

ENGINEERING AT THE NANOSCALE: A STRATEGY FOR DEVELOPING HIGH PERFORMANCE FUNCTIONAL POLYMERIC MATERIALS

Abitha VK and Sabu Thomas

International and Interuniversity Centre for Nanoscience and Nanotechnology, School of Chemical Sciences, Mahatma Gandhi University, Kottayam -686560, Kerala, India

Abstract

The paper will concentrate on various approaches being used to engineer materials at the nanoscale for various applications in future technologies. In particular, the case of clay, carbon nanostructures (e.g. nanotubes, graphene), metaloxides, bionanomaterials (cellulose, starch and chitin) will be used to highlight the challenges and progress. Several polymer systems will be considered such as rubbers, thermoplastics, thermosets and their blends for the fabrication of functional polymer nanocomposites. The interfacial activity of nanomaterials in compatibilizing binary polymer blends will also be discussed. Various self assembled architectures of hybrid nanostructures can be made using relatively simple processes. Some of these structures offer excellent opportunity to probe novel nanoscale behavior and can impart unusual macroscopic end properties. Also about various applications of these materials, taking into account their multifunctional properties. Some of the promising applications of clay, metal oxides, nano cellulose, chitin, carbon nanomaterials and their hybrids will be reviewed. Finally the effect of dewetting up on solvent rinsing on nano scale thin films will also be discussed.

1.Introduction

Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometer range. Normally, the term nano encompasses the range 1–100 nm .Nanoscience and nanotechnology can be considered as a revolutionary science in the multidisciplinary area combining chemistry, physics, material science, electronics and biosciences. It is a fascinating technology of the twenty first century, ranging from novel building materials to medicine. With respect to diversity in technological applications, nanotechnology offers novelty and versatility not observed in any other field. Nanocomposite materials have emerged as suitable alternatives to overcome limitations of microcomposites and monolithics, while posing preparation challenges related to the control of elemental composition and stoichiometry in the nanocluster phase. The surface area/volume ratio of reinforcement materials employed in the preparation of nanocomposites is crucial to the understanding of their structure–property relationships. This review mainly focuses on the studies carried out in my lab to prepare high performance polymer nanocomposites for various applications.

2. Types of Nanocomposites

Nanocomposite materials can be classified according to their matrix materials as given below

1. Ceramic matrix nanocomposites
2. Metal matrix nanocomposites
3. Polymer matrix nanocomposites

Ceramic matrix nanocomposites are a subgroup of composite materials. They consist of ceramic fibers embedded in a ceramic matrix. Carbon (C), special silicon carbide (SiC), alumina (Al_2O_3) and mullite ($\text{Al}_2\text{O}_3\text{-SiO}_2$) fibres are most commonly used for CMCs. The matrix materials are usually the same that is C, SiC, alumina and mullite. Metal matrix nanocomposites (MMNC) refer to materials consisting of a ductile metal or alloy matrix in which some nanosized reinforcement material is implanted. These materials combine metal and ceramic features. Metal matrix nanocomposites are suitable for production of materials with high strength in shear/compression processes and high service temperature capabilities.

Polymer nanocomposites (PNC) consist of a polymer or copolymer having nanoparticles or nanofillers dispersed in the polymer matrix. These PNC's belong to the category of multi-phase systems (MPS, viz. blends, composites, and foams) that consume nearly 95% of plastics production. These systems require controlled mixing/compounding, stabilization of the achieved dispersion, orientation of the dispersed phase, and the compounding strategies for all MPS, including PNC, are similar. The transition from micro- to nano-particles leads to change in its physical as well as chemical properties. Two of the major factors in this are the increase in the ratio of the surface area to volume, and the size of the particle. The increase in surface area-to-volume ratio, which increases as the particles get smaller, leads to an increasing dominance of the behavior of atoms on the surface area of particle over that of those interior of the particle¹.

