

Polymer Nanocomposites: From Synthesis to Applications

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1. Introduction

Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometer range (Roy et al., 1986). These are high performance materials that exhibit unusual property combinations and unique design possibilities and are thought of as the materials of the 21st century. With an estimated annual growth rate of about 25% and huge demand for engineering polymers, their potential is so promising that they are useful in several applications ranging from packaging to bio-medical. Literature survey reveals that about 18,000 publications, including papers and patents, have been published on nanocomposites in the last two decades. It has been reported that at the nanoscale (below about 100 nm), a material's property can change dramatically. With only a reduction in size and no change in the substance itself, materials can exhibit new properties such as electrical conductivity, insulating behavior, elasticity, greater strength, different color, and greater reactivity-characteristics that the very same substances do not exhibit at the micro- or macroscale. For example,

1. By the time gold crystals are just 4 nm across, the melting point drops to 700 K from its "encyclopedia value" of 1337 K (Mulvaney, 2001).
2. White crystals such as those of ZnO and TiO₂ are used as paint pigments or whitening agents, but they become increasingly colorless as the crystals shrink in size, and ZnO and TiO₂ colloids become invisible to the human eye below about 15 nm (Mulvaney, 2001).
3. Aluminum-can spontaneously combust at the nanoscale and has been used as rocket fuel.

Additionally, as dimensions reach the nanometer level, interactions at interfaces of phases become largely improved, and this is important to enhance materials properties. In this context, the surface area/volume ratio of reinforcement materials employed in the preparation of nanocomposites is crucial to the understanding of their structure-property relationships. Further, discovery of CNTs (carbon nanotubes) (Iijima, 1991) and their subsequent use to fabricate composites exhibiting some of the unique CNT related mechanical, thermal and electrical properties (Biercuk et al., 1991; Ounaies et al., 2003; Weisenberger et al., 2003) added a new and interesting dimension to this area. The possibility of spinning CNTs into composite products and textiles (Dalton et al., 2003) made

further inroads for the processing and applications of CNT-containing nanomaterials. Rubber based nanocomposites are attracting considerable interest in polymer science research. Incorporation of different nanoreinforcements such as layered silicate clays, carbon nanotubes, nanofibers and silica nanoparticles into elastomers significantly enhances their mechanical, thermal, dynamic mechanical, and barrier properties along with noticeable improvements in adhesion, rheological and processing behavior (Bhowmick et al., 2010). Nowadays, nanocomposites offer new technology and business opportunities for all sectors of industry, in addition to being environmental- friendly (Choa et al., 2003). This chapter concentrates on some of the recently studied polymer nanocomposites and highlights their synthesis, properties and applications.

2. Varieties of polymer nanocomposites

Almost all types of polymers, such as thermoplastics, thermosets and elastomers have been used to make polymer nanocomposites. A range of nanoreinforcements with different shapes have been used in making polymer nanocomposites. An important parameter for characterizing the effectiveness of reinforcement is the ratio of surface area (A) of reinforcement to volume of reinforcement (V) [McCrum et al., 1996]. A plot of A/V against aspect ratio [defined as the ratio of length (l) to diameter (d)]. It can be seen from figure 1 that the predicted optimum shape for the cylindrical reinforcement to maximize A/V is

- $a \gg 1$ (a fiber), and
- $a \ll 1$ (a platelet).

Therefore, it can be understood that the two main classes of nanoreinforcement are fibers (e.g., carbon nanotubes) and platelets (e.g., layered silicate clays).

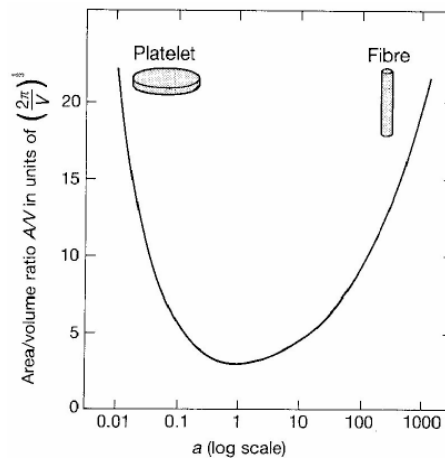


Fig. 1. Surface area to volume ratio A/V of a cylindrical particle of given volume, plotted versus aspect ratio $a=l/d$ (from McCrum et al., 1996)

Polymer-layered inorganic platelet nanocomposites are bio-inspired materials. Mother of pearl (nacre) is a bio-nanocomposite made of: 95 percent aragonite (calcium carbonate), a brittle ceramic, and 5 percent flexible biopolymer (conchiolin). But, it is several times stronger than nylon; its toughness is almost equal to silicone. It is built like a "brick-and-

mortar" structure, where millions of ceramic plates stacked on top of each other with each layer of plates glued together by thin layers of the biopolymer (Figure 2). Mixture of brittle platelets and the thin layers of elastic biopolymers make the material strong and resilient. The "brickwork" arrangement also inhibits transverse crack propagation.

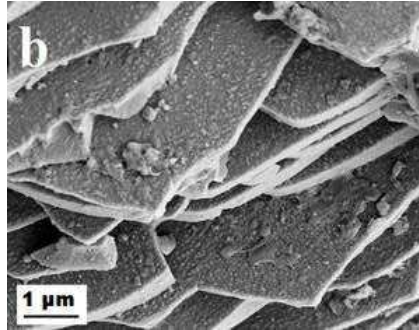


Fig. 2. Scanning electron microscope view of the fractured surface of nacre.

Table 1 presents a non-exhaustive list of possible layered host crystals that can be intercalated by a polymer. Most important one among them is layered silicate clay (figure 3). Amongst all the potential nanocomposite precursors, those based on clay and layered silicates have been more widely investigated probably because the starting clay materials are easily available and because their intercalation chemistry has been studied for a long time. Montmorillonite (MMT) is a naturally occurring 2:1 phyllosilicate, which has the same layered and crystalline structure as talc and mica but a different layer charge [Giese and Van Oss, 2002]. The MMT crystal lattice consists of 1 nm thin layers, with a central octahedral sheet of alumina fused between two external silica tetrahedral sheets (in such a way, that the oxygens from the octahedral sheet also belong to the silica tetrahedral). These layers organize themselves in a parallel fashion to form stacks with a regular van der Waals gap in between them, called interlayer or gallery (figure 4). The Na^+ or Ca^{2+} ions residing in the interlayers could be replaced by organic cations such as alkyl ammonium ions or phosphonium ions by an ion-exchange reaction to render the hydrophilic layered silicate organophilic, so that polymer chains could be intercalated, thus causing the clay layer to be either swollen or exfoliated [Ma et al, 2004].



Fig. 3. Layers of naturally occurring phyllosilicate clay as seen under SEM.

