# CONCLUSION

B lending two or more polymers to obtain a new material with improved properties is an important practical concept in polymer science and technology. A new system of a polymer blends has been developed from acrylonitrile butadiene rubber (NBR) and poly(ethylene-co-vinyl acetate) (EVA). The results of a systematic and detailed investigation carried out on NBR/EVA blends are presented in this thesis. The mechanical, rheological, dynamic mechanical, transport and thermal properties of the blends were evaluated. The influence of blend composition, cure systems and fillers on these properties have been studied.

The morphology of NBR/EVA blends indicates a two phase structure in which the minor component is dispersed within a continuum of the major component. A co-continuous morphology is obtained when the NBR content is between 40-60%. The mechanical properties such as tensile strength, Young's modulus, elongation at break, tear strength and hardness increase with increase in EVA content. The increase is sharper when the EVA content is more than 40% where it formed a continuous phase. The stress-strain curves of blends with high EVA or NBR content exhibit behaviour similar to that of pure EVA or NBR. The 50/50 blend with a co-continuous morphology shows an intermediate stress-strain behaviour. The variation in properties is related to the morphology of the system. The tear failure mechanism is investigated using scanning electron microscopic examination of the failure surfaces. The fracture patterns are related to the strength and nature of the failure mode of these materials. The high tear strength of EVA is manifested as sinusoidal folds and striations. Of the various theoretical models

used to predict the modulus of the blends the series model predictions are found to be close to experimental results. The recyclability of the blends is studied; it is interesting to note that the properties of the blends are little affected by the recycling process.

The curing behaviour, mechanical properties and failure mode of NBR/EVA blends have been studied with special reference to blend composition, crosslinking systems and fillers. From the cure characteristics it is observed that the peroxide cure system shows the lowest cure time. Enhanced scorch safety is exhibited by the sulphur cured system. The deformation characteristics of NBR/EVA blends is clear from the stress-strain curves. In the EVA rich blends there is an increase in stress with increasing strain which is due to the orientation of crystalline region of EVA in the direction of stress. The effects of different crosslinking systems on the stress-strain behaviour have been explained on the basis of the nature of crosslinks (polysulphidic, C-C linakges, etc.) formed during vulcanisation. The mechanical properties such as tensile strength, elongation at break, Young's modulus, tear strength and hardness increase with an increase in the EVA content. However, in the case of sulphur cured system there is a drop in tensile strength and elongation at break beyond 50% EVA content. This is due to the fact that at high concentration of EVA, it tends to be the continuous phase which cannot be crosslinked by sulphur.

The extent of reinforcement is determined using the Kraus equation and it is found that the reinforcing ability of the fillers is in the order of HAF > SRF > silica > clay. The mechanical properties of the filled systems are in good agreement with reinforcing ability of the filler as established by Kraus equation. The tensile and tear failure surfaces are observed under a scanning electron microscope to follow the failure mechanism. The $N_0P$ exhibits a cracked tensile fracture surface due to its crystallinity and $N_{100}P$, a smooth fracture surface which is characteristic of rubbers. In the tensile fracture surfaces of all the filled systems dewetting phenomenon is observed which is associated with the poor matrix-filler adhesion. In the HAF filled system the dewetting is less predominant because of

its better reinforcing ability. The tear fractograph of $N_0P$ shows tear fronts with folds and striations, characteristic of high tear strength materials. $N_{100}P$ exhibits a smooth tear fracture surface. In the filled systems, crack deviation is observed due to the restrictions to crack propagation by the filler particles. Applicability of various theoretical models to predict the properties of the unfilled and filled blends is also examined. It is found that the Young's modulus of the blends can be predicted using the Kerner model. For the filled systems, the experimental values are higher than the theoretically predicted ones.

The rheological properties of NBR/EVA blend systems have been studied with special reference to the effect of blend composition, curative systems and shear rate. The viscosity of NBR/EVA blends decreases with increasing shear rate i.e., the system exhibits a pseudoplastic behaviour. At a given shear rate, a negative deviation in the viscosity of the blends is observed. Thus, NBR/EVA blends are not miscible systems. The effect of the presence of curative prior to crosslinking, viz., sulphur, peroxide and mixed systems, on the viscosity of NBR/EVA blends is negligible. The flow behaviour index (n') of NBR/EVA system decrease as the NBR content in the blend increases. The n' values of the system are below 1 which is characteristic of pseudoplastic materials. The addition of different curative systems has little effect on the flow behaviour index of these blends prior to crosslinking. The experimental viscosity data of the blends are found to deviate from the viscosity calculated using series model, Hashin's upper and lower limit models. The melt elasticity of these blends is characterised in terms of the die swell, principal normal stress difference, elastic shear modulus and recoverable elastic shear strain. Addition of NBR to EVA results in an increase of the melt elasticity of the system. EVA and EVA rich blends show a higher critical shear rate. A lower critical shear rate is observed for NBR rich blends and pure NBR. As the shear rate increases the extrudate surface exhibits a higher degree of deformation which is associated with the melt fracture that occurs at high shear rates. The extrudate morphology as a function of shear rate and blend composition is studied using a scanning electron microscope. It is seen that the size of the