3. Methods of Preparation of polymer nanocomposites

Many methods have been described for the preparation of polymer nanocomposites. The most important ones are i) Intercalation of the polymer or pre-polymer from solution; ii) In-situ intercalative polymerization; iii) Melt intercalation (Figure 1); iv) Direct mixture of polymer and particulates; v) Template synthesis vi) Sol Gel process etc.

3.1 Polymer Nanocomposites

3.1.1 Clay based polymer nanocomposites

Clay/polyaniline nanocomposites were prepared by Jlassi et al. using in-situ oxidative polymerization of aniline in the presence of 4-diphenylamino diazonium-exchanged clay (DPA). This exfoliated and conductive nanocomposites were used for the first time as nanofiller of DGEBA matrix. This DPA modified bentonite clay improves the dielectric and mechanical properties of DPA bentonite clay/polyaniline composites. The mechanism behind this is aryl groups from the diazonium precursor significantly modify the interface by acting as an efficient stress transfer medium. The mechanism of modification of the composite is as shown in **figure 1**.²

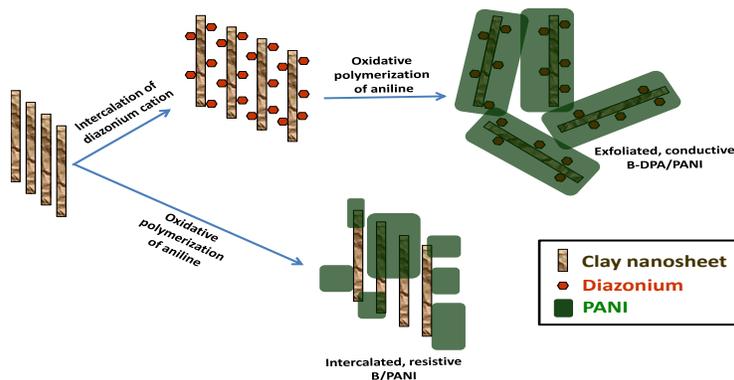


Figure 1: Proposed mechanism of modification of clay using DPA

In another study epoxy/clay/carboxyl-terminated poly (butadiene-co-acrylonitrile) (CTBN) hybrids were prepared with two different organically modified clays. Octadecyl amine and trimethyl stearyl ammonium-modified nanoclays (Nanomer I.30E and I.28E, respectively) were used. It was found that the octadecyl amine modifier in I.30E initiates the homopolymerization of epoxy pre-polymers to generate cross-link via ether linkage which reduce the cross-link density of the matrix. The plasticizing effect of clay modifier/dissolved liquid rubber and the interfacial adhesion between the polymer and the clay platelets were found to control the T_g of epoxy/ clay (1.3E)/CTBN hybrid. Epoxy/ trimethyl stearyl ammonium modified clay (I.28E) nanocomposites showed superior thermal degradation properties than epoxy/I.30E due to the low cross-link density in later case³.

Zachariah et al. studied on the NR/CIIR blend for tyre inner liner applications. Clay was added in different concentrations and upon addition the gas permeation through the inner liner membrane has decreased. The values were comparable to the current rubber (CIIR/BIIR) membranes being used in the tyre industry⁴⁻⁵.

The major applications of clay based composites are tyre inner liner, epoxy based coatings etc.

3.1.2 Silica based polymer nanocomposites

Meera et al. have prepared natural rubber/ TiO_2 / nano silica composites. The stress relaxation behavior of the composites under tension was studied with reference to the filler loading and strain level. It was observed that the rate of stress relaxation increases with increase in filler loading. The rate of stress relaxation was found to be higher for silica-filled NR compared to TiO_2 -filled NR. This is due to the high degree of agglomeration in silica compared to titanium dioxide filler. The effect of ageing on the stress decay was also investigated and the rate of stress relaxation was found to decrease after ageing. The nonlinear viscoelastic behavior of the composites of natural rubber filled with surface-modified nanosilica was studied with reference to silica loading. The effect of temperature on the nonlinear viscoelastic behavior has been investigated. It was observed that Payne effect becomes more pronounced at higher silica loading. The filler characteristics such as particle size, specific surface area, and the surface structural features were found to be the key parameters influencing the Payne effect. A nonlinear decrease in storage modulus with increasing strain was observed for unfilled compounds also. The results reveal that the mechanism which include the breakdown of different networks namely the filler-filler network, the weak polymer-filler network, the chemical network, and the entanglement network⁶⁻⁷. In another study by Swapna et al., polyhedral oligomeric silsesquioxane (POSS) encapsulated PVA nanocomposite was successfully prepared by solution blending method. Octa tetramethylammonium (Octa TMA) and polyethylene glycol were used as

