Polymer-clay Nano Composites

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ABSTRACT

Nano has now become a theme in almost all the established discipline. The confluence of innovative methodologies, sophisticated characterisation techniques, and potential technological utility has resulted in intense research activity in the field of polymer nano composites. Polymer composites made out of nano materials display unique properties in terms of improved tensile strength, flexibility, and flexural endurance. The paper discusses the development of polymer-clay nano composites, both from the conceptual point of view as well as practical methods for the synthesis of nano composites. These are monomer intercalation, monomer modification, common solvent, and melt-intercalation methods. Various models have been discussed that describe improvements in mechanical and barriers properties due to the incorporation of nano materials. Ongoing R&D work in the two DRDO laboratories on the development of nano composites has been briefly mentioned. The emerging use of polymer-nano composites has also been described.

Keywords: Nano composites, polymer-clay composites, nano technology, nano materials, polymer-clay nano composites

1. INTRODUCTION

Nano composites have received considerable attention in the recent years, both from scientific as well as industrial perspective [1-4]. These composites are formed through the union of two different materials with organic and inorganic pedigrees. The integration of a second component into a host system allows for the combination of physical or chemical properties that can not be achieved by modification of the matrix alone.

The modern interest in nano composite materials can be traced back to the development of backalite or phenolic resins in 1906. Bakelite was hard and brittle material and could not find any practical application on its own. The addition of short cellulose fibres, and subsequently, the wood powder, however, improved Backalite's processability and physical, chemical, and electric properties, as well as reduced the cost.

In the early 1960's, research work on advanced composite materials started with the availability of strong and stiffer fibres such as carbon, boron, aramid, and glass. For conventional composites, phase mixing typically occurs on a macroscopic (mm) scale, as a result, the filled materials lack from an intense interaction at the interface between the two partners. In general, macroscopic reinforcing elements always contain imperfections that affect their load-bearing capability and other properties. In spite of these limitations, the traditional polymer

composites filled with micrometer-sized fillers often show improvements in their mechanical properties[5,6] in the form of increase in modulus, yield strength, and glass transition temperature (T_g).

The goal of micro-composites has been to produce tough, flaw-insensitive materials that fail in ductile manner by virtue of crack deflection and crack-tip shielding. However, improvement in properties are usually accompanied by losses in ductility and toughness. In addition, large amounts of filler are required to achieve the desired properties, often offsetting the weight savings gained in usually low-density polymers. Theory of reinforcement in composites suggests that filler volume fraction, which is a quantitative measure of degree of reinforcement of the matrix, determines the enhancement of properties[7,8]. In the form of fibre-reinforced unidirectional and multi-directional composites, very high values of strength and stiffness can be achieved[8] with volume fraction of about 60 per cent.

Takayanagi[9] proposed the concept of molecular composite for the intimate mixing of two different materials that can produce synergistic effect, which was subsequently defined as a nano composite. For a nano composite, phase mixing occurs on a nanometer length scale. It is known that more and more structural perfection is reached if the reinforcing composite elements become smaller and smaller.

The two major findings that pioneered the revival of polymer-clay nano composites are the successful preparation of nylon-6/montmorillonite nano composites, for obtaining improved product by Toyota Chemical Research, and experiments by Giannelis, *et* al. which showed that melt-mixing of polymers with clay is possible without using organic solvents[10-12]. Another route adopted was to modify the clay by making these organophilics using organic solvents[13-15].

The subject of nano composite is of great vitality and offers immense opportunity because a variety of compounds can be synthesised by combining a wide variety of host materials as well as polymers.

Due to the ability of certain minerals to organise and direct polymer synthesis, these have been used extensively for the preparation of nano composites. Some of these typical minerals are montmorillonite, sapotite, makatite, octosilicate, magadite, and kenyaite group of clay[16]. All these comprise silicate layers in which the functional unit is about 1 nm thick planer structure. These also interact with a variety of natural and synthetic organic compounds. Uptake of a solvent by the clay gives the individual platelets mobility wrt one another and provides a mechanism for rearrangement of reactive sites into a variety of patterns. Usually, the lattice energy of swellable clay minerals is so high that it is stable even at high temperature[17] up to about 1000 °C. Wide acceptance of these inorganic nano particles is also due to the low cost and ease of incorporation. Also, the use of a variety of clays and polymeric matrices have produced similar results in terms of property enhancement[17-19]. Interaction of inorganic layered materials with polymers has the following characteristics.

• Polymers can be accommodated in the inter layer region with the retention of the structural features of the layered hosts.

• Inter layer spaces are adaptable to the size of guest polymer.

• Accommodation of guest species in the inter layer spaces is influenced by the characteristic environment surrounded by the adjacent host layers.

