Chapter 9

Conclusions and Future Scope

Abstract

A brief account of the major conclusions drawn from the present study on the nitrile rubber nanocomposites is summarised in this chapter. Scope for the future investigations and possible applications are also mentioned.
9.1 Conclusions

Nitrile rubber is one of the most widely used, commercialised and mass produced special purpose elastomers. Because of its good processability, resistance to oil, fuel, and chemicals as well as its good mechanical properties after vulcanization, NBR has found a variety of applications in sealants, hoses, belts, shoes, and brake linings. However, NBR exhibits poor mechanical properties without vulcanization and reinforcing fillers. Consequently, fillers, such as polymers, metals and ceramics are often used to modify certain properties of NBR. For example, carbon black is an excellent reinforcing agent due to its strong interaction with NBR. But they suffer from limitations associated with the decreased processability at higher filler loading. Recently, silica has been employed in NBR composites because of its good physical properties and environmental issues caused by carbon black. The reinforcing properties of silica are similar to those of carbon black and they also enable the production of coloured materials. However, it is difficult to obtain a uniform dispersion of silica particles in NBR due to particle aggregation presumably caused by hydrophilic and polar hydroxyl groups on the particle surfaces. Therefore, much attention has recently been given to the preparation of nitrile rubber nanocomposites using some other suitable nanofillers. These nanocomposites exhibit outstanding mechanical properties, improved thermal resistance, low gas permeability and reduced molecular transport. A detailed and systematic study of the impact of filler size and shape as well as filler loading on the properties of nitrile rubber has been presented in this thesis.
The cure behaviour analysis revealed that the torques maximum value was associated with layered silicate filled system, which could be attributed to the intercalation/exfoliation of the nitrile rubber matrix in the LS. Morphology of the different systems was studied using transmission electron microscopy and X-ray diffraction method. XRD results showed presence of intercalation of NBR matrix in to the layers of the silicate filler at low filler loading. The mechanical properties of the nanocomposites show remarkable changes due to the differences in particle geometry and the chemical nature of the fillers. The filler geometry has significant effect on the mechanical properties of the composites owing to the enhanced availability of interfacial area per unit volume. The layered silicate showed maximum enhancement in mechanical properties because of the very high surface area to volume ratio in comparison with calcium phosphate and titanium dioxide. In CP nanocomposites a moderate increase was noticed whereas in TO composites the increase was minimum due to larger particle size, which resulted in a weak filler-matrix interaction. All these observed mechanical properties were well supported by the morphological analysis results. Transmission electron microscopy provided clear evidence for the intercalation of NBR matrix in layered silicate in comparison with CP and TO fillers. The crosslink density results determined by swelling method of different systems were in agreement with the observed tensile properties. Kraus plot analysis revealed the interactive nature of the different fillers from the slopes of the curves. The mathematical modelling of different fillers was almost in agreement with the experimental values.
The dynamic mechanical properties of nanocomposites were analysed. The results showed that particle geometry has pronounced effect on the loss modulus, storage modulus and glass transition temperature values. It was observed that upon the addition of nano fillers, the storage modulus increased considerably. The results clearly showed that the addition of layered silicate into NBR matrix resulted in a remarkable increase in the stiffness of material. This might be due to the enhanced surface area available with layered silicate filler for effective interaction with the polymer matrix. The loss tangent curves of the nanocomposite samples indicated a shift in tan δ peak to higher temperatures, which is proportional to the filler loading. The layered silicate showed maximum enhancement in the dynamical mechanical properties because of the very high aspect ratio in comparison with CP and TO fillers. The rheological behaviour of the nanocomposites were analysed with special reference to filler loading, particle size, and chemical nature of the filler. It has been observed that loss modulus of the filled systems show the same trend as that of storage modulus and it magnitude increases with the increase in frequency. The value was higher for filled system compared to neat polymer. In comparison with spherical particles, layered silicate filled system showed good loss modulus. The surface-to-volume ratio of the layered silicate filler is abnormally high and hence it provides sufficiently high surface area for the effective heat transfer process. Viscosity of the particle filled system is found to decrease with the increase in frequency. For a specified frequency, the viscosity increases with filler loading and is found to be maximum with layered clay loading. This can be attributed to the degree of compatibility
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between the matrix and the filler particle. The viscosity gain was found to be maximum with layered silicate filled system.

