Elastomers are generally reinforced with particulate fillers like carbon black, silica etc. The full reinforcing effect from these fillers is not observed due to their tendency for agglomeration. Thus the use of nanofillers in polymers to obtain beneficial mechanical and physical properties is becoming crucial. Use of organic and inorganic fillers has become ubiquitous in polymer systems. Parallel to the development of polymer layered silicate composites, there has been rapid growth in the use of other nanofillers like carbon nanotubes, nanosilica etc. in polymers.

First part of the study is the characterization of fillers used, optimisation of the cure time of latex compounds, and the methods used for the preparation of rubber nanocomposites.

XRD analysis of nanokaolin gave characteristic peaks at 2θ = 12°, 20° and 25° corresponding to the interlayer spacing 7.05, 4.41 and 3.55Å respectively. Grafting of vinylsilane did not increase the interlayer spacing of modified nanokaolin. Diffraction peak of MWCNT was obtained at 25.7° and the XRD curve of graphene showed its similarity to graphite in interlayer spacing. From XRD analysis, particle sizes of nanokaolin, vinyl silane grafted nanokaolin, MWCNT and graphene were found as 16, 21, 40 and 15 nm respectively.
Peaks of same intensity were observed for nanokaolin and vinyl grafted nanokaolin (FTIR spectrum). It showed that grafting of vinylsilane groups had taken place only to some of the OH groups in nanokaolin. Eventhough virgin MWCNT showed no characteristic peak, acid treated MWCNT showed the presence of hydroxyl and carbonyl groups on MWCNT surface. Presence of these groups assisted in the formation of MWCNT dispersions.

SEM analysis of these fillers showed agglomeration. Grafting seemed to reduce agglomeration in nanokaolin. MWCNT showed less purity and the samples remained as bundles. But after purification they remained as entangled lose curly thread like entities. SEM images of graphene had a wavy or wrinkled appearance and consisted of thin stacks anchored with each other at the edge of the platelets.

Cure time of the latex compounds were optimised by measuring the variation in mechanical properties of XNBR and SBR vulcanizates. Cure time of XNBR based nanocomposites were taken as 30min at 100°C and that of SBR nanocomposites as 40min at 110°C. Both ball milled and sonicated clay were used in the preparation of latex composites and it was found that sonicated clay gave better properties than the ball milled sample. Examination of the dispersions of ball milled and sonicated clays showed that ball milled sample had a higher tendency to settle down than the sonicated clay. Cure time of dry rubber composites were determined by using RPA 2000.

Different methods were used for the preparation of filler dispersions and the methods adopted for the preparation of latex based and dry rubber
Chapter 3, Part 3. MWCNT dispersions were made in SDBS and graphene dispersions in Vulcastab VL.

Chapters 4 and 5 gave a detailed study of the effect of these fillers on the mechanical and thermal properties of XNBR and SBR latices and the different methods for the characterization of the nanocomposites.

Enhancement in the mechanical properties of XNBR and SBR latices by the incorporation of clay showed that nanokaolin and vinylsilane grafted nanokaolin could be used as good reinforcing fillers in XNBR and SBR. Even though there was enhancement in mechanical properties; nano effect was not observed in the composites. Tendency of the clay particles to agglomerate and the non swellable nature of nanokaolin contributed to the decrease in nano effect.

Compared to SBR latex based composites, XNBR composites showed good improvement in properties. This might be due to the higher interaction of the polar CN and COOH groups in XNBR with the OH groups of clay. Non polar nature of SBR and the presence of bulky styrene group reduced the compatibility of clay in SBR latex. In latex nanokaolin composite there was greater interaction between the hydrophilic clay and the aqueous latex medium. But in modified nanokaolin, the introduction of organic moiety in nanokaolin made it hydrophobic and reduced the interaction with the latex. So for XNBR and SBR latex composites mechanical properties were lower for vinyl modified clay composite. Tensile strength, elongation at break, modulus at 300% elongation and tear strength, showed a similar trend in XNBR and SBR. The only variation was found for elongation at break of SBR–vinyl grafted nanocomposite. The
value declined with clay loading showing poor adhesion of the modified clay to SBR matrix.