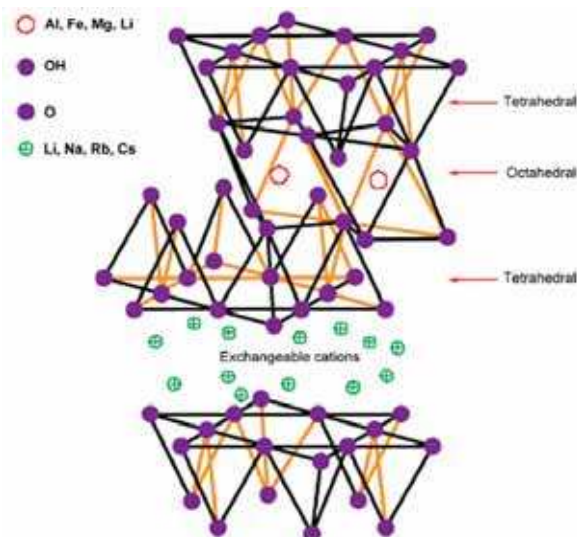


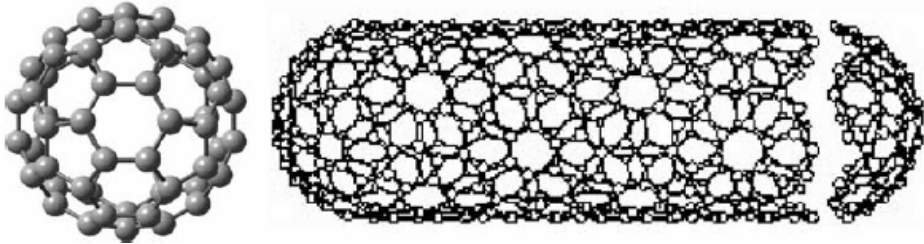
Fig. 4. The structure of a 2:1 layered silicate (from Koo, 2006).

Chemical nature	Examples
Element	Graphite
Metal chalcogenides	(PbS) _{1.18} (TiS ₂) ₂ , MoS ₂
Carbon oxide	Graphite oxide
Metal phosphate	Zr(HPO ₄) ₂
Clays and layered silicates	Montmorillonite, hectorite, saponite, fluoromica, fluorohectorite, vermiculite, kaolinite, magadiite.
Layered double hydroxides	M ₆ Al ₂ (OH) ₁₆ CO ₃ .nH ₂ O; M = Mg, Zn

Table 1. Examples of layered host crystals susceptible to intercalation by a polymer.

Carbon nanotubes are hexagonally shaped arrangements of carbon atoms that have been rolled into tubes. Carbon nanotubes are allotropes of carbon with a cylindrical nanostructure (scheme 1). Nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1, significantly larger than any other material. The first polymer nanocomposites using CNT as reinforcement were reported in 1994 (Ajayan et al., 1994). CNTs possess high flexibility (Cooper et al., 2001), low mass density (Gao et al, 1998), and large aspect ratio (typically ca. 300-1000). CNTs have a unique combination of mechanical, electrical, and thermal properties that make nanotubes excellent candidates to substitute or complement the conventional nanoreinforcements in the fabrication of multifunctional polymer nanocomposites. Some nanotubes are stronger than steel, lighter than aluminum, and more conductive than copper. For example, theoretical and experimental results on individual single-walled CNTs (SWNT) show extremely high tensile modulus (640 GPa to 1 TPa) (Uchida and Kumar, 2005) and tensile strength (150-180 GPa) (Walt, 2004). Depending on their structural parameters, SWNT can be metallic or semiconducting, which further expands their range of applications. Because of the nearly one-dimensional electronic structures, metallic nanotubes can transport electrons over long tube lengths without

significant scattering (McEuen, 1999). Chemical pretreatments with amines, silanes, or addition of dispersants improve physical disaggregation of CNTs and help in better dispersion of the same in polymer matrices (Ganguly et al., 2008). Figure 5 is a transmission electron micrograph of a portion of a nanotube showing the multiwall structure surrounding the hollow core. Figure 6 is a scanning electron micrograph showing the curvilinear structure of multi-walled nanotubes (MWNT).



Scheme 1. Ideal structures of a fullerene and a carbon nanotube (from Wang et al., 2004).

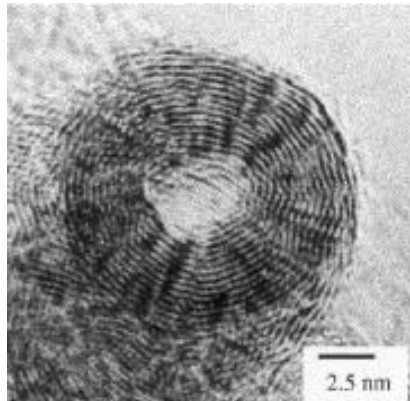


Fig. 5. TEM end-on view of a MWNT.

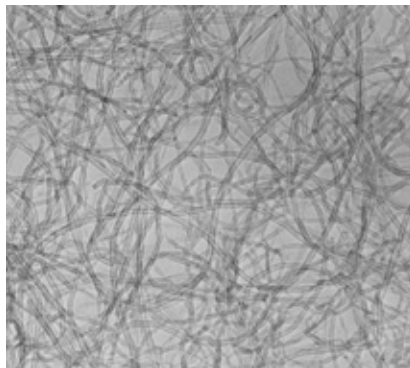
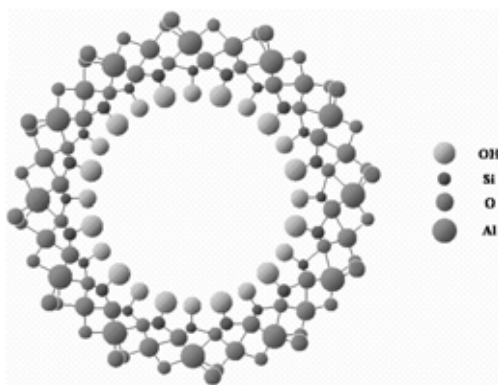


Fig. 6. Scanning electron micrograph of MWNT.

Wang et al. (2004) reviewed various methodologies for incorporating fullerene and CNT structures into polymers. The results of studies on fullerene and CNT based polymer nanocomposites show that the combination of the unique properties of CNTs and fullerenes with functional polymers will lead to novel materials with unusual mechanical, electrical, magnetic, and optical properties. Both conducting and conventional polymers can be used as matrices in the preparation of functional composites. The structures and properties of these hybrids are strongly dependent on the properties and concentrations of the active components. The combination of the unique properties of fullerenes and CNTs with polymers makes these materials potential candidates for many applications, such as data storage media, photovoltaic cells and photodiodes, optical limiting devices, photosensitive drums for printers, and so on.

Imogolite, consisting of hollow tubes with an external diameter of 2 nm and length of a few micrometers, is a naturally occurring hydrous aluminosilicate polymer found in soils of volcanic origin with a net composition $(\text{HO})_3\text{Al}_2\text{O}_3\text{SiOH}$ (Yamamoto et al., 2005). Imogolite can also be synthesized by various routes (Suzuki and Inukai, 2010). The tubes have curved gibbsite sheets with SiOH groups on the inner surface and AlOH groups on the outer surface (scheme 2). Atomic force microscope image of synthetic imogolite is shown in figure 7.

