

Efficient dispersion of nanofillers in the polymer matrix plays a major role in the preparation of high performance polymer nanocomposites. Conventional methods of composite preparation were found to be ineffective due to the severe agglomeration of nanofillers in the polymer. In the present investigation an attempt has been made to prepare rubber nanocomposites with segregated structure of nanofillers. Segregated structure has more significance in the case of conductive fillers because of the ultra-low percolation threshold exhibited by these composites. Segregated electrically conductive polymer composites (s-CPCs) have conductive fillers segregated at the interfaces of the polymeric particles instead of being randomly dispersed in the polymer matrix. In the present investigation NR and XNBR were used as polymer matrices, MWCNT was chosen as the conductive nanofiller and nanosilica as the modifier to MWCNTs. In order to ensure efficient dispersion of nanofiller in the rubber, aqueous dispersion of the nanofiller was prepared and mixed with the rubber latex. A second processing route was adopted to study the effect of processing method on the distribution of nanofillers in the rubber nanocomposite and hence the properties, especially, the mechanical and electrical properties was studied.

MWCNTs are known for their exceptional mechanical and electrical properties and can contribute outstanding properties to polymer matrices.

The main difficulty in obtaining a homogeneous dispersion of CNTs is their tendency to remain as bundles due to strong van der Waals force of attraction. To overcome this difficulty two types of modifications were done on MWCNTs to disperse them uniformly in water so that these can be mixed with NR and XNBR latices efficiently. The use of non-ionic surfactant, Vulcastab VL as a dispersant for MWCNT in water is described in Part A of chapter 3. Concentration of VL and sonication energy required for stable nanotube dispersion has been optimised with the help of UV-vis spectral studies and particle size analysis based on dynamic light scattering. CNT to VL weight ratio has been optimised to be 1:1 for getting stable aqueous dispersions of MWCNTs. Minimum sonication energy required was 85000 J. Morphological studies using TEM confirmed the formation of surfactant wrapped exfoliated MWCNTs.

Surfactant treated nanotube dispersions were mixed with NR latex, compounded and film cast to get NR-MWCNT composites. TEM images of the composites revealed the presence of a segregated network of nanotubes throughout the NR matrix. The composites exhibited very good mechanical properties with 68% increase in tensile strength, 80% increase in tensile modulus and 55% increase in tear strength at 0.1phr MWCNT loading. A very low percolation threshold of 0.043 vol% obtained from electrical conductivity studies confirmed the presence of segregated nanotube network in which the individual CNTs are aligned along the periphery of the rubber particles in the composite. Dielectric properties of the composites were promising but the DC conductivity and AC conductivity (at low frequency) were far below the expected values due to the presence of insulating surfactant coating over the nanotubes.

The electrical properties of MWCNT based NR composites were improved by chemical modification of MWCNT (Chapter 4A), which involved acid treatment of MWCNTs. Polar hydrophilic groups such as

hydroxyl and carboxyl moieties introduced on the nanotube surface by oxidation with H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> mixture assisted in getting stable aqueous dispersions of MWCNTs. FTIR spectra, Raman spectra, XPS and TGA confirmed the presence of carboxyl groups on the MWCNT surface. Morphological studies of MWCNTR using SEM and TEM further proved that the acid treatment shortens and purifies the nanotubes and helps in debundling of the MWCNTs into individual tubes.

Aqueous dispersions of oxidised MWCNTs (MWCNTRs) were mixed with NR latex, compounded and film cast to prepare NR-MWCNTR composites. The composites exhibited beautiful segregated MWCNTR network in NR giving rise to low electrical percolation threshold (0.086 vol% or 0.2 phr), good electrical conductivity and high dielectric constant. Along with increase in dielectric constant, there has been proportional increase in the dielectric loss for these composites. The composites exhibit good mechanical properties with 61% improvement in tensile strength, 75 % in tensile modulus and 59 % in tear strength at 0.5 phr of MWCNTR. The DC conductivity increases from  $1.7 \times 10^{-12}$  to  $5.65 \times 10^{-7}$  Sm<sup>-1</sup> with 0.3 phr MWCNTR (0.1293 vol%). The inclusion of 1.0 phr MWCNTR in the NR matrix increased the dielectric constant from 4.7 for pure NR to 918 at 100 Hz. The AC conductivity reached a value of 10<sup>-4</sup> S/m for the nanocomposite at 1 kHz. These, nanoscale, flexible, reinforced natural rubber based composites with high dielectric constant and dielectric loss can find application as electromagnetic wave absorbers in the low frequency region.

