

Conclusions and Future Outlook

The major conclusions that are drawn from the present study are summarized in this chapter. Future scope and possible applications are also mentioned herewith.

10.1 Conclusions

Nanotechnology is a future manufacturing technology that will make most products lighter, stronger, cleaner, less expensive and more precise.

Over the past decade, nanomaterials have been the subject of enormous interest. These materials, notable for their extremely small size, have the potential for a wide range of industrial, biomedical and electronic applications. Nanomaterials can be metals, ceramics, polymeric or composite materials. Their defining character is its very small feature size in the range of 1-100 nanometers (nm).

At the nanomaterial level, some material properties are affected by the laws of atomic physics, rather than behaving as traditional bulk materials do. Physical substances with at least one characteristic dimension between 1-150nm can be defined as nanomaterials. Nanomaterials properties can differ

from those of the same materials with micron scale dimensions. Nanomaterials are the building blocks of practical nanotechnology and can be physically and chemically manipulated for specific applications.

Nowadays, composite materials have replaced traditional ones in a variety of applications. Lightweight coupled with enhanced properties are the main reasons for their market acceptance and growth, and the optimization of their performance is a challenge worldwide. Composite materials are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct at the macroscopic, microscopic, nanoscale within the finished structure. Composites are made up of individual materials referred to as constituent materials, namely matrix and reinforcement. The high aspect ratio of the reinforcing particle and its adhesion to the matrix are of great importance, because they control the final properties of the composites.

Polymer/clay nanocomposites are formed through the union of two very different materials with organic and mineral pedigrees. The hybrid compositions, however, exhibit large increase in tensile strength, modulus, and heat distortion temperature as compared with the pristine polymer. Polymer/clay nanocomposites meet these requirements due to the shape (platelet, disc) and nanometer- scale dispersion of the clay layers in the polymeric matrix. This type of composite has raised significant scientific interest due to the improved physical properties that can be achieved by adding a small fraction of clay (<10wt. %) into the polymer matrix. Among the nanocomposites, polymer/clay nanocomposites have received a lot of attention due to their excellent mechanical and barrier properties. Organically modified layered silicates are also used as excellent reinforcing materials in elastomers.

Best performance of the polymeric nanocomposites is achieved when the silicate layers are dispersed in the polymer matrix without agglomeration. An essential step in the preparation of a nanocomposite is the delamination of the layered silicates (LS), which is usually termed exfoliation in literature. Both the layer thickness and the space (galleries) between the layers are of ca. 1nm. The galleries are occupied by hydrated cations, which counterbalance the negative charge of the layers generated by the isomorphous substitution of some atoms in the silicate crystals.

The environment of the galleries is hydrophilic and thus inappropriate for the hydrophobic macromolecular chains to penetrate therein. The replacement of the inorganic cations by organic onium ions (surfactant, intercalant) overcomes this inconvenience. The cationic head of, e.g., an alkylammonium compound is tethered to the layers *via* coulombic interactions, leaving the aliphatic tail to hover between the layers. The longer the surfactant chain length and the higher the charge density of the clay, the further apart the clay layers will be forced. The presence of these aliphatic chains in the galleries renders organophilic, the originally hydrophilic silicate. A value that characterizes each LS is the cation exchange capacity (CEC), expressed in meq/100g, referring to the moderate negative charge of the clay layer surface. The effect of CEC has been checked for different types of clay. It was claimed that a well exfoliated silicate structure can be obtained in polymers when layered silicates of optimum CEC (ca. 90 meq/100g) are rendered organophilic.

Various models have been developed to trace the parameters forcing the macromolecular chain in the silicate layers and then causing their delamination. The interplay of entropic and energetic factors determines the outcome of

polymer intercalation/exfoliation. The entropy decrease due to confinement of the polymer molecules when entering between the galleries is over-compensated by the increase in the entropy of the tethered chains of the surfactant while the silicate layers are moving apart prior to their final separation. In addition, energetically favored interactions between the surfactant and polymer molecules may yield a negative mixing enthalpy. It should be noted that a molecular dispersion requires that the Gibbs' free energy of mixing become negative.

Vulcanized rubbers are usually reinforced by carbon black and inorganic fillers. Carbon blacks are excellent in reinforcement owing to the strong interaction with rubbers, but their presence often reduces the processability of rubber compounds, especially at high volume loadings. On the other hand, minerals of various shapes (e.g., fibrous, platy) are suitable for rubber filling, but they have a poor interaction with rubbers ("inactive fillers"). Therefore, it is of paramount interest to disperse layered silicate in rubber on a nanometer level. The required level of reinforcement in rubbers can be achieved at very low LS loadings, which offers easier processing without any property deterioration compared to traditional "active" fillers.

Sulphur prevulcanized natural rubber latex (PVNRL) nanocomposites were produced by mixing dispersions of layered silicates with prevulcanized latex. Layered silicates used were bentonite and fluorohectorite along with English Indian clay as reference material. Nanocomposites based on sulphur prevulcanized natural rubber latex and layered silicates were subjected to mechanical, swelling, XRD and TEM analysis. Rubber nanocomposites showed higher modulus and tear strength with incorporation of layered silicate and 3 phr loading was found to be the threshold level for optimum mechanical properties.

Higher loading leads to agglomeration or filler networking in the rubber. The rate of relaxation of stress and tension set were higher for layered silicate incorporated composites. The solvent resistance of the rubber nanocomposites was better compared to the microcomposite. The filler-rubber interactions are strong in layered silicate-incorporated vulcanizate. It was found that the fine silicate layers form a skeleton network structure (house of cards) in the vulcanizates.