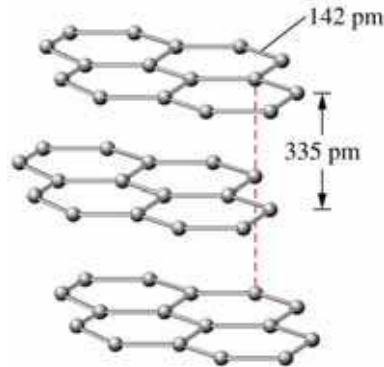


Scheme 2. Side view of the chemical structure of imogolite (from Lee et al., 2006).



Fig. 7. Atomic force microscope image of synthesized imogolite.

The structure of graphite (scheme 3) reveals that it is made of several graphene layers those are held together by van der Waals forces (www.benbest.com, 2011) and can be exfoliated similar to layered silicate clay by chemical modification.



Scheme 3. 3D structure of graphene layers in graphite.

High crystallinity of graphite is disadvantageous in forming nanocomposites with polymers, as giant polymer molecules do not find spaces within the graphene sheets. This has been overcome by modifying graphite flakes with several oxidizing agents (Inagaki et al., 2004). The effective method of preparing the polymer-expanded graphite composite is by rapidly heating the pretreated (oxidized) graphite to a high temperature. The exfoliation of graphite is a process in which graphite expands by up to hundreds of times along the c-axis, resulting in a puffed-up material with a low density and high temperature resistance (Chung, 1987). The graphite thus resulted contains nanodimensional flakes (expanded graphite) providing greater surface/volume ratio for interaction with suitable polymer matrices.

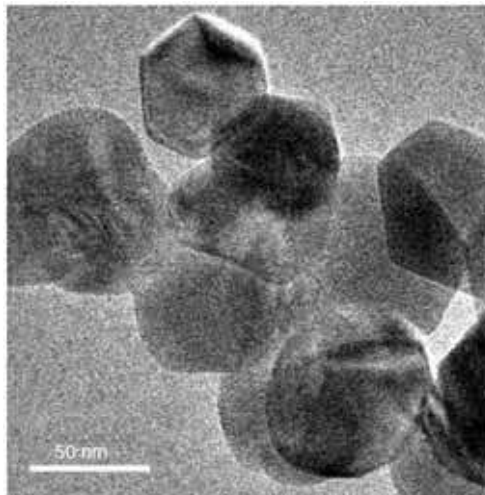


Fig. 8. Transmission electron microscopic (TEM) image of nano-zinc oxide (ZnO) (from Sahoo and Bhowmick, 2007).

Recently, several metal oxides apart from silica have been investigated and reported for rubber-based nanocomposites. Some important and commercially meaningful oxides used in rubber are ZnO, Mg(OH)₂, CaCO₃, zirconate, iron oxide, etc. When used in carboxylated nitrile rubber as curative, ZnO nanoparticles (figure 8) show excellent mechanical and dynamic mechanical properties [Sahoo and Bhowmick, 2007]. Different polymer-nano-ZnO hybrid systems based on epoxy [Liufu, 2005], poly(styrene-*co*-acrylic acid) [Ali and Iliadis, 2005], polyurethane [Zheng et al., 2005], etc. have been reported. Recent development of rubber nanocomposites by other nanoreinforcements includes piezo-rubber application by incorporating lead-zirconate by Tandon et al. [1993], Fe-containing silicone rubber by Yurkov et al. [2006], and crab shell whisker-reinforced natural rubber nanocomposites by Nair and Durfreshe [2003]. Thomas et al (2008, 2009 and 2010) extensively studied the properties of poly(ethylene-*co*-vinyl acetate) (EVA) and polystyrene nanocomposites based on nano calcium phosphate.

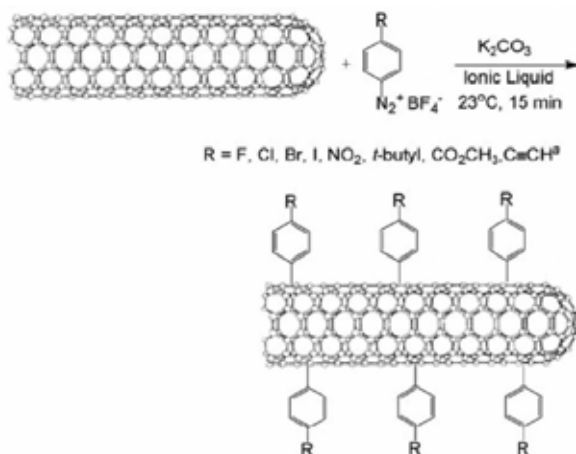
3. Functionalization of nanoreinforcements

On most occasions, nanoreinforcements need to be surface modified before incorporating them in to polymer matrices. This is because of the polarity difference between nanoreinforcements and majority of the polymer matrices. There are several approaches used in modifying surfaces of nanoreinforcements. The following paragraphs discuss some of the recent progresses made in the field of surface modification of nanoreinforcements.

In order to enhance the compatibility between clay and an organic polymer, one typically must ion exchange the sodium counter ion of the clay for an organophilic ion, usually an 'onium' ion, such as alkyl ammonium, sulfonium, phosphonium and imidazolium. The most common treatments that have been used to produce the organically-modified clays are ammonium salts, and this cation contains at least one long alkyl chain. The use of phosphonium salts and stibonium salts provides a marginal increase in thermal stability (Zhu et al., 2001). The formation of a nanocomposite requires the clay to be well-dispersed throughout the polymer matrix. A nanocomposite is described as intercalated if the registry between the clay layers is maintained and it is called exfoliated, or delaminated, if this registry is lost. For some properties, notably flexural modulus and permeability, it is believed that an exfoliated system shows more enhanced properties while, for fire retardancy, there is apparently no difference in behavior between exfoliated and intercalated systems. Zhang and Wilkie (2004) reported the preparation of nanocomposites of polystyrene with carbocation substituted clay. The thermal stability of this clay was greatly enhanced compared to the normal, ammonium-modified clays.

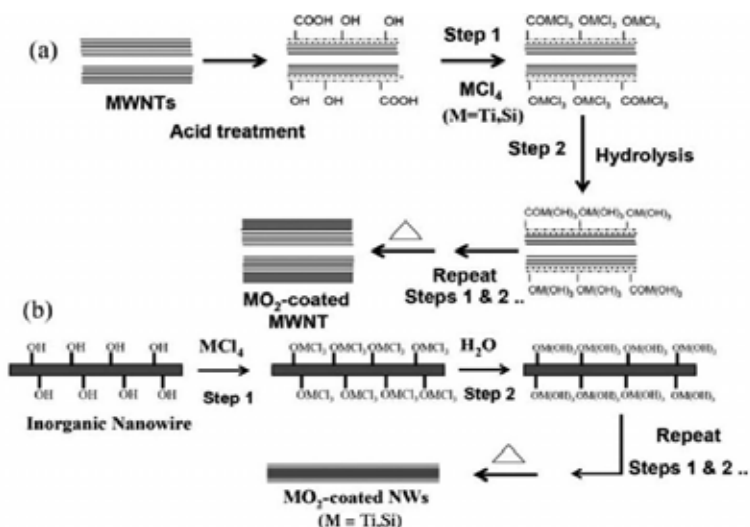
Wypych and Satyanarayana (2005) proposed a strategy to the use of synthetic and natural layered compounds, taking into account their ability to be exfoliated in the form of single layers, which can be chemically grafted with key molecules; a similar procedure can also be applied to fibrous materials. These surface-grafted molecules can carry reactive groups to be bonded to the polymer matrices. Thus adhesion between the reinforcement and the polymer matrix can be achieved.

