Conclusions

Nanoparticles are finding wide applications in diverse areas of science and technology including drug delivery, diagnostics, sensors, catalysts, as fillers and additives in structural components such as polymers, rubbers, concrete etc. Nanoparticles for various applications are synthesized by the chemical route popularly known as *bottom up* synthesis. In the chemical route also the solution based synthesis techniques are more commonly used technique and easier to implement.

Since nanoparticles have very high surface energies it is difficult to retain their small size over a period of time, as particles have tendency to agglomerate. One idea forwarded for retaining the size of nanoparticles is to synthesize them in the inner droplets of reverse micelles and microemulsions. These entities are often referred as microheterogeneous systems which are small aggregate system of molecules within a solvent.

Microemulsions are clear, thermodynamically stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant with dispersed domain diameter varying approximately from 1 to 100 nm. Aqueous phase may contain salt(s) and/or other ingredients, and the "oil" may actually be a complex mixture of different hydrocarbons In contrast to ordinary emulsions, microemulsions form upon simple mixing of the components and do not require the high shear conditions generally used in the formation of ordinary emulsions.

In the present investigation standard microemulsion formulations have been used to synthesize nanoparticles of titania and cadmium selenide in the inner phase of microemulsions and reverse micelles. Further the application of commercially available nanomaterial - organoclay having pillared structure, was explored for the synthesis of nanocomposites for use as tire inner liners. The summary of experimental work and significant conclusions drawn from the work are listed below.

6.1 Experimental

Microemulsion for titania synthesis was formulated with cyclohexane as the continuous phase, Triton X-100 was the surfactant and n-hexanol was used as cosurfactant and electrolyte solution as the dispersed phase. Two microemulsions (microemulsion I and microemulsion II) with identical composition but in a different aqueous phase are taken. The aqueous phase in microemulsion I was an aqueous solution of $TiCl_4$, whereas the aqueous phase in microemulsion II was the precipitating agent aqueous ammonium hydroxide solution.

The two microemulsions were mixed with vigorous stirring at room temperature. The microemulsions II which serves as the precipitating agent was slowly added to the microemulsion I. Due to the continuous collisions and coalescence of the droplets of water-in-oil micro-emulsions, the reacting species in microemulsions I and II ($TiCl_4$ and ammonium hydroxide, respectively) come in contact with each other and react. This leads to the precipitation of titanium hydroxide within the aqueous cores of the microemulsion.

Microemulsion synthesis of CdSe proceeded with taking n-heptane as the solvent, Triton X 100 as surfactant and aqueous solution of cadmium nitrate tetrahydrate as the dispersed phase to form reverse micelle with Cd salts in the inner core of micelle, to this solution was added a mixture of sodium selenite mixed with hydrazine hydrate leading to formation of deep red precipitate of CdSe.

Sol-gel synthesis of titania was also attempted reacting $TiCl_4$ and different alcohols. Hydrothermal synthesis of titania was used for reference. Particles formed were characterized using XRD, FTIR, Raman IR and SEM. Photoluminescence spectra of the CdSe particles were determined.

6.2 Synthesis of particles in microheheterogeneous media

Titanium hydroxide precipitates were synthesized by varying the titanium precursor concentration as well as the ammonia solution concentration since titania particles were the end product the precipitates had to be calcined. Calcinations temperatures above 680^{o} C ensured the formation of rutile phase of titanium dioxide lower temperatures led to formation of mixed phases as revealed by XRD.

Differential thermal analysis of the product indicated prominent endotherms below 180^{0} C which can be mainly due to the free adsorbed water. However, there was only one sharp endotherm for the sample. There is a broad exothermic shoulder from $200\text{-}380^{0}$ C which corresponds to the decomposition of residual –OH groups and the condensation of non-bonded oxygen. The process continues with the exothermic shoulder which indicates the increase in crystallization of anatase phase. At round 580^{0} C, the product completely transforms into anatase. After 620^0 C, there is a constant exotherm which indicated the appearance of rutile phase and there after no significant thermal effects were observed.

The titanium hydroxide samples prepared with different concentration of precursors showed different morphologies SEM images of samples dispersed in acetone and propanol showed that agglomeration of the particles was more in case acetone as the dispersed medium the particle size was estimated to be around 100 nm.

Sol-gel method resulted in greater yield of titania particles with greater crystallinity. However, FTIR-Raman spectra did not reveal an significant difeerence in particles synthesized from different alcohols. In this case also only particles calcined above 700^o C were converted to rutile phase.

CdSe particles were formed with equimolar concentration of Cd and Se and also with excess of Cd as well as with excess of Se. XRD revealed that there is lesser degree of crystallinity when Cd precursor is in excess. Matching the experimental XRD data with ICDD standard indicates that CdSe formed in this case had cubic structure. The CdSe phase in these particles was only 47.7%. Excess of Se leads to formation of particles having distinct diffraction peak of CdSe particles with 69.7% phase of CdSe of which 56.3% of hexagonal structure and 13.4% of cubic structure are shown by XRD. There is also formation of CdSe oxides that were also formed when Cd was in excess.