NR-MWCNTR composites prepared were of high dielectric loss and an attempt to reduce the dielectric loss by incorporation of insulating nanosilica along with carboxylated MWCNTs was done. Influence of colloidal nanosilica on the properties of NR is described in Chapter 5. NRSF composites prepared by film casting and curing of the nanosilica/natural rubber latex compound show segregated structure of nanosilica within the NR matrix. The rigid

network imparted significant improvement in tensile strength (60%), tear resistance (157%) and tensile modulus (90%) at 5 phr silica. The mol% uptake of toluene ( $Q_t$ ) is reduced for the composite by 67% which could be explained in terms of the reduction in the ease of penetration of solvent due to the increase in tortuosity created by the segregated silica network in NR.

In order to understand how the processing method influences the filler morphology inside a rubber and hence the properties of the composites, NR/nanosilica composites were prepared using Haake mixer. Here also latex stage mixing of colloidal nanosilica with NR was done as the first step and then instead of film casting the mix was coagulated and the dried coagulum was mixed in the Haake internal mixer to get NRSH nanocomposites. Microstructure analysis of the composite using TEM revealed randomly dispersed nanosilica inside the rubber. This shows that the web-like nanosilica network in the coagulum has been broken by the intense shear forces in the internal mixer and the final sample contains uniformly distributed nanosilica in NR matrix. The composites exhibit significant improvement in the mechanical properties at 5 phr silica loading. NRSH5 nanocomposite exhibited good mechanical properties with 28% enhancement in modulus, 38% in tensile strength and 29% in tear strength. Difference in the filler morphology in NRSF and NRSH composites was supported by the SEM images of the tensile and tear fractured surfaces and strain sweep studies. On comparing NRSF and NRSH composites it is found that regardless of the processing conditions mechanical properties of both composites increased with silica loading and good mechanical properties were obtained at 5 phr.

Ultrasonication assisted mixing of carboxylated MWCNTs and colloidal nanosilica was done to coat nanotubes with nanosilica (CS hybrid) to reduce dielectric loss. Preparation of CS hybrid fillers involved very simple and environment friendly method using water as the solvent and ultrasonication as the processing tool. Hydrogen bonding possible between carboxyl groups

on the nanotube side walls and silanol groups on nanosilica helped in the adsorption of nanosilica particles on the nanotube surface. These hybrid fillers gave stable aqueous dispersions on ultrasonication. Film casting method adopted in this case resulted in NRCSF composite with a segregated CS hybrid filler network. TEM and SEM images, and strain sweep studies of the composites revealed the segregated network of the hybrid filler. The NRCSF2 composite exhibited excellent mechanical properties with 65% increase in tensile strength, 122% in tensile modulus and 86% in tear strength compared to neat NR and further addition of the nanohybrid filler reduced the properties. 58% reduction in swelling index was observed for NRCSF2 composite supporting the solvent resistance offered by the segregated CS hybrid in NR. The NRCSF composites exhibited high dielectric constant (417 at  $10^3$  Hz) and low electrical percolation threshold (0.80 vol%). Insulating nanosilica coated nanotubes reduced the dielectric loss for the composite and NRCSF composite exhibited better dielectric performance than the NR based composites reported elsewhere (Table 6.5). Comparison of dielectric properties of NRCSF with NR-MWCNTR at 1 kHz indicated that the dielectric loss of NRMWCNTR composite was very high (2.20) at a dielectric constant of 133 whereas the dielectric loss of NRCSF composite was low (1.6) at a dielectric constant of 417. At 1MHz frequency both NRMWCNTR and NRCSF exhibited same dielectric permittivity, but the dielectric loss tangents were quite low for the NRCSF composite compared to NRMWCNTR. In NRCSF, nonconducting silica can form insulating sheath around the carbon nanotubes and avoid direct contact of the conducting nanotubes. This reduces the leakage of current and the composite shows low dielectric loss. These elastomeric nanocomposites with high dielectric constant and low dielectric loss can find application as capacitors for energy storage.