Functionalization of MWNTs using mineral acids such as H₂SO₄ and HNO₃ is well documented in the literature. Vivekchand et al., (2007) have extensively reviewed functionalization of nanotubes and nanowires by various methodologies. For example, SWNT can be functionalized in ionic liquid using a mortar and pestle (Scheme 4) (Price et al., 2005). SWNTs can be cut into short segments by controlled oxidation by piranha (HNO₃/H₂SO₄) solutions [Ziegler, 2005].



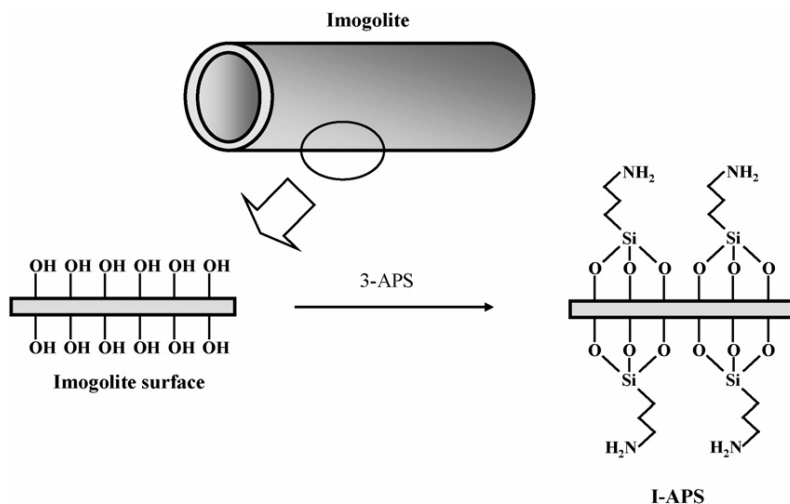
Scheme 4. Functionalization of CNT.

Metal oxide coated CNTs and inorganic nanowires can be prepared as shown in scheme 5 (Gomathi et al., 2005). The ceramic oxide coating provides improved compatibility with polar matrices as well as improved thermal stability of the nanotubes and nanowires. Natural graphite as such is not reinforcing in nature. But when modified to expanded graphite by high temperature heat treatment, this could be used as reinforcing nanoreinforcement in various polymer matrices. Recently George et al. (2007 & 2008) synthesized EVA/graphite nanocomposites using both tailor-made and commercially available expanded graphite. In both the cases, well-dispersed, fine graphite flakes were seen within the EVA matrices and this resulted in superior mechanical, dynamic mechanical, and processibility characteristics over the systems having natural graphite.



Scheme 5. The ceramic oxide coating process for (a) carbon nanotubes and (b) metal oxide nanowires (from Gomathi et al., 2005).

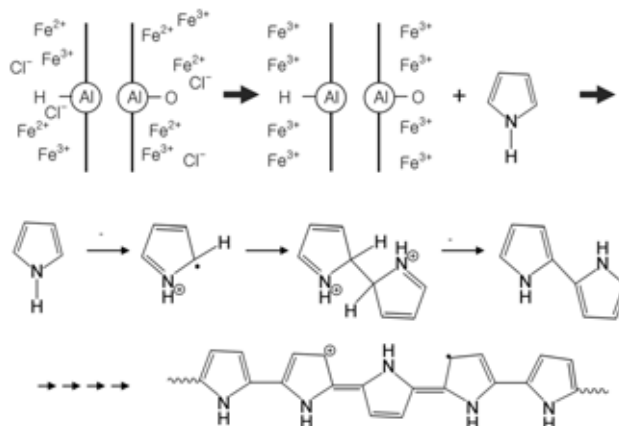
Imogolite nanotubes can be surface modified by 3-aminopropyltriethoxysilane (3-APS) in anhydrous toluene at 100 °C as shown in scheme 6 (Qi et al., 2008). Such surface modifications help compatibilize the inorganic nanotube imogolite with organic polymer matrices so that nanocomposites with a good interphase could be developed.



Scheme 6. Modification of imogolite surface by 3-APS (from Qi et al., 2008).

4. Synthesis of nanocomposites

Basically there are three methods to prepare nanocomposites. They are: solution casting, melt blending and in-situ polymerization. In solvent casting, a polymer, a solvent and nanoreinforcement are combined and thoroughly mixed by ultrasonication and the solvent is allowed to evaporate leaving behind the nanocomposite typically as a thin film. The solvent chosen should completely dissolve the polymer as well as disperse the nanoreinforcement. The solvent used will help in the mobility of the polymer chains which in turn helps in the intercalation of the polymer chains with the layered nanoreinforcement. In the case of melt blending, extruder or an internal mixer is used. Polymer and nano reinforcement are added in the extruder and subjected to intensive mixing for some time and nanocomposite comes out from the die. In this method, polymer mobility simply comes from thermal energy. In case of in-situ polymerization, which is widely used for PLS nanocomposite synthesis, initially the monomer and nano reinforcement are mixed. The monomer is allowed to intercalate between the silicate layers. Once the monomer is intercalated it is polymerized. The polymerization may be due to some surface modification at silicate surface or due to any functionalities present which catalyze the reaction (Alexandre and Dubois, 2000). There have been numerous reports on the synthesis of conducting polymer nanocomposites (Fang et al., 2008; Gangopadhyay and De, 2000). In an interesting work by Lee et al (2006), polypyrrole coated imogolite was synthesized by exposing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ absorbed imogolite to pyrrole vapor under ambient conditions (scheme 7).

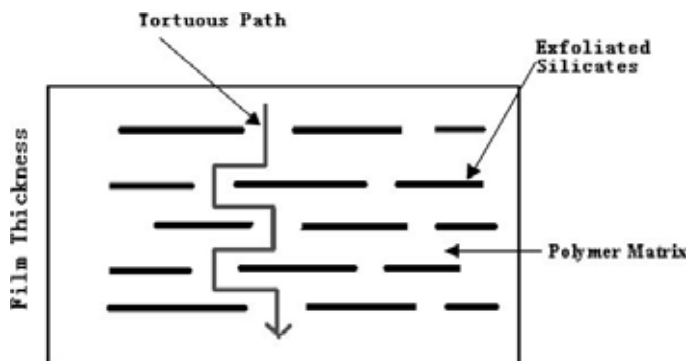


Scheme 7. Scheme to prepare polypyrrole-imogolite in a doping state with an acceptor dopant (FeCl_3) (from Lee et al., 2008).

