CHAPTER 9
CONCLUSION
Thermoplastic elastomers (TPEs) have tremendous commercial importance since they exhibit thermoplastic processability and rubber like behaviour. They have quickly filled many product requirements formerly held by conventionally cured rubbers. Thermoplastic elastomers from nylon and acrylonitrile-co-butadiene rubber (NBR) produce a new class of material having excellent oil resistance, ozone resistance, good toughness and mechanical properties. In this thesis, efforts are made to investigate the morphology and properties of unmodified and modified nylon/NBR blends. Emphasis has been given in the study of interfacial modification by means of compatibilisation and dynamic vulcanisation and the efficacy of these modifiers to change the morphology, mechanical and viscoelastic properties, flow behaviour, ageing, thermal and crystallisation behaviour.

Morphology of unmodified nylon/NBR blend system indicates a two phase structure in which NBR is dispersed as domain in the continuous nylon phase at lower proportions, but as the proportion of the rubber increases beyond 40%, this component also exists as a continuous phase. It is found that the minor component appears as the dispersed phase and its domain size increases with increase in its concentration. The mechanical properties of the unmodified blends are found to increase rapidly beyond 40% of nylon. This abrupt rise in mechanical properties is associated with the fully continuous nature of the nylon matrix. Mechanical properties such as tensile strength, Young’s modulus, tear strength, elongation at break, hardness and tension set are higher for blends containing higher proportions of nylon.
The modulus also is found to be maximum for composition of higher plastic content. Almost all mechanical properties are found to decrease with the addition of NBR, which is due to the reduced crystallinity of nylon and also due to the poor interfacial interaction at the blend interface. Almost all the mechanical properties except hardness are found to have a negative deviation. The influence of strain rate on the mechanical properties have been analysed. The properties like tensile strength, tear strength and Young's modulus are maximum when the testing speed is 500 mm/min. Various theoretical models have been used to predict the tear strength, tensile strength and Young's modulus of the blends. It is found that the Coran's model fits the experimental results.

Dynamic vulcanisation has imparted significant morphological transformation to the blend. Dynamic vulcanisation of nylon/NBR blends leads to a fine and uniform distribution of rubber particles in the plastic matrix. Further, dynamic crosslinking has prevented the dispersed particles from coalescence. Chlorinated polyethylene (CPE) is used as an effective compatibiliser in such a manner to improve the interfacial adhesion between nylon and NBR and to provide stability against gross segregation of the domains. Compatibilisation reduced the average size of the dispersed phase, provided a uniform and stable morphology by the break-up of the largest particles and it narrowed the size distribution of the dispersed phase. At 3 wt% of the compatibiliser concentration, the domains showed their smallest size and beyond 3% the domain size was found to increase. The compatibilising effect of CPE in nylon/ NBR system is attributed to the formation of a graft between CPE on the NBR surface and nylon. The CPE is adhered on the surface of NBR as a result of radical interaction. Further CPE is found to be an efficient compatibiliser in nylon/nitrile rubber blends as they provided stability against coalescence during annealing. Compatibilisation increased the mechanical properties of the blends due to the increased interfacial adhesion. The mechanical properties of the blends are increased by the addition of compatibilisers followed by a levelling off at
higher concentrations. Dynamic vulcanisation also improved the mechanical properties of nylon/NBR blends. The 70/30 nylon/NBR system shows 160% improvement in tensile strength values as a result of dynamic vulcanisation.

Dynamic mechanical properties of nylon/NBR blends have been investigated with special reference to the effect of blend ratio, compatibilisation, dynamic crosslinking of the elastomer phase and temperature. The dynamic mechanical studies of the uncompatibilised blends indicate two separate transitions corresponding to the T_g's of nylon and NBR phases. This indicates the incompatible nature of the two components of the blends. As the concentration of the NBR phase increases the storage modulus decreases and the damping characteristics and the loss modulus increase. The change in viscoelastic properties are correlated with the morphology of the blends. Various composite models have been used to fit the experimental viscoelastic data. The Coran's model was found to fit with the experimental data. The addition of chlorinated polyethylene as a compatibiliser improved the viscoelastic properties of the nylon/NBR blends, indicating improved interaction between the two components in the compatibilised system. The dynamically crosslinked blends using DCP also showed high modulus values compared to unmodified blends, in spite of the two separate transitions corresponding to nylon and NBR. These results indicate immiscibility of the blends. However, some degree of miscibility is achieved as a result of dynamic crosslinking which is evident from the peak broadening and peak shifting. The activation energies correspond to nylon and NBR transitions increased as a result of compatibilisation and dynamic vulcanisation. The peak width at half height increased as a result of interfacial modification. Dynamic vulcanisation shows two T_g peaks which have come more closer to one another compared to uncrosslinked system.