Polymers-clay nano composites show unique combinations of mechanical and thermal properties, often at very low filler weight fractions. Small amounts (typically less than 5%) of nanometre thin layered inorganic fillers give rise to the same levels of mechanical and thermal improvements as are typically achieved with loadings of 30 per cent to 50 per cent of micron-sized fillers[20-24]. The polymer-clay nano composites also exhibit other enhanced properties including high heat distortion temperature, enhanced flame resistance, better barrier property, and decreased thermal expansion coefficient due to structural, chemical, and thermal stabilities induced by rigid inorganic framework[25-26]. The enhanced properties are presumably due to the synergistic effects of the nanoscale fillers and polymer molecules.
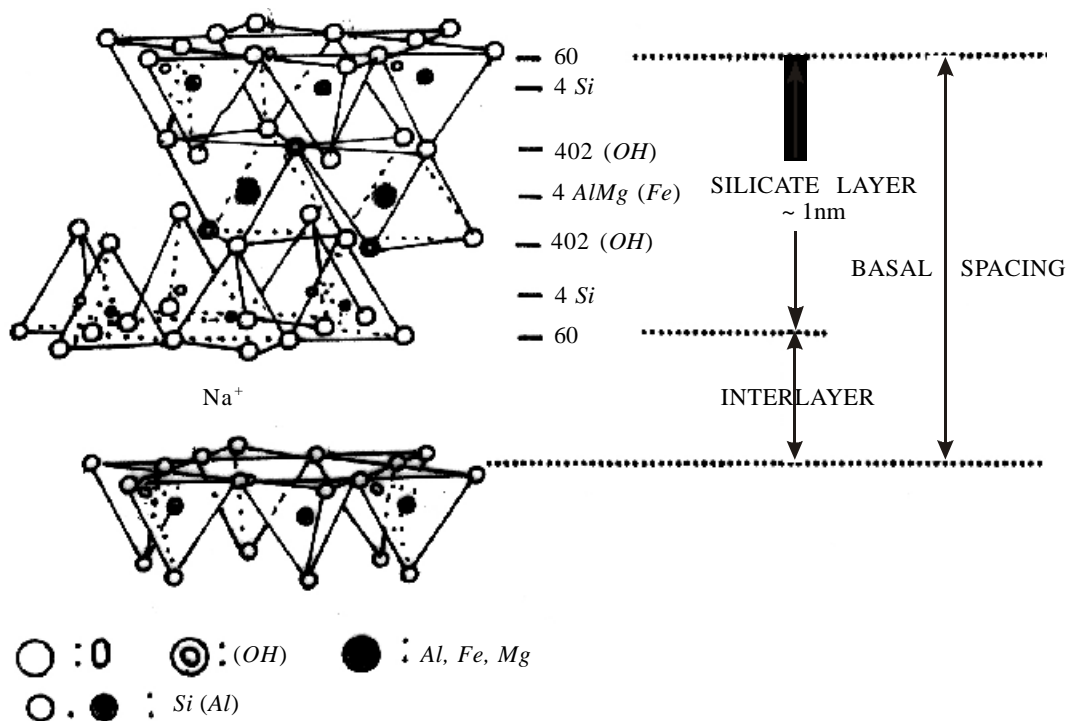
Figure 1. Structure of layered silicate like montmorillonite showing interlayer distance and basal spacing.

2. SYNTHESIS OF POLYMER-CLAY NANO COMPOSITES

Kato and Usuki[19] described four methods for the synthesis of polymer-clay nano composites. These are monomer intercalation, monomer modification, common solution, and polymer intercalation. Another method is also utilised for making rubber-based nano composites using co-vulcanisation.

2.1 Monomer Intercalation Method

Monomer intercalation method deals with incorporation of monomer and their polymerisation in the inter layer of the clay. A clay mineral is a potential nanoscale additive because it comprises silicate layers in which the fundamental unit is 1 nm thick planer structure (Fig.1). Natural *Na*-montmorillonite is hydrophilic and not compatible with most organic molecules. However, *Na* cations in the inter layer space of montmorillonite can be exchanged with organic cations to yield organophilic montmorillonite. The smectite clays, such as montmorillonite and hectorite, also have the ability to organise and direct polymer synthesis due to unique structural and chemical properties[27]. Polymerisation of a monomer occurs in the inter layer of the clay mineral, resulting in an expanded inter layer gap and silicate layers that get homogeneously dispersed on a nanometer level at the end of polymerisation.

Some of the earliest works on inorganic toughening were performed in 1987 at Toyota Chemical Research Centre (TCR). It was demonstrated that an inorganic nano material, suitably