5. Properties of polymer nanocomposites

5.1 Barrier properties and flame retardancy

The search for non-halogenated flame retardants has led to nanoclays, one nm thick by 1000 nm diameter. Initial research showed that the addition of as little as 5% of nano-sized clay particles could produce a 63% reduction in the flammability of nylon-6. More recent studies have shown that flame retardancy in many other polymers can be boosted by dispersing clay at the molecular level. Clays are believed to increase the barrier properties by creating a maze or ‘tortuous path’ (Scheme 8) that retards the progress of the gas molecules through the matrix resin (Neilson, 1967). For example, polyimide/layered silicate nanocomposites with a small fraction of O-MMT exhibited reduction in the permeability of small gases, e.g. O_2 , H_2O , He, CO_2 , and ethyl acetate vapors [Ray and Okamoto, 2003].



Scheme 8. Neilson’s tortuous path model for barrier enhancement of nanocomposites (from Neilson, 1967).

Kashiwagi et al. [2002] studied multiwall nanotubes in polypropylene. A comparison of heat release rate curves among the three samples is shown in Figure 9. The results show that the

heat release rates of the PP/MWNT nanocomposites are much lower than that of PP even though the amount of MWNTs in PP is quite small. This reduction in heat release rate is at least as much as what was previously found for clay nanocomposites in a maleic anhydride modified PP. Kashiwagi attributed the performance of the MWNT more to the presence of the small amount of iron catalyst in the MWNT. This iron may form iron oxides during combustion and iron oxides have been used as flame retardant additives. Another possibility that has been suggested is that the nanotubes function by conducting heat away from the flame zone.

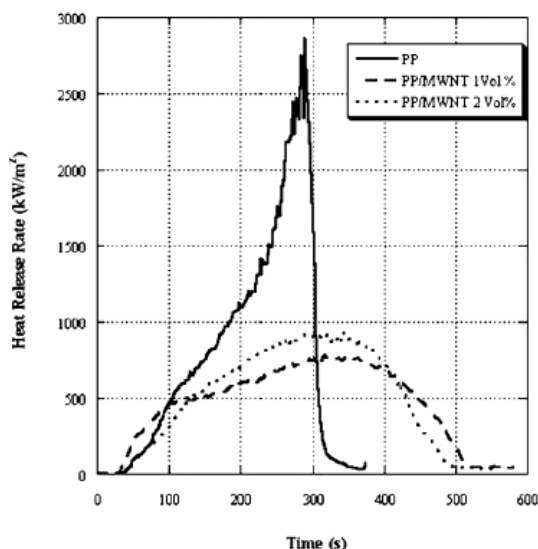


Fig. 9. Heat Release Rate for PP with CMWNT (from Kashiwagi et al., 2002).

Beyer [2002] studied the effect of adding montmorillonite nanoclays modified with a quaternary ammonium compound and carbon multiwall nanotubes in ethylene-vinyl acetate (EVA). Beyer made several observations:

1. Nanotubes did not accelerate the time to ignition like the nanoclays (the clay's acceleration was attributed to the decomposition of the quaternary ammonium compound within the nanoclay.)
2. Nanotubes are better than nanoclays at reducing the peak heat release rate at either 2.4% or 4.8% loading. The char showed much lower crack density for nanotubes. The hypothesis is that the high aspect ratio of the nanotubes formed a reinforcing composite that made the char more resistant to cracking. The reduced cracking provided better insulation to the unburned polymer surface and hence reduced the emission of volatile gasses into the flame area.
3. An equal mixture of 2.4% nanotubes and 2.4% nanoclay gave a synergistic reduction in peak heat release rate. The char showed the least amount of cracking, due to the combined reinforcement effect of both fillers. Das and Bandyopadhyay (2011) and Das et al. (2011) developed poly(methyl methacrylate) (PMMA)/MWNT nanocomposites and investigated their thermogravimetric and resistivity properties.

5.2 Optical clarity

The presence of reinforcement incorporation at nano-levels has been shown to have significant effects on the transparency and haze characteristics of films. In comparison to conventionally filled polymers, nanoclay incorporation has been shown to significantly enhance transparency and reduce haze. With butyl rubber, polyamide and acrylic rubber based clay nano composites, this effect has been shown to be due to modifications in the crystallization behavior brought about by the nanoclay particles; spherulitic domain dimensions being considerably smaller. Clays are just into thin, albeit their micro- lateral size. Thus, when single layers are dispersed in a polymer matrix the resulting nanocomposite is optically clear in the visible region (Figure 10). At the same time, there is a loss of intensity in the UV region (for $\lambda < 300$ nm), mostly due to scattering by the MMT particles. There is no marked decrease in the clarity due to nano-dispersed reinforcements compared to that of the neat-unfilled-polymer (for any relevant o-MMT loadings $\phi \leq 9$ wt%). This is a general behavior as seen by UV/vis transmittance for thick films (3–5 mm) of polymer/MMT nanocomposites, based on PVA [poly(vinyl alcohol)] (Strawhecker and Manias, 2000), PP (Manias et al, 2001), and several epoxies. Recently, Anandhan and Arunjunairaj (2011) have obtained similar results on poly(ethylene-co-vinyl acetate-co-carbon monoxide)/O-MMT hybrid nanocomposites.

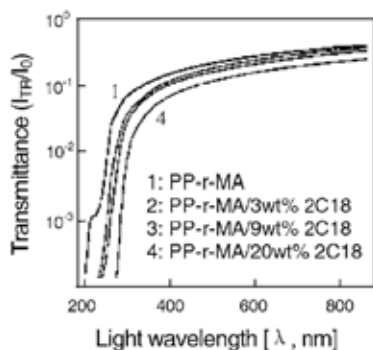


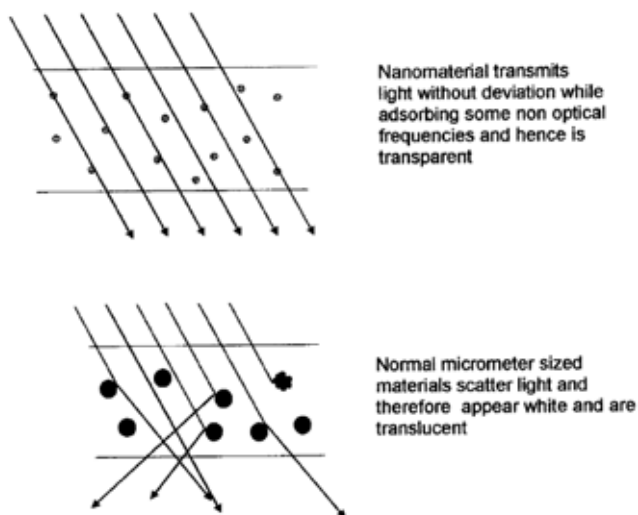
Fig. 10. UV-visible transmittance for MA-functionalized PP and its MMT nanocomposites as a function of MMT loading (from Manias et al., 2001).

Thermoplastic elastomeric polyurethane (TPU) and O-MMT nanocomposites were synthesized and characterized by Lee et al (2004). They found out that the light transmittance of TPU/O-MMT did not reduce appreciably even after incorporation of 5 wt% clay in TPU matrix (figure 11).



Fig. 11. Visual appearance of TPU/O-MMT nanocomposite films: a) TPU, b) TPU/3wt%O-MMT, c) TPU/5 wt% O-MMT.