Morphological observation shows dendritic growth of nanorods of CdSe having sizes significantly lower than 100 nm. Photoluminescence measurements were carried out on the samples using an excitation wavelength of 400 nm. The average peak in the Emission PL spectra is centered around 250 nm. The average peak in the excitation PL spectra is centered around 400 nm. There is deviation of these peaks with the PL peak from bulk wurtzite CdSe. This may be due to oxides and hydrates forms of CdSe particles present in the reaction system. However, the sharp peak of PL spectra in the cases inferred about the existence of semiconductor particles.

6.3 Application of Nanoparticles in Synthesis of Rubber Nanocomposites

Rubber nanocomposites were synthesized for application as tire inner liners using Natural rubber and Bromobutyl rubber other ingredients were sulfur, zinc oxide, MBTS Accelerator, 6 PPD and antioxidant. The fillers used in this study carbon black and nanoclay.

Compounding was done in a laboratory mixer. The nanoclay was used in the above formulations at 2, 4, 6 and 8 phr respectively the study was oriented to focus on the possible substitution of carbon black by nanoclay.

Characterization of the rubber nanocomposites were done based on physical testing, rheological testing, dnamic mechanical analysis, wide angle XRD, transmission electron microscopy and atomic force microscopy.

Hardness of rubber nanocomposites was maximum with carbon black loading of 40% and declined when the carbon black content was decreased interestingly a linear relationship appears between amount of filler and the hardness. Nanoclay reinforcement is reasonably good even at low filler loading, the problem however is to incorporate nano filler in the rubber matrix. The tensile strength increases considerably in the presence of nanoclay than in the presence of carbon black and over here also we find a more or less linear relationship existing between tensile strength and mixed filler loading. Same is the case with tear strength, but we observe that carbon black influences tear strength more significantly than nanoclay.

The addition of nanoclay to the rubber compound causes faster curing as indicated by the torque development time Tc10, Tc50, Tc 90. Curing is faster in presence of nanoclay in comparison with carbon black. Mooney viscosity (MV) also shows decrease in value with the substitution of carbon black with nanoclay indicating a rubber which has ease in its processability, this behavior is attributed to the greater homogeneity of the rubber matrix as carbon black component declines and nanofiller loading increases.

Viscoelastic properties of nanocomposites were determined by dynamic mechanical measurement at two temperatures 30^{o}C and 60^{o}C. The dynamical properties such as storage modulus ($G^{'}$), loss modulus (G”), Tan δ and loss compliance (J) have great influence on the performance of the nanocomposites during application. Tan δ which is the ratio of loss modulus to storage modulus of the compound i.e the ratio of viscous response to elastic response of the material represents the hysteresis loss of the compound. Hysteresis loss is greatly influenced by filler-filler interaction, higher the filler-filler interaction higher will be the hysteresis loss.

Wide angle X-ray diffraction (WAXD) was performed on the nanocomposite containing 8 phr of nanoclay and the same is compared with the diffraction pattern of the nanoclay. The basal spacing value of nanoclay obtained experimentally and from the literature of the supplier is 3.15 nm. The increase in the basal spacing d_{001} of the nanocomposite sample shows that the clay has intercalated in the rubber matrix.

The filler dispersion in the nanocomposites was studied by transmission electron microscopy (TEM). The TEM image of sample M5 that contains only nanoclay (8 phr) reveals the intercalation of nanoclay layers resulting in hair like structures. AFM was performed using the tapping mode (intermittent contact –AFM), the high sensitivity of this technique results in high resolution images of even very soft samples. The surface roughness parameters of the nanocomposites show that even in absence of fillers the gum rubber compound of BIIR-NR has considerable roughness addition of fillers in a way smoothens the sheet surface. When only nanoclay is present as filler in the sample the roughness is considerably reduced, it appears that the nano filler induces a very fine scale of mixing of the polymer and consequently influences the physical properties of the sample significantly.

It was concluded that there is a good case of replacing the inner liner formulations currently incorporating carbon black by either carbon black- nanoclay dual filler system or by nanoclay alone. All the relevant physical, rheological and elastic properties are satisfied by these nanocomposites.

6.4 Future Work

Nanoparticle synthesis is a rather new branch of science and technology. Although, the chemistry is reasonably well understood but the engineering of such reactions is in a nascent stage of development. There is a need to properly classify these reactions in a fashion that appropriate techniques are adopted for synthesis. Reactions with multiple steps lose their novelty when synthesized in microheterogeneous media like microemulsions and the advantage gained from restricted reaction volume is lost. More focused and rigorous investigations are necessary to resolve engineering problems with respect to nanoparticle synthesis.

Use of nanoparticles to develop nanocomposites is being extensively investigated. The results obtained in this study are very encouraging to focus attention to develop nanocomposites on commercial scale for tire inner liners. Additional experiments on the permeability of the nanocomposites and its relation to viscoelastic properties needs to be evaluated prior to a commercial weightage of the new genre of inner liners.