Radiation prevulcanized natural rubber latex (RVNRL) nanocomposites were produced by mixing dispersions of layered silicates with radiation vulcanized latex. The XRD and TEM analysis of radiation vulcanized natural rubber nanocomposites revealed the NR chains get intercalated into the galleries of the layered silicate. Dynamic mechanical analysis revealed that layered silicates nanocomposite has higher storage modulus and minimum $\tan\delta$ values when compared to the corresponding non-layered grade. From the TEM photomicrograph, it was clear that the layers form a network structure and was concentrated around the boundary of the rubber particles. The air permeability studies showed that the layered silicate nanocomposites had higher gas impermeability than radiation vulcanized natural rubber gum vulcanizates and their composite with commercial clay.

The rheological behavior of sulphur prevulcanized natural rubber (NR) latex nanocomposites was compared with the nonlayered clay latex compound. The flow behavior of latex nanocomposites was depend on the nature of the silicates (layered or non-layered). It was found that viscosity decreased with shear rate and layered silicates registered the higher shear viscosity values. The higher viscosity of layered silicates nanocomposites was due to the intercalation/

exfoliation of rubber hydrocarbons. Natural rubber latex nanocomposites showed shear thinning behaviour at higher shear rates due to orientation of the exfoliated or intercalated structure along the direction of shear. As the loading of layered silicate increased, the viscosity of the compound also increased especially at lower shear rates. The intercalation/ exfoliation can be related to the higher zeroshear viscosity, high yield stress, high activation energy and high pseudoplasticity index.

The dipping characteristics of prevulcanized latex compounds containing layered silicates behaved almost similar to conventional latex compounds. The effect of variation in the speed of immersion and withdrawal of the glass former, dwell time and concentration of the coagulant etc on the thickness of the latex deposit was investigated using a semi- automatic dipping machine. The results of the studies showed that the deposit thickness depends on the withdrawal speed of the glass former, and the viscosity of the latex compound. Bentonite, formed filler network in NR latex showed higher compound viscosity and greater film thickness. The thickness of the deposit was found to increase with dwell time as well as increased concentration of the coagulant. Swelling studies showed that fluorohectorite incorporated vulcanizate (dipped film) have high reinforcement. Superior mechanical properties were observed with layered silicate incorporated vulcanizates.

The degradation behaviour of natural rubber latex nanocomposite against various degrading agents *viz.* thermal, gamma and UV radiation, chlorination and solvents was investigated. During thermal ageing, layered silicate nanocomposite showed better retention of tensile strength especially after prolonged ageing periods. Modulus and elongation at break of nanocomposites

were hardly affected by thermal ageing. Nanocomposites retained their tensile properties up to a radiation dose of 40 kGy and thereafter it decreased. On exposure to UV radiation the performance was inferior for ordinary clay compounds. Kraus plot revealed a strong rubber-silicate interface. As the penetration of oxygen through the nanocomposite was hindered by the silicate layers, they showed good retention of tensile properties after ozone atmosphere. The retention effect was more pronounced in fluorohectorite nanocomposites, which might be due to the high aspect ratio of the platelets. The introduction of nanoclays improved the thermal stability of the nanocomposites compared to microcomposites. This was confirmed by XRD, TEM, SEM and TGA analysis.

Prevulcanized natural rubber latex, chloroprene latex and their blend nanocomposites were prepared using layered silicates. It was observed that layered silicates delaminate in NR, CR and also in their blends. This was evident from the shifting of peaks from higher 2θ values to lower in XRD spectra and also from higher to lower wave numbers in FTIR spectra. It was also observed that, the performance of a layered silicate in a polymer system depends on the nature of the polymer and also on the interlayer distance of the clay. The tensile strength of NR and CR and their blends loaded with 10 phr of layered silicates showed superior TS value when NR phase predominates (strain crystallizing effect). Due to the polar nature of layered nanosilicates they are more compatible with CR and 50/50 NR/ CR blends than pure NR and 80/20 NR/CR blends. The blend showed low elongation values than their corresponding gum and amorphous clay vulcanizates. The layered silicate composite showed high ageing resistance. This might be due to the higher crosslink formation at the elevated temperature. NR nanocomposites showed faster relaxation compared

to the composites of virgin rubbers and their blends. In all cases the solvent intake of nanocomposites was lower than the virgin compounds, since there was less restriction for the solvent absorption in the gum compound. In the blend as the amount of NR increased tear strength values decreased. In NR, CR and their blends crosslink density was higher in layered silicate nanocomposites than the amorphous clay.

Latex Foley catheters requires good modulus and strength properties which are usually met by blending suitably compounded NR latex with synthetic polymers. As latex nanocomposites have good modulus and strength properties Foley catheters were developed from the latex nanocomposite which confirms to BIS (Bureau of Indian Standards) specification.

10.2 Future outlook

The development of organoclay/ rubber composites is still in its embryonic stage. The methods practiced so far are related to various solution (including the latex route) and melt intercalations. No direct (*in situ*) intercalation during rubber synthesis was reported in the literature. Irrespective of the success with latex and solution assisted compounding, the research and development activities in the near future will likely to focus on rubber melt intercalation techniques. Here the target issues are to clarify the role of polar rubbers as additives and the effects of curing components, to perform sulfurless vulcanization, to study the effects of processing oils, and to get experience with *in situ* melt intercalation (rendering the clay organophilic and achieving its intercalation/exfoliation during mixing/curing).

Since the related research in the field of nano-reinforcement is far more advanced with thermoplastic resins than rubbers, attention should be paid to the related achievements, which may serve as guidance for the development of rubber-based nanocomposite. Latex compounding will likely to focus on rubber blends, whereas for solution intercalation, pristine layered silicates will be tried in the future. The other critical issues in the area of nanocomposites are given in section 1.5.1 (page-66).

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