A plausible reason for the above observations could be that the size of nanoclay particles is less than the wavelength of visible light; hence, visible light rays are not appreciably scattered by nanoclay particles. But, visible light rays could be appreciably scattered by regions where clay particles form agglomerates. This fact could be understood by looking at scheme 9 (Wilson et al., 2002).



Scheme 9. Light rays passing mostly undeflected through an array of nanoparticles, so the array is transparent. When the particle size of the same material increases, light rays are scattered and the material becomes translucent (from Wilson et al., 2002).

5.3 Miscellaneous properties

Razafimahefa et al (2005) found out that a polyamide-6/clay nanocomposite fiber yarn dyes itself faster with disperse dyes than unfilled polyamide-6 yarns. Aqueous coatings of intercalated smectite clay particles in poly(N-vinyl pyrrolidone) and poly(ethylene oxide) matrices were found to have the potential to be used in inkjet media with improved receptor properties (Majumdar et al., 2003). Modification of elastomer surfaces (having low surface energy) using nanoreinforcements to increase their adhesive behavior is relatively a new approach. In a recent work, two different nanoclays such as Cloisite-15A (modified nanoclay) and Cloisite-NA (unmodified nanoclay) were incorporated into the vulcanized EPDM matrix and the adhesion strength between vulcanized EPDM to unvulcanized EPDM was investigated. It was found that Cloisite-NA showed better peel strength as compared to Cloisite-15A. A maximum of 56% improvement of peel strength was accomplished with 4 wt% Cloisite-NA concentration in EPDM. A similar improvement of adhesion is also observed with other rubbers (Bhowmick et al., 2010). For example, adhesion of thiokol rubber with aluminum was enhanced by five folds with the incorporation of 8 wt% of Cloisite-30B nanoclay (Figure 12).

PVA/Na⁺-MMT nanocomposites of various compositions were studied by Strawhecker and Manias (2000). The clay layers promote a new crystalline phase different than the one of the respective neat PVA, characterized by higher melting temperature and a different crystal

structure. This new crystal phase reflects on the composite materials properties. Namely, the hybrid polymer/silicate systems have mechanical, thermal, and water vapor transmission properties, which are superior to that of the neat polymer and its conventionally filled composites.

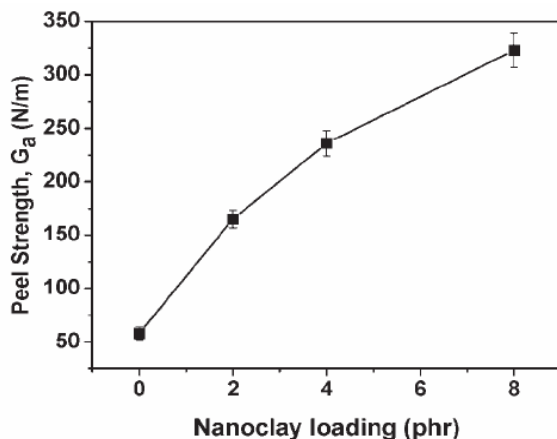
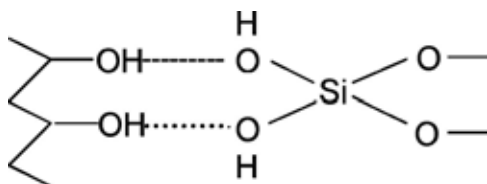


Fig. 12. Effect of concentration of Cloisite-30B nanoclay on adhesion strength of thiokol rubber against aluminum (from Bhowmick et al., 2010).

The improvement in properties of PVA could be attributed to the hydrogen bond formation between PVA and silicate layers (scheme 10). Heat distortion temperature (HDT) is the temperature at which a polymer sample deforms under a specified load. In general, improvements of HDT are reported by nanocomposite formation. Usually, a significant increase is achieved for clay contents of approximately 5 wt%, and then HDT values level off for higher clay loadings (Kojima et al., 1993; Ray et al., 2003; Nam et al., 2001).



Scheme 10. Hydrogen bonded poly(vinyl alcohol/clay) organic-inorganic hybrid structure.

Atieh et al. [2005] studied the properties of natural rubber (NR)/MWCNT nanocomposites. Mechanical test results show an increase in the initial modulus for up to 12-fold in relation to neat NR. The composites containing 10–20 wt% uniformly dispersed CNT exhibited significant drop of volume resistivity [Kazumasa et al., 2005]. The effect of CNTs on the mechanical and electrical properties of ethylene-propylene-diene monomer (EPDM) rubber in comparison to that of high-abrasion furnace carbon black was studied by Ying et al. [2002]. Kar and Bhowmick [Ganguly et al., 2008] developed MgO nanoparticles and investigated their effect as cure activator for halogenated butyl rubber and obtained promising results.

Many nanocomposites based on conducting polymer matrices have been reported in the literature (Gangopadhyay and De, 2000). Lee et al (2006) studied electrical properties of polypyrrole coated imogolite and found that conductivity after modification with polypyrrole increased with polypyrrole thickness at various voltage conditions. They opined that the resultant conducting nanofibers can be utilized in electronic applications. Sengupta et al. (2010) have extensively reviewed mechanical and electrical properties of graphite and modified graphite reinforced polymer composites.

6. Applications of polymer nanocomposites

The improvements in mechanical properties of nanocomposites have resulted in major interest in numerous automotive and general/industrial applications. It includes potential for utilization as mirror housing on various types of vehicles, door handles, engine covers, and belt covers. More general applications include: packaging, fuel cell, solar cell, fuel tank, plastic containers, impellers and blades for vacuum cleaners, power tool housing, and cover for portable electronic equipment such as mobile phones and pagers.

6.1 Gas barriers for plastic bottles, packaging and sports goods

Hybrids made of poly(dimethyl siloxane) rubber and nanosilica generated in-situ by hydrolysis of tetraethyl orthosilicate can be specifically shaped, giving objects such as golf balls (figure 13) (Hu and Mackenzie, 1992; Chung et al, 1990; Mackenzie et al, 1992).



Fig. 13. Rubbery hybrids with different shapes (from Sanchez et al., 2005).

A number of polymer nanocomposites based on polymers, such as butyl rubber, styrene butadiene rubber, ethylene propylene diene monomer rubber, ethylene vinyl acetate copolymer, ethylene-octene copolymer, have been used commercially for barrier applications. These polymers can act as excellent barriers for many gases such as CO_2 , O_2 , N_2 , and chemicals such as toluene, HNO_3 , H_2SO_4 , HCl , etc. Due to excellent solvent barrier properties PNCs have been utilized in chemical protective and surgical gloves in order to protect against chemical warfare agents and for avoiding contamination from medicine.

PNCs also have been widely used in food packaging and plastic containers, both flexible and rigid. Specific examples include packaging for processed meat, cheese, cereals and dairy products, printer cartridge seals, medical container seals for blood collection tubes, stoppers for medical containers and blood bags, baby pacifiers and drinking water bottles.

The incorporation of layered silicate clay reduces diffusion rate of small molecules, such as water and oxygen, through polymer films. Clay based polymer nanocomposites have been used in plastic bottle manufacturing industries for improving barrier, mechanical properties and self life of the product. To improve the bottle's properties and seek an alternative solution, plastic bottles have been tried in the beer package industry. The shelf-life of a clay based nanocomposite plastic beer bottle is more than 6 months. The first plastic beer bottle based on clay has been introduced by Honeywell. Nanocomposites have been used for beer bottle manufacture to solve many problems, such as the beer colloids instability, including biological and non-biological aspects, oxygen permeation and bad taste due to light exposure (Ke and Stroeve, 2005). A study on nitrile rubber/organoclay nanocomposites (in 10 wt % organoclay) reveals that the relative vapor permeability for water and methanol was reduced up to 85% and 42%, respectively, compared to the neat polymer.

One of the recently commercialized sports goods is double core Wilson tennis ball (figure 14). The clay nanocomposite coating of the Wilson tennis balls maintains the internal pressure for an extended period of time. The core is coated by a butyl rubber-clay (vermiculite) nanocomposite that acts as a gas barrier, doubling its shelf life. By polymer nanocomposites, more flexible coatings with gas permeability 30-300 times lower than butyl rubber has been produced. These coatings have been shown to be undamaged by strains up to 20%. This double core new tennis balls using this coating retain air longer, and it able to bounce twice as long as ordinary balls (improvement in air retention). It is anticipated this technology can be extended to the rubber industry and be incorporated into soccer balls or in automobile or bicycle tires [Koo, 2006]. Another important application in sports good is basketball shoe pouch manufactured by Triton Inc. from EVA/clay nanocomposites. Figure 15 shows clay nanocomposite pouch filled with helium inserts that fits into basketball shoe. The ultimate property of the pouch is that it can give good resilience for basket ball player while jumping; meantime, it exhibits excellent gas barrier properties. The Converse system developed this process, but, Triton System has manufactured it first [Koo, 2006].

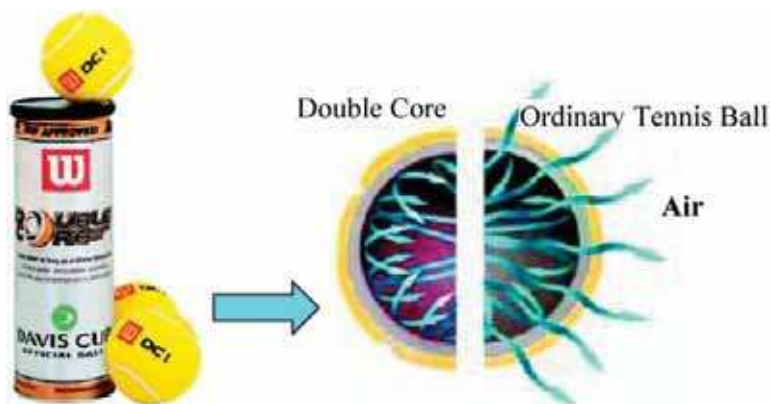


Fig. 14. The core of this Wilson tennis ball is covered by a polymer-clay nanocomposite coating (from Sanchez et al., 2005).

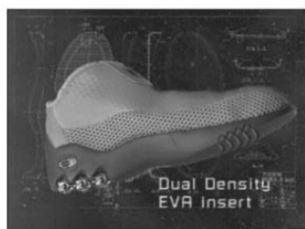
On the other hand tire industry is another very important application field for rubber/clay nanocomposites for improving barrier and mechanical properties of tires and tubes. The excellent air retention properties of butyl/halo butyl and chemically modified rubbers with incorporated clays are very well known in the tire industries as these nanocomposites are widely used in the inner tube and inner liner in automotive tires for improving many properties such as tensile, tear resistance, rolling resistance, dimensional stability, improved flame resistance and enhanced air retention.

6.2 Energy storage systems and sensors

Fuel cells act as electrochemical devices, which convert chemical energy of carbon, hydrogen and oxygen directly and efficiently into useful electrical energy with heat and water as the only byproducts. Due to incorporation of nano materials their efficiency increases considerably. In fuel cells, proton exchange membrane's role is to allow proton transport from the anode to the cathode, to be an electron nonconductive material and to act as a gas separating barrier (Prater, 1990). Typical membranes are made of organic polymers containing acidic functions such as carboxylic, sulfonic or phosphonic groups which dissociate when solvated with water, allowing H_3O^+ (hydrated proton) transport. Therefore, the membrane performance is related to the ionic group amount and to the hydration rate. Moreover, the membrane needs to be chemically (highly acidic medium) and thermally (from 80 to 140 °C) stable. Membranes made of silylated-sulfonated poly(ether ether ketone) (Premchand et al., 2008), poly(benzimidazole)/sulfonated silica nanoparticle nanocomposite (Suryani and Liu, 2009), fluorinated polybenzimidazole/silica nanoparticle composites (Chuang et al., 2007) were used as proton conducting membranes for fuel cell applications and were reported to be superior in terms of proton conductivity than pristine polymer membranes.



Nanocomposite pouch filled with helium



Insert that fits into the shoe



Fig. 15. Converse basketball shoe pouch by Triton Systems Inc (from Koo, 2006).

Sulphonated polystyrene ethylene butylene polystyrene/montmorillonite nanocomposites can be used as proton exchange membranes [www.azom.com, 2010] due to their superior

proton exchange capacity. Several polymers are being used in fuel cell applications, such as hyperbranched polymer with a hydroxyl group at the periphery, cross linked sulphonated poly(ether ether ketone), sulfonated polybenzimidazole copolymer, phosphoric acid doped polybenzimidazole, sulfonated polyarylenethioethersulfone, sulfonated polybenzimidazole, etc. Clay incorporated thermoset polymer fuel cells exhibit higher proton conductivity, better ion exchange capacity and rate of conductivity is high even at higher humidity and improved mechanical properties [Bai and Ho, 2008]. Anis et al. (2008) developed PVA/nano heteropolyacid nanocomposites that could be used in fuel cell electrolyte membranes.

Another important storage application of clay based nanocomposite is solar cells. PLS nanocomposites based solar cells have the potential to become one of the leading technologies in conversion of sunlight to electrical energy. Because of their ease of processing from solution, fast and low cost mass production of devices is possible in a roll-to-roll printing fashion. They exhibit high efficiency, enhanced light absorption and possess excellent barrier cum mechanical strength [Yang and Loos, 2007]. Even though solar cells are used outdoors, one need not worry about damage from any mechanical actions or UV rays for clay based thermoset nanocomposites. Various polymers have been used for solar cell manufacturing, such as poly(phenylene-vinylene), polythiophene, polyfluorene, polyaniline, polypyrrole, etc. PLS nanocomposites have been widely used in sensor technology too. Many novel polymers, such as polyamidoamine dendrimer, silicone, hyper branched polymers, polyacrylamide, etc. have been used for sensing gas, atmospheric moisture, detection of solvent leaking in pipe line application, etc. Clay incorporated elastomers are being developed as sensors to detect fatigue, impact and large strain for aerospace applications.

6.3 Optical glass and membranes

Clay incorporated polymers have been shown, when employed to coat transparent materials, to enhance both toughness and hardness of these materials without sacrificing light transmission characteristics. An ability to resist high velocity impact combined with substantially improved abrasion resistance of PLS nanocomposites was demonstrated by Triton Systems. Owing to this reason and improved optical properties it has been widely commercialized in contact lens and optical glass applications (Haraguchi, 2011).

Polymer/clay nanocomposites can also be used to fabricate various types of membranes, such as solvent filters, filters for bacteria and virus (www.nanowerk.com), solid electrolytes for fuel cells, membrane for gas separation, etc (Cong et al., 2007). Organic membrane technology is used to design membranes for separating synthetic gas from natural gas. The transformation of natural gas into liquid materials requires design of inorganic membrane catalysts. Lot of research has been done on membranes based on thermoset clay nanocomposites. Polymers, such as polyimide, polybenzimidazole, cross-linked sulfonated poly(ether ether ketone), and polyacrylate, have been widely used for membrane applications. The creation of nanopores in nanocomposites by the use of nanoreinforcement is the main mechanism in gas, solvent separation and transportation. The nanopores decide the sensitivity and quality of the membrane (www.nanowerk.com).

6.4 Products with low flammability

The ability of nanoclay incorporation to reduce the flammability of polymeric materials is incredible. Gilman demonstrated the extent to which flammability behavior could be

restricted in polymers like polypropylene with as little as 2% nanoclay loading. The improvement of flame resistance by incorporation of clay has been commercialized in various applications including cable wire jacket, car seats (Hard Foams), packaging films, textile cloths, surface coatings for many steel products, paints; one of the higher end applications is rocket ablative materials core manufacturing (Koo, 2006). Na⁺-MMT in nitrile rubber nanocomposites showed higher flame retardancy with good oil resistance as compared to a control sample [Wang et al., 2009]. Figure 16 shows nanocomposite power cable developed by Kabelwerk Eupen.

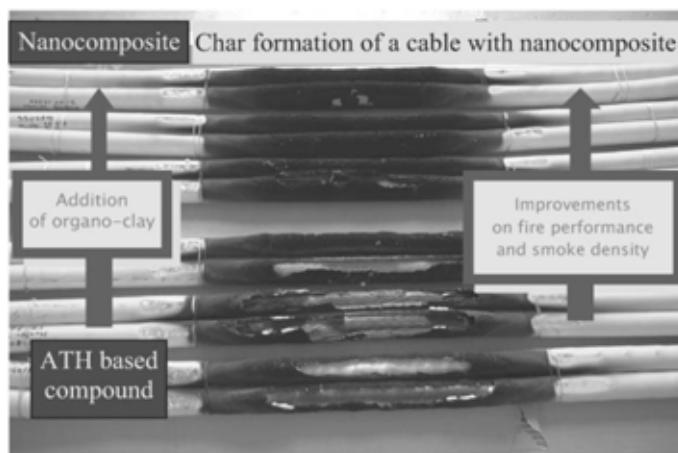


Fig. 16. Nanocomposite power cable by Kabelwerk Eupen (from Koo, 2006).

Polyurethane/clay based nanocomposites also exhibit superior flame retardancy and they have already been commercialized in automobile seats manufacturing (hard foam). Borden Chemicals' SC-1008, a resole phenolic, was selected as the resin for manufacturing rocket ablative material with MMT. The nano scale distribution of silicate layers leads to a uniform char layer that enhances the ablative performance. The formation of this char was only minutely influenced by the type of organic modification on the silicate surface of specific interactions between the polymer and the aluminosilicate surface, such as end-tethering of a fraction of the polymer chains through ionic interaction to the layer surface. The same formulation has also been used for simulated solid rocket motor casing. It exhibited excellent flame retardancy. The ablative test was performed at around 2200°C, and the results showed that the motor has not burned.

6.5 Electronics and automobile sectors

Application of thermoset/clay nanocomposites for electronics and automobile sectors is another big milestone. The ability of nanoclay incorporation to reduce solvent transmission through polymers such as specialty elastomers, polyimides, poly urethane, etc. has been demonstrated. A study reveals the significant reductions in fuel transmission through polyamide-6/66 by incorporation of nanoclay reinforcement. The major driving force for the usage of PNCs by tire companies is reduction of weight and processing costs. Clay is one of the naturally available materials and also it possesses very low density; it facilitates reduction in weight. Clay incorporated tires exhibit excellent mechanical properties as

compared to ordinary tires as well as improved gas barrier performance for tubeless tire applications. Generally styrene butadiene and natural rubber based clay nanocomposites are mostly preferred for automobile tire manufacturing and butyl rubber is for tubes. It is due to improved abrasion resistance and thermal properties of the tires combined with their longer life (Koo, 2006).

The addition of clay into conducting polymers such as polypyrrole, polythiophene polyaniline, etc. sensibly increases conductivity and impedance effect with improved mechanical properties such as elongation, impact, scratch resistance and results in longer life of the product. These PNCs find many applications in solar cells, wind mills, electronic circuit boards, battery manufacturing, micro chips, transistor, etc. Nanocomposites consisting of spatially confined liquid crystals are of great interest due to the prospects of their application in optoelectronic devices, photonic crystals, depolarizers, scattering displays, information storage and recording devices such as compact disk, universal serial bus storage, and windows with adjustable transparency [Merhari, 2009].

6.6 Coatings

Coatings are important for modifying properties of surfaces. Several strategies have been tried by researchers for improving surface properties of products. One of the well versed developments is nanoclay based polymer coatings. Plenty of work has been done in this area [Jin et al, 2010; Turri et al., 2010]. Nanoclay incorporated thermoset polymer nano coatings exhibit superior properties such as superhydrophobicity, improved wettability, excellent resistance for chemicals, corrosion resistance, improved weather resistance, better abrasion resistance, improved barrier properties and resistance to impact, scratch, etc. Coating thickness depends on process parameters such as dipping time, temperature, nature of surfactant, purity of nanomaterial, etc. Turri et al. [2010] developed nano structured coatings based on epoxy/clay on steel substrates. The scratch strength of epoxy/clay nano structured coating was two times greater than the pristine epoxy coating. These kinds of coatings are best candidates for various applications, such as construction, thermal barriers for aerospace applications, automobile, and pipe line coatings for marine applications, sometimes for decorative purpose, textiles, etc. Clay and nano silver incorporated thermoset polymer nano coatings could be used to improve antibacterial properties and it has been widely used in medical sectors. At present these kinds of hybrid coatings are one of the promising ones for improving shelf life and antibacterial properties in medical field.

7. Conclusion

Among many highly hyped technological products, polymer nanocomposites are one of those, which have lived up to the expectation. Polymer nanocomposites exhibit superior properties, such as mechanical, barrier, optical, etc. as compared to micro- or macro-composites. Owing to this, polymer nanocomposites have shown ubiquitous presence in various fields of application. Polymer nanocomposites for various applications could be synthesized by proper selection of matrix, nanoreinforcement, synthesis method and surface modification of either the reinforcement or polymer (if required). Many products based on polymer nanocomposites have been commercialized. This review has tried to highlight various types of nanoreinforcements and their surface modification procedures, some unique properties of nanocomposites, various technological applications of polymer nanocomposites with some specific examples of commercialized products. Though it is not a

comprehensive one, this review could give a basic idea about polymer nanocomposites to a beginner.

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