Layered silicate filled nanocomposite showed higher thermal resistance in comparison with nanocomposites having more spherical fillers. The nano fillers acted as a barrier by forming a coating on the surface of the polymer. Since the $T_g$ values are an indication of segmental mobility of polymer in presence of fillers, the addition of layered silicate restricted the segmental mobility more effectively than TO and CP. This also resulted in the minimum heat capacity value of the layered silicate filled system. The activation energy needed for the thermal degradation of the layered silicate filled sample is found to be higher than that of gum and other filled samples.

The molecular transport properties of nano-structured layered silicates and more spherical CP and TO reinforced nitrile rubber were investigated using solvents such as benzene, toluene and $p$-xylene. The unexpected decrease in molecular transport through layered silicate filled nanocomposites was because of increased polymer/filler interaction, which resulted in tortuosity of path and the reduced transport area in polymeric membrane. The diffusion coefficient of filled samples decreased as a function of filler concentration. It was found that the polar–polar interaction between the solvent and the polymer matrix played an important role in the molecular transport. The addition of filler decreased the swelling coefficient of the nanocomposites and hence the oil repellence of the matrix. The swelling coefficient values in commercial oil indicate that the incorporation of layered silicate further increased the oil repellence of nitrile rubber.
The gas permeability of the nanocomposites was investigated using permeant gases such as oxygen and carbon dioxide. The results highlighted the fact that the layered silicate showed reduced gas permeability in comparison with CP and TO filled systems. This could be attributed to very high aspect ratio of the layered silicate that resulted in better matrix-filler interaction. The relative fractional free volume measurements revealed that layered silicate filled system could provide minimum free volume hence showing good barrier property. An increase in filler loading could enhance the barrier property considerably in the case of layered silicate filled system. But the same trend was very weak with CP and TO filled system.

The dielectric properties of the nitrile rubber nanocomposites were studied at a frequency range of 500Hz–5MHz. The nanocomposites showed a decrease in volume resistivity with the addition of fillers. In comparison with TO and CP filled nitrile rubber composites, layered silicate filled system exhibited much decrease in volume resistivity indicative of more conductivity of the system. It has been observed that layered silicate filled system showed enhanced conductivity in comparison with CP and TO filled systems. Maximum dielectric permittivity is shown by layered silicate filled system. The presence of fillers in nitrile rubber leads to an overwhelming presence of polar groups giving rise to dipole or orientation polarizability.

To conclude with the present thesis the major observations of the various studies were the following. The filler geometry played an important role on the properties of the nitrile rubber system. Among the fillers, layered silicate imparted maximum filler – matrix interaction
owing to the high aspect ratio. NBR/LS system showed better mechanical, dynamic mechanical, gas barrier, solvent and thermal resistance in comparison with NBR/CP and NBR/TO systems.

9.2 Future scope

NBR is and will continue to be a complex family of workhorse elastomers. The unique balance of oil, chemical, heat and cold resistance allows it to work well in a wide variety of automotive and industrial applications. The family is well differentiated to include general purpose types for cost sensitive applications and specialty products for more demanding service conditions.

9.2.1 Solid state nuclear magnetic resonance studies

Solid state NMR is highly useful for the determination of crosslink density present in a system. The detailed mechanism of vulcanization can be drawn from solid state $^{13}\text{C}$ NMR. This is a powerful method for the investigation of structural changes upon vulcanisation especially in presence of fillers. The magnetic field near the filler particle is different from the rest of the sample. Therefore the polymer chains near the filler particles experience a different resonance frequency. This change in frequency causes a shift in NMR spectrum.

9.2.2 Flame retardant properties

The decreased flammability of nanocomposites is one of the most important properties of nanocomposites. The Cone calorimeter is one of the most effective methods for the analysis of the fire retardant properties of polymeric materials. The properties such as the heat release rate (HRR), smoke production and CO$_2$ yield are vital to the evaluation of the
fire safety of materials. The flame retardant mechanism of nanocomposites involves a high performance carbonaceous silicate char which builds upon the surface of the polymeric material upon burning. This offers a coating to the underlying material and slows the decomposition due to burning.

9.3 Applications

NBR nanocomposites find lot of applications in the areas requiring oil, fuel, and chemical resistance. In the automobile field NBR nanocomposites can be used in fuel and oil handling hose, seals and water handling applications. On the industrial side, nitrile rubber nanocomposites find applications in roll covers, hydraulic hoses, conveyor belting, graphic arts, oil field packers, and seals for all kinds of plumbing and appliance applications.