modifiers for POSS. The relaxation corresponding to the crystal–crystal slippage characteristic of semicrystalline polymers were observed in storage modulus curves of PVA/POSS system, suggesting the crystalline nature of matrix even in the presence of POSS. Less polar, inert, and stiff inorganic center core of POSS contributes to the reduced energy dissipation and dielectric constant of PVA/POSS system⁸.

3.1.3 CNT based polymer nanocomposites

Multiwalled carbon nanotubes filled PC/PP composites were prepared and the effect of polypropylene-grafted maleic anhydride (PP-g-MA) as a compatibilizer were studied by Arif et al. High-performance electromagnetic shielding PC/PP blend nanocomposite was developed via melt blending method. The substantial effect of compatibilization on the dispersion of MWCNTs has resulted in higher conductivity values of 0.33 Scm⁻¹ which is a major requirement for designing electromagnetic interference shields. The addition of PP-g-MA into the PC/PP blend causes the refinement of the co-continuous morphology, decreased interfacial tension and suppression of coalescence. The co-continuous morphology of PC/PP/PP-g-MA has been unchanged by the inclusion of MWCNT. Both the uncompatibilized blends and compatibilized nanocomposites showed viscoelastic phase separation due to the dynamic asymmetry of the PC phase and PP phase⁹.

The mechanical and morphological characteristics of ionic liquid modified MWCNT based SBR nanocomposites have been investigated by Abraham et al. The mechanism of ionic liquid modified CNT is shown in **figure 2**. Tensile strength increased with f-MWCNT loading and reached up to a value of 6.801 MPa (T10IL1) from 1.626 MPa (neat SBR), an improvement of about 318% over the neat polymer. The plasticizing effect of ionic liquid reduces the mechanical properties at its higher loadings. The quantity of macromolecular chains adsorbed on the filler surface was calculated from DMA, which further supports the substantial enhancement in the mechanics¹⁰.

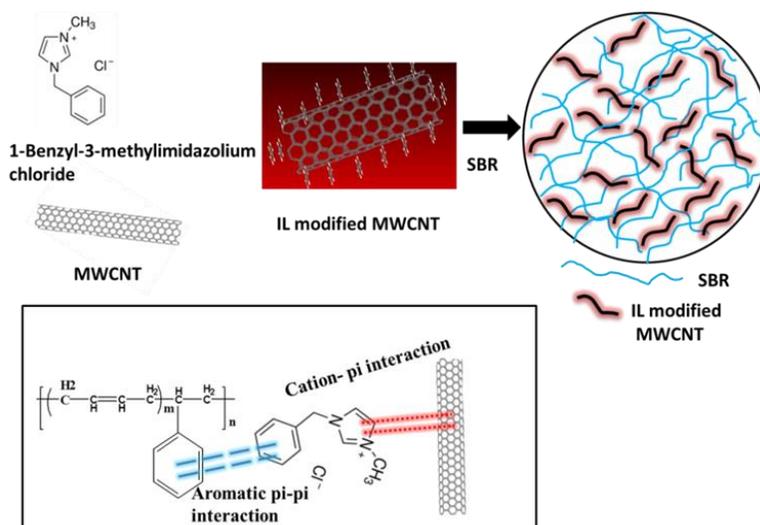


Figure 2: Mechanism of Ionic liquid modified CNT SBR compsite

Battacharya et.al demonstrated an efficient and successful way to prepare reinforced and conducting natural rubber composite materials through incorporation of up to 8.3 wt% MWCNT activated by oxidation. The electrical percolation behaviour of this composites is due to CNT network formation(**Figure3**).The nanocomposites showed a very high degree of increase both in the tensile and storage modulus in the rubbery region at room temperature, probably due to rigid networking effect favored by segregation effects coming from latex structure and cross-linking via functional groups at the surface of CNT and organic molecules present in the natural latex

solution¹¹.

