Chapter 9

Summary and Conclusions

A novel route for preparing maleated natural rubber (MA-g-NR) was developed by grafting maleic anhydride onto natural rubber (NR) by γ-radiation. This route is cleaner (avoids the use of chemicals), faster (higher throughput in a single batch) and versatile (product quality can be controlled by the radiation dosage). The maleated natural rubber thus produced has very attractive properties due to its polarity compared to unmodified natural rubber and can be utilized for a variety of applications. The major finding of the study is that the maleated natural rubber can be successfully utilized for developing nanocomposites based on nanoclay.

The field of nanotechnology is one of the most popular areas for current research and development in basically all technical disciplines. This obviously includes polymer science and technology. Polymer nanocomposites have received much attention due to the nanoscale dispersion and very high aspect ratio of nanofillers. Polymer layered silicate (PLS) nanocomposites often exhibit remarkable improvement in material properties when compared with the virgin polymer or conventional micro-and macro-composites. These improvements can include high moduli and electrical properties, increased tensile strength, heat resistance, tear strength, decreased gas permeability, swelling to solvents and flammability.

A key factor in the polymer-organoclay interaction is the affinity polymer segments have for the silicate surface. The degree of dispersion of layered silicate in a particular polymer matrix depends on the interlayer cation. To support intercalation and exfoliation the interlayer distance should be greater than 1.5nm and the layered structure should be broken down. Thus the polymer interaction might be made more effective by increasing the interlayer distance.
detailed and systematic study of maleated natural rubber clay nanocomposites by direct and masterbatch technique varying the maleic anhydride content and clay content in order to optimize its properties is presented in the thesis.

The grafting of maleic anhydride (MA) on natural rubber by gamma (γ) radiation has been the first part of this investigation. The modification of rubber using maleic anhydride improves its compatibility with different types of fillers. The effect of radiation dosage (0.5-10kGy) and MA concentration on grafting efficiency was evaluated. The MA content in MA-g-NR increased from 0.7% to 9.1% on increasing the MA concentration (from 1 to 10% of NR) in the reaction mixture. But high MA content retards the curing reactions of the rubber compositions. The MA grafted polymers also have been used extensively in the area of polymer reactive blending, as blend components or as compatibilizers. Grafted rubber can also be produced through chemical route. When compared to chemical routes, the novel radiation route adopted in this study is pollution free and adaptable for bulk production. It is observed that the MA grafting reaction strongly dependant on the radiation dosage. The MA content increases sharply up to a radiation dose of 2.5kGy and then decreases on further increasing the dosage. Highest grafting efficiency was observed at a dosage of 2.5kGy from IR and titration method. When concentrations of 1, 3, 5 and 10percentages were taken the MA content proportionately increased from 0.7% to 9.1%.

Even though maleated natural rubber can be utilized for a variety of applications, this study mainly focused on the preparation and characterization of maleated natural rubber organoclay nanocomposites using hydroxyethyl substituted tallow ammonium as the organo-modifier. Effect of inter layer distance of the layered clay on the cure characteristics, mechanical properties and transport properties of natural rubber and maleated natural rubber by direct and master batch method were investigated. The improvement in properties were in the order NR <MA-g-NR direct <MA-g-NR master batch. Maximum torque of nanoclay filled compounds increased with increase in clay content while the cure time
reduced, which shows the accelerating effect of organoclays in the curing of rubber. This reduction in cure time marginally increased with the increase in interlayer distance of clay. It is seen that the nanocomposite with clay having higher interlayer distance show better mechanical properties. This shows that as the interlayer distance increases, the polymer chains penetrate more easily into the clay layers, which make the formation of intercalated structure. The morphology of filler dispersion in rubber matrix was analyzed using the transmission electron microscopy.

The mechanical properties such as tensile strength, elongation at break, modulus at 300% elongation, and tear strength of the nanocomposites were analyzed. The tensile strength increased with the concentration of clay for MA-g-NR and NR systems.

10% MA concentration was taken in the masterbatch technique. An increment of 87.33% in tensile strength is observed for 10MA-g-NR at 5wt% nanoclay in 40phr batch when compared to the pure NR gum sample. While on the other hand 10MA-g-NR nanocomposites when compared to the 5MA-g-NR at 5wt% nanoclay loading shows an increase in tensile strength of 12.14%. 10MA-g-NR in 40phr batch & 5MA-g-NR with 5wt% nanoclay shows a decrement of 26.83 & 7.20% respectively in the case of elongation at break. The decrease at higher loading is due to the enhancement in rigidity of the material and is possibly caused by the reduction in tensile crystallization. All the systems show the same trend. The increase in d-spacing for these layered clays is evident from X-ray results. TEM photographs also confirm the formation of an intercalated structure.

The thermal stability of nanofilled samples was higher due to the obstructed diffusion of volatile decomposition products within the nanocomposite. However, for a few samples at higher concentration of nanofiller, thermal stability decreased due to the reduced degree of delamination of clay in the matrix. The nanofillers act as a barrier by forming a coating on the surface of the polymer. As a result the thermal stability of the polymer nanocomposite
increases. The activation energy required for thermal degradation of MA-g-NR nanocomposites was determined by Coats-Redfem and Freeman Carroll plots. The activation energy required for thermal degradation of nanofilled samples was found to be higher than that of unfilled systems. Higher the activation energy the greater was the thermal stability. The ageing resistance of MA-g-NR nanocomposites was found to be higher than the unfilled system. The flame retardancy of MA-g-NR nanocomposites is not much improved when compared to unfilled sample.

The transport properties of MA-g-NR nanocomposites with a low level of filler loading were studied in detail. A considerable decrease in diffusion, permeation and sorption coefficients were observed for nanocomposites. The permeation resistance of the nanocomposites was confirmed by the gas permeability testing and it fits with the Nielson's model, which describes the tortuosity effect of plate like particulates on the gas permeability of polymer composite structures. The percentage mass of oil absorbed with nanoclay for 5, 3, and 1% MA in MA-g-NR nanocomposites were studied in transformer oil, hydraulic oil and engine oil. It is observed that the swelling values of 5MA-g-NR nanocomposites are found to be much less when compared to 3MA-g-NR and 1MA-g-NR nanocomposites and also the swelling index values is lower for transformer oil and higher for engine oil. This can be explained in terms of the polar-polar interaction between the polymer and filler. The increase in filler content (1-7wt%) also shows reduced swelling index values. The reduction of swelling upon the addition of layered silicates is due to the enhanced rubber/filler interaction. This can also be explained in terms of the higher tortuosity of path and the reduced transport area in the rubber matrix in presence of nanoclay.

The dielectric property for MA-g-NR nanocomposites is higher for unfilled system when compared to gum in all cases. The dielectric property of maleated NR gum is higher than pure NR gum due to the polar nature of maleated rubber. When nanoclay is added to maleated system the polarity is reduced due to the
interaction of OH group of organoclay with acid group of maleated rubber. The hydrogen bonding takes place here and this directs to the interaction between the maleated rubber and filler. Filled MA-g-NR nanocomposites show increased storage modulus. Here the tan δ value is reduced owing to the better dispersion of clay layers in the matrix. The loss modulus also shows the same trend as tan δ.