Rheological properties of the blends have been investigated using a capillary rheometer and melt flow indexer. All the blends show a decrease in viscosity with increase of shear stress indicating pseudoplastic behavior. The
viscosity of the system was found to increase with increase of rubber content. The viscosity-blend composition profile exhibits a positive deviation due to the weak polar-polar interaction in spite of the immiscibility between the two components. The experimental viscosity values are compared with theoretical predictions. The experimental viscosity values fit well with the Mashelkar model. The use of chlorinated polyethylene as compatibiliser increases the melt viscosity of the blends. This increased viscosity has been attributed to the increased interaction between the nylon and NBR as a result of decreased interfacial tension and coalescence due to the introduction of the compatibiliser. The extrudate morphology analyses reveal that the domain size decreased with increase in concentration of the compatibiliser and finally gets levelled off beyond a critical value. The temperature dependency of viscosity of different blend systems was studied using the Arrhenius equation and activation energy measurements. The compatibilised system showed higher values of activation energy compared to the uncompatibilised system which means that the blends become less temperature sensitive in the presence of the compatibiliser. Melt flow index studies are in good agreement with the capillary rheometer data. Master curves have been drawn using the MFI and rheometer data and this could be helpful to construct the rheograms of nylon/NBR blends by simply knowing the MFI values. Among the dynamic crosslinked blends, the DCP cured blends show the higher viscosity compared to sulfur crosslinked systems. Dynamic vulcanisation reduced the die swell values of the nylon/NBR blends. The morphology of both the compatibilised and dynamically vulcanised systems are found to be stable at various shear rates.

The thermal degradation of nylon/NBR blends was investigated using thermogravimetric method. The incorporation of NBR into nylon improved the thermal properties of nylon. All the blend systems show improved initial decomposition temperature ($T_D$) upon the addition of NBR to nylon phase.
The effect of the compatibiliser, chlorinated polyethylene (CPE), on the thermal degradation of nylon/NBR blend was also investigated. The CPE has been found as an effective compatibiliser in nylon/NBR systems as it improves the thermal stability of the systems by providing improvement in the interfacial interaction between nylon and NBR. The compatibiliser increased the decomposition temperature of these systems especially at a critical value of its concentration in the blends. Dynamic vulcanisation using sulphur and DCP also found to provide improvement in the decomposition temperature. DCP cured systems show higher decomposition temperature. Attempts have been made to correlate the thermal behaviour of the dynamically crosslinked systems with the type and strength of the crosslinks and the crosslink density. The kinetic studies of degradation show random nucleation as the mechanism of degradation is the rate controlling process. DSC was also employed to follow the melting behaviour of the nylon/NBR systems. The heat of fusion values (ΔH) decreased with the NBR incorporation. Nylon exhibits cold crystallisation temperature at 75.86°C. The crystallisation temperature decreases with NBR incorporation, but compatibilisation and dynamic vulcanisation increased these values. X-ray diffraction studies reveal the reduction in crystallinity and increase in the interplanar distance of the crystalline nylon as a result of NBR addition. Compatibilisation causes an increase in spherulitic size of nylon as the compatibilised systems exhibit lower width at half height in the WAXS pattern.

Since nylon is a hygroscopic thermoplastic, there is tremendous practicable importance in investigating the water sorption behaviour of nylon based blends. The transport of water through nylon and nylon rich nylon/NBR blends has been investigated. It was found that as the NBR content in the blend increases the final water uptake values increases in spite of the higher initial rate of sorption behaviour exhibited by nylon and nylon rich blends. This has been explained in terms of overshoot effect exhibited by
nylon as a result of the penetrant rejection during chain relaxation. The penetrant overshoot effect was influenced by polymer blend ratio and temperature. All the transport characteristics, except sorption coefficient, are found to vary inversely with increasing elastomer addition. The values of ‘n’ is nearly equal to 0.5, which shows that the diffusion mechanism follows a Fickian trend. The diffusion coefficient increases with temperature and is found to be increasing with increase in concentration of nylon. The presence of water molecules in the blend causes a reduction in the mechanical properties. The mechanical properties such as tensile strength, modulus and yield stress of nylon and the blends are found to decrease due to the water uptake. As expected, the elongation at break increases as a result of water absorption. These effects are attributed to the plasticising action of water molecules and consequent molecular chain flexibility.

Chlorinated polyethylene (CPE) is found as a very effective interfacial modifier in nylon/NBR systems. This increased the viscosity, thermal stability, mechanical properties, viscoelastic behaviour of nylon/NBR blend systems. Therefore, the use of this compatibiliser in nylon/NBR thermoplastic elastomer will broaden the applicability of the blend system.

9.1. Future scope of the work

9.1.1 Vapour sorption studies

Since phase morphology is one of the prominent decisive aspects of the material property, there is considerable importance in the modification of blend morphology and investigating the effect of these changes in morphology on the sorption behaviour of the blend towards the permeation of vapours of various organic solvents. Vapour sorption experiment is also useful to understand the continuity of the phases in the blends. The barrier properties of these blends can be studied to extend its application for the
separation of various gases and liquids. Pervaporation and gas permeation studies can be carried out for this purpose in addition to vapour sorption.

9.1.2 Effect of various fillers

Being an engineering plastic, there is considerable importance in the studies regarding the improvement of material strength of nylon based blends. So the effect of various fillers like, carbon black, silica, clay, cork etc. on dynamically vulcanised nylon / NBR blends are worth attempting. Further studies of interfacial modification like the effect of filler treatment on polymer/polymer and polymer/filler interfaces can be conducted. Striking improvements in mechanical properties can be obtained by incorporating glass fibre with the blends containing high proportions of nylon. This improvement can be achieved without the sacrifice of electrical, frictional and chemical properties.

9.1.3 Fabrication of useful products

Attempts can be made for the fabrication of automobile parts like gears, bearings where feed lubrication is difficult. Besides, the fabrication of dash board panels, seat slides, door handles etc. can be attempted.