NRCSH composites were prepared using the same method adopted for the preparation of NRSH nanocomposites. Here also the segregated CS filler network in the coagulum was disturbed by the intense shear forces between the rotors in the internal mixer resulting in random distribution of fillers in the composite. TEM, SEM and strain sweep studies provided clear picture of the difference in filler morphology of NRCSF and NRCSH nanocomposites. Tensile strength, modulus (300%) and tear strength increase with CS hybrid filler loading whereas elongation at break decreases. 19% enhancement in tensile strength, 57 % in modulus, and 37 % in tear strength were exhibited by NRCSH3 composite. Tensile strength, tear strength and modulus of NRCSF were higher compared to NRCSH which can be credited to the segregated structure. Higher modulus of NRCSH compared to NRCSF can be explained in terms of the crosslink density difference in the two; because more crosslink formation is possible in the case of compression moulded samples compared to the film cast ones. But the relative increase in modulus with respect to neat rubber is still higher for the NRCSF composites and that can be credited to the segregated structure of the composites. DC conductivity values obtained for the NRCSH composites are in good agreement with the arrangement of fillers proposed for the composite. There is no significant change in the conductivity with filler loading suggesting the absence of continuous conductive network for the composites. Moreover the presence of insulating silica particles around carbon nanotubes can hinder the proper contact between the conducting nanotubes and can result in poor conductivity. Comparison of dielectric permittivity and AC conductivity of NRCSF and NRCSH composites proves that the nature of filler distribution plays a major role in determining electrical properties of the composite. Significant improvement in dielectric constant and AC conductivity has been observed for the segregated structured NRCSF

composites while only a marginal increase is observed for NRCSH composites with non-segregated structure.

Possibility of segregated filler network formation during latex stage mixing and the effect of processing method on the filler morphology were studied using carboxylated nitrile rubber (XNBR) which is a polar rubber. XCF composites prepared by ultrasonication assisted latex stage mixing of MWCNTR aqueous dispersion with XNBR and film casting show segregated MWCNTR network in XNBR matrix. TEM of the composite film and SEM of the fracture surface along with strain sweep studies proved the presence of network. The rigid filler network along with good rubber-filler interaction possible via H-bonding between the surface groups on MWCNTR and XNBR contributed to the enhancement in mechanical properties of the composites. 65 % improvement in tensile strength and 32% in modulus were observed for XCF0.3. Tear strength also increased by 22% for XCF0.7. The composites exhibited excellent dielectric properties at ultralow percolation threshold ( $f_c=0.05$  vol%  $\sim 0.1$  phr) which is credited to the existence of 3D segregated MWCNTR network inside the rubber. Dielectric constant at 100Hz increased from 23 for pure XNBR to around 490 for 1 phr and 7000 for 7 phr MWCNTR.

XCH composites prepared by co-coagulation method and Haake mixing exhibited random nanotube network leading to excellent mechanical properties. Tensile strength at break increased by 35% at 1.5 phr MWCNTR and tear strength improved by 34% at 1.0 phr MWCNTR. Low electrical conductivity behaviour shown by all Haake mixed samples viz. NRSH, NRCSH and XCH composites indicate the absence of conductive network. Dielectric properties were also poor for these composites. The study reveals that the processing method has a significant impact on morphology which in turn affects the properties of the composites. Random network of filler is

beneficial in getting good mechanical properties whereas it has a detrimental effect on electrical properties.

Presence of segregated filler network in all the composites prepared by film casting was supported by strain sweep studies. These composites exhibited increase in Payne effect with filler loading suggesting decrease in modulus due to breakage of filler–filler networks with applied strain. Segregated structure had no significant influence on the thermal stability of the rubber. Improved solvent resistance and crosslink density of all the nanocomposites indicate good rubber filler interaction. The mechanical properties decrease after reaching an optimal concentration in all the composites which can be due to the agglomeration of the fillers.

This study could develop a technique for the successful fabrication of an elastomer composite with segregated network of nanofillers. The work has proved the efficacy of non-ionic surfactant in debundling the nanotubes and obtaining a good aqueous dispersion. Mechanical properties of the composites could be improved substantially even with very low filler concentrations. The segregated network of MWCNTs resulted in very low percolation threshold and improved electrical properties. Carboxylated MWCNTs could impart good dielectric properties barring an increase in dielectric loss. Nanosilica modified MWCNTs were successful in reducing the dielectric loss to considerably low values but not to the expected level for capacitor applications. An alternate processing method adopted (coagulation followed by mixing in Haake) proved that the method of processing a composite strongly influences the distribution of fillers in the polymer. The Haake mixing method resulted in random filler network which had a reducing effect on electrical properties.

### **Future scope of the work**

There is ample scope for continuation of the studies on the rubber nanocomposites with segregated structure. Some of the possibilities are listed below.

- Preparation of Rubber/CNT nanocomposites with segregated network having high CNT content without sacrificing mechanical properties.
- Optimisation of silica coating over MWCNT and study of dielectric performance of the hybrid filler.
- Tuning the dielectric properties of the CNTs by modification to make them suitable for capacitor applications
- Study of actuated strain of the rubber/CNT composites for application as dielectric elastomer actuators.
- EMI shielding studies of NR/MWCNT composites with high CNT content.

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