Incorporation of MWCNT and graphene at low concentration ranging from 0-1.5 phr increased the mechanical properties of XNBR and SBR latex based nanocomposites. Compared to XNBR/graphene, XNBR/MWCNT nanocomposites gave good enhancement in properties due to the polar interaction of XNBR with the OH and CO groups introduced in MWCNT during purification. SBR/graphene and SBR/MWCNT nanocomposites showed similar change in mechanical properties.

Grafting of bulky, vinyl groups increased the tortuosity of path leading to greater reduction in swelling for XNBR/vinyl grafted nanokaolin composites. But for SBR latex nanocomposites, the lower compatability of organophilic vinyl grafted nanokaolin increased swelling.

Greater reduction in swelling for XNBR/MWCNT might be due to the greater adhesion between XNBR and MWCNT. A discrepancy was shown in the swelling studies of graphene nanocomposites in SBR. Here filled nanocomposites gave higher swelling than the unfilled sample. This might be due to the weak interface created by vulcastab which allowed greater penetration of solvent.

Thermal studies conducted on the nanocomposites showed an increase in thermal stability of XNBR and SBR containing clays. Usually the incorporation of inorganic components into organic materials improve thermal stability.

Thermal studies of all MWCNT and graphene nanocomposites showed an increase in the thermal stability, except for SBR graphene
Summary and Conclusions

nanocomposite where the decrease in thermal stability was an evidence of composite heterogeneity and lack of filler protective action.

DSC studies showed $T_g$ of XNBR clay nanocomposites remained a constant while there was small increase in $T_g$ for SBR clay nanocomposites. Incorporation of MWCNT and graphene showed marginal increase in $T_g$ for XNBR nanocomposites while $T_g$ decreased for SBR nanocomposites. Literature reports that chain mobility depends on polymer cohesive forces and in non polar elastomers the cohesive forces are low and therefore no change in $T_g$ was expected for SBR/MWCNT and SBR/Graphene nanocomposites.

XRD analysis confirmed the intercalation/exfoliation of polymer chains. The increase in interlayer spacing was small for the vinyl modified clay composites showing the reduced compatability of hydrophobic organophilic clay with the hydrophilic polymer.

FTIR studies showed the interaction of OH groups in nanokaolin with the polar CN and COOH group in XNBR, and styrene units in SBR. In vinyl grafted nanokaolin composites the interaction was between the vinyl groups of clay and butadiene double bonds in XNBR and SBR. In MWCNT and graphene nanocomposites there were interaction of the pi electrons with the butadiene double bond of XNBR and SBR. Morphological studies of the composites showed good dispersion of fillers in the latices. In the SEM image of SBR-vinyl grafted nanocomposite the clay particles projected out from the matrix showing the low compatability of organophilic clay with non polar SBR.

Clay showed a cure retarding effect in NBR. The adsorption of curatives on the surface OH groups of clay decreased the effective
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concentration of curatives leading to an increase in cure time and scorch time. Presence of thermally conducting MWCNT and graphene accelerated the curing reaction and decreased the scorch time and cure time. Thermal stability increased slightly for clay nanocomposites but for low concentration of MWCNT and graphene the increase was negligible. DSC analysis showed that there was no change in $T_g$ for all the nanocomposites. XRD of clay nanocomposite showed a slight increase in interlayer space, showing intercalation of polymer chain into the clay gallery. FTIR of NBR/clay nanocomposites showed interaction of OH groups and vinyl group in clay with the butadiene double bond of polymer chain, while FTIR of NBR/MWCNT/graphene nanocomposites showed the interaction of pi bonds with the butadiene double bond of polymer chain.