domain decreases with the increase in shear rate at lower rates of shear. At a high shear rate of 367 s$^{-1}$ the dispersed domains were elongated due to the increased shearing force. It is observed that in $N_{30}$ and $N_{70}$ the minor component is dispersed within the major component and $N_{50}$ exhibited a co-continuous morphology.

The dynamic mechanical analysis of the uncrosslinked and crosslinked NBR/EVA blends has been carried out as a function of blend composition, and crosslinking systems over a wide range of temperature and frequency. The glass transition temperatures of the pure components are very close to each other. Hence the blends also exhibit a single, sharp transition. The variation in tan $\delta_{max}$ with the weight percentage of NBR exhibits transition corresponding to the phase inversion in morphology of the system. This is also evident from the scanning electron micrographs. The damping properties of the blends increase with increasing nitrile rubber content. The modulus curves for all the compositions have three distinct regions: a glassy region, a transition region and a rubbery region. In the glassy and transition region all the blends exhibit nearly same modulus. In the rubbery region (above $T_g$) NBR rich blends exhibit lower modulus. The glass transition temperature is shifted towards higher temperature region with increasing frequency. The damping characteristics of the blends are not much affected by the variation in frequency. The $T_g$ and tan $\delta_{max}$ are shifted towards the higher side with increasing crosslink density. Applicability of various models to predict the storage modulus of the blends is examined and it is found that the experimental values lie close to the Coran's model. Cole-Cole plots does not show any tendency for the formation of a semi-circle which indicates the heterogeneous nature of NBR/EVA blends. A master curve is constructed for the storage modulus of $N_{50}P$ based on the time-temperature superposition principle.

The influence of blend composition, crosslinking systems, filler type, loading, temperature and penetrants on the diffusion process has been analysed. At room temperature, the mode of diffusion is found to be Fickian for the cyclohexanone-NBR/EVA blend systems. At higher temperatures a deviation from the Fickian mode of diffusion is observed. The sorption behaviour of the blends is related to the morphology of the system. The variations in the equilibrium uptake values are explained on the basis of volume fraction of polymer in the swollen

mass, crosslink density and crystallinity. The equilibrium uptake of the filled system decreases upon loading due to reinforcement. The transport coefficients increase with the increase in NBR content. The activation energies for diffusion and permeation processes are estimated. Thermodynamic parameters are determined using Van't Hoffs relationship. Chemical crosslinks are determined using affine and phantom models and it is found that the experimental values lie close to affine model. For different solvents, the variations in the equilibrium uptake are explained based on solubility parameter values.

The thermogravimetric analysis and thermal ageing of NBR/EVA blends have been carried out with special reference to the effect of blend composition, crosslinking systems, filler type and loading. Both NBR and EVA exhibit a two step degradation process. An increase in NBR content of the blend increases the initial and final decomposition temperatures. Among the various crosslinking systems, the peroxide cured system shows the highest initial decomposition temperature indicating a better thermal stability. The activation energy of degradation for the blends is higher than that of the pure components indicating the enhanced thermal stability achieved by blending. The thermal behaviour of the uncrosslinked and crosslinked NBR/EVA blends is analysed by differential scanning calorimeter. The results from DSC also indicates that the introduction of crosslinks shifted the $T_g$ towards a higher temperature. The peak due to melting appears around 80°C. Thus the DSC results corroborate those obtained by DMA.

Among the various filled systems, silica filled system shows the highest thermal stability. The properties are not affected by the mild ageing condition (50°C for 72 h). However, under severe ageing condition (100°C for 72 h) a deterioration in property is observed due to the degradation of the crosslinks. The peroxide cured system exhibits better retention in properties even after severe ageing condition. The oil resistance of the blends is also examined. As expected a considerable improvement in the oil resistance is observed with the addition of NBR.