness. The interfacial tension can be measured using highly specialised pendant drop apparatus or breaking thread methods.

9.2.4 **Fabrication of useful products**

The application of PP/NBR blends for the fabrication of automobile parts such as dash boards, bumpers, etc. can be attempted.