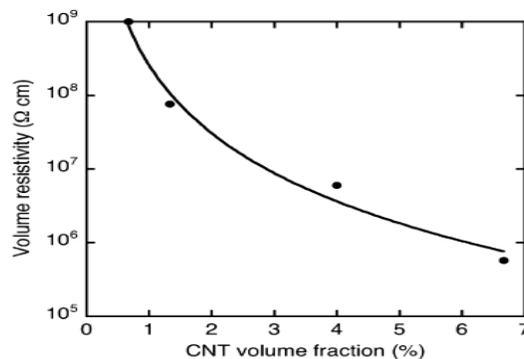


Figure 3: Resistivity vs. CNT volume fraction, showing an electrical percolation behavior due to CNT network formation.

The main applications of CNT based composites are in EMI shielding, sensors etc.

3.1.4 Graphene based polymer nanocomposites

Thermally reduced graphene oxide (TRG) was incorporated into dry natural rubber (NR) by mechanical melt mixing method. NR TRG composites were exhibited gas barrier properties. Excellent O₂ gas barrier properties were observed for 3% w/w TRG. The mechanical properties, especially modulus values from tensile test were found to be high at 3% w/w of TRG sacrificing the tensile strength. It was concluded that the alignment of high aspect ratio TRG platelets leads to a tortuous path for the gas molecule inside NR¹².

Nanocomposite films using ammonia functionalized nano graphene oxide (NGO) into cellulose nanofibre matrix was prepared by Beeran et al. Increasing concentration of NGO upto 3 wt% increases mechanical strength and thermal stability. Besides, the high dielectric constant and AC conductivity at a relatively high frequency region (1 MHz) with comparable electrochemical energy storage capacity demonstrated that such ultra-strong and ultra-stiff composite films are suitable cost-effective alternative green materials for flexible energy storage devices¹³.

PU nanocomposite filled with unmodified and modified GOs were prepared by simple solution mixing method. The methylene diphenyl diisocyanate modified GOs offered better interactions with the urethane skeleton. Correlating this with the dielectric constant showed the significance of these characterization techniques in manufacturing super capacitors and electrically applicable materials. Payne effect observed for these thermoplastic elastomer composites explained the confinement effect of filler platelets in immobilized polymer chains¹⁴.

3.1.5 Bio based polymer nanocomposites

Polyvinylidene fluoride (PVDF) electrospun membrane, unmodified cellulose nanofiber (CNF) based PVDF membrane, and Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) modified CNF-based PVDF membranes were used for the Fe₂O₃ nanoparticle filtration and crystal violet (CV) dye adsorption. With the 10 mg/L of crystal violet (CV) aqueous solution, CV adsorption of PVDF electrospun membrane, and unmodified CNF-based PVDF membrane was around 1.368 and 2.948 mg/g of the membrane respectively, whereas it was 3.984 mg/g of the membrane by Meldrum's acid CNF-based PVDF membrane. The demonstrated Meldrum's acid modified CNF based PVDF membrane was proven to be the efficient media that can concurrently eliminate the Fe₂O₃ nanoparticles and CV dyes from the water¹⁵.

An active functional adsorbent membrane developed by combining both hydrophilic bio polymer filler such as chitin nano whiskers (ChNW) which contains two functional groups and a

hydrophobic polymer matrix such as polyvinylidene fluoride (PVDF) using electrospinning technique. Characterization of PVDF/ChNW electrospun membrane indicated high probable of these nanowhiskers/porous structures to be used in adsorption technology¹⁶.