One of the most referred applications of MWCNT and graphene is in electronic devices. Although rubbers were known to be thermal and electrical insulators, incorporation of conductive fillers would produce composite materials with some electrical properties. Potential applications of rubber nanocomposites might vary from industrial application to electrical shielding and electrical heating. The dielectric properties of XNBR/MWCNT/graphene, SBR/MWCNT/graphene, NBR(dry)/MWCNT/graphene and SBR (dry)/MWCNT/graphene were evaluated by Cavity Perturbation technique in the microwave frequency (Sband 2-4GHz). Dielectric permittivity, dielectric loss and AC conductivity of all the nanocomposites increased with increase in frequency and in most cases with increase in concentration. Maximum values were obtained for XNBR based nanocomposites. Presence of conducting fillers reduced the penetration of electromagnetic waves into the material and skin depth decreased with
increase in frequency. Maximum value of conductivity and minimum value of skin depth were obtained at a frequency of 4 GHz. The nonpolar SBR latex showed some discrepancy in their behaviour.

In Chapter 8, the preparation of layered silicates by microwave technique using Na$_2$SiO$_3$ as the precursor was reported. The prepared silicates were designated as LS1 (containing Mg and Li), LS2 (containing Mg and Al) and MLS2 (LS2 modified with CTAB). XRD analysis of LS2 gave the typical pattern of a synthetic hectorite and it showed greater interlayer spacing than LS1. Particle size of LS2 was 36.1nm as determined by Debye Scherrer equation. SEM image of LS1 showed a layer structure and LS2 showed small particles in an agglomerated state. Modification of LS2 by CTAB was confirmed by IR analysis. TEM images of LS2 and MLS2 also showed agglomeration of particles.

The effect of these fillers on the mechanical properties of XNBR/SBR latices, and NBR/SBR dry rubber, revealed, that the best performance was obtained with LS2 in dry rubber. Incorporation of LS2 enhanced the tensile strength of NBR by 100% and SBR by 119% and elongation at break increased by 74% and 91% for NBR and SBR respectively. Organomodified silicate did not give expected result, might be due to the agglomeration of the silicate particles. The incorporation of these fillers declined the properties of latex composites especially in XNBR. Lack of a proper dispersion of filler and the tendency for the silicates to agglomerate in latex medium might have contributed to the decline in properties of the latex composites.

Although nanofillers have a myriad of applications, the use of nanokaolin and vinyl grafted nanokaolin in the production of gloves is part...
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of the research work. Increase in tensile strength, elongation at break, modulus at 300% elongation and tear strength of the gloves showed that nanokaolin and vinyl grafted naokaolin could be used as a good reinforcing filler in glove production.

Usually compatibilizers are introduced in nanocomposites to reduce the surface tension between the immiscible polymers and fillers as well as to improve the surface adhesion of filler. The simple latex stage mixing adopted for the preparation of nanocomposites and the effectiveness of ultrasonication for preparing filler dispersion contributed to optimum filler dispersion and improvement in the properties of the nanocomposite.

Exceptional physical properties associated with CNTs, their highly graphitic structure and very high aspect ratio holds good for applications requiring unique electrical and mechanical properties. As a robust, yet flexible material, graphene also provides infinite applications. Cost effective composites could be fabricated using MWCNT and graphene as they alter properties at very low concentration.
Response to Comments

1. Equation 6 on page No: 51 may need correction. Do you need molar mass of solvent? If needed why not molar mass of polymer?

   - Solvent uptake Qt % = \( \frac{\text{Mass of solvent sorbed}}{\text{Molar mass of solvent} \times \text{Mass of polymer}} \) \times 100

   Solvent uptake Qt % is expressed as the molar % uptake of solvent per gram of polymer.

References


   - Industrial applications of polymer nanocomposites: In packaging industry, automobiles, aerospace, as coatings, fuel tanks, stoppers for medical containers, sensors etc.

3. Several spelling mistakes may be corrected. Page 6 and some other places.

   - Corrections are made.

4. Page 45. Do the plate thickness / particle size match with BET surface area? Or what would be the theoretical surface area?

   - Plate thickness, particle size and BET surface area of nanokaolin and vinylsilane grafted nanokaolin given in Table 2.3. is taken from specification given in literature.

   As per literature there is a difference between the theoretical surface area and surface area obtained by BET equation. BET surface area depends on many factors like particle size, plate thickness, porosity, density etc. So the particle size and plate thickness are not entirely responsible for the given BET surface area.