The effect of ZnO nanoparticles on the degradation of electrospun polycaprolactone membranes have been investigated by Augustin et al. PCL/ZnO nanocomposite membranes have shown higher degradation rate than the neat PCL membranes. The enhanced degradation of the PCL membrane containing ZnO nanoparticles might be due to multiple factors such as production of ROS by the ZnO nano particles and decrease in the crystallinity of the polymer¹⁷

In another study electrospun PCL tissue engineering scaffolds containing EHNs were fabricated and characterized for various morphological and physico-chemical properties. Furthermore, biological studies showed enhanced cell growth and a greater density of endothelial cells grown on the scaffolds incorporated with EHNs (PCL-EHNs). The PCL-EHNs also exhibited good hemo compatibility towards blood cells¹⁸.

4. Hybrid Nanocomposites

XLPE/Al₂O₃ nanocomposites showed increase in contact angle values with increase in nanofiller concentration for both the solvents water and DMSO. Among different spherical nanofillers TiO₂ and Al₂O₃ showed higher values for contact angle. Comparing interfacial energy and interaction parameter, and all other properties XLPE/Al₂O₃ nanocomposite is the best candidate having higher non-wetting property¹⁹.

Transport properties of hybrid nanoparticle based cross-linked polyethylene (XLPE)–Al₂O₃–clay binary and ternary nanocomposites have been investigated with special significance to the hybrid effect and synergism of hybrid nanofillers. Compiling the temperature and filler effects demonstrates the self assembly of hybrid nanofillers in confining the polymer chain dynamics. Experiments confirmed the extra stability of the ternary hybrid nanocomposites against the process of solvent penetration. Thermodynamic and kinetic investigations reveal that the nanofillers are competent to alter the thermodynamic feasibility and rate constant parameters. The morphology and the network density estimation confirm the presence of filler networks and the trapped polymer chains inside them, in ternary systems, which elucidate the microstructure assisted solvent resistant properties of the ternary hybrid nanocomposites²⁰.

5. Nanostructured polymer blend materials

Styrene-block-butadiene-block-styrene (SBS) triblock copolymers epoxidized at several epoxidation degrees by hydrogen peroxide in water/dichloroethane biphasic system were blended with epoxy based on diglycidyl ether of bisphenol A (DGEBA) and DDM (4,4'-diaminodiphenyl methane) as curing agent. The incorporation of epoxidized block copolymers in epoxy resulted in the formation of nanostructured blends. The key factor controlling the morphology is the mole percentage of epoxidised butadiene units in SBS. In fact, the morphologies changed from macroscopic phase separated domains in unmodified SBS to nanostructured domains in epoxidised SBS and the resulting morphologies were fixed by the cross-linking reaction. Nanostructured morphologies such as worm-like and spherical micelles (radius 8 nm) were generated due to reaction induced phase separation of PS phase followed by the self-assembly of PB sub chains²¹

6. Thin films

The significance of choosing solvents for deconstructing polymer thin films along with their stability was investigated by Unni et al. Solvents such as toluene, chloroform, tetrahydrofuran, and acetone were used for rinsing the polystyrene coated silicon wafer. The solvents are chosen

according to their relative energy difference with the polymer. Fine tuning of rinsing time leads to a progressive decrement of film thickness that allows the investigation of stability of the residual film resulting from different solvent leaching. The stability of these films is found to be dependent on various interactions involved in the system such as van der Waals dispersive forces, steric repulsions, acid–base interactions, etc²².

7. Conclusion

Nano technologies have been successfully used for the development of polymeric materials having novel properties and/or improved performance compared to conventionally processed components. In fact, nanocomposites are suitable materials to meet the emerging demands arising from scientific and technological advances. They offer improved performance over monolithic and microcomposite counterparts and are consequently suitable candidates to overcome the limitations of many currently existing materials and devices. A number of applications of polymer nanocomposites already exists, while many potentials are possible for these materials, which open new high performance material for the future. In view of their unique properties such as very high mechanical properties even at low loading of reinforcements, gas barrier and flame related properties, many potential applications and hence the market for these materials have been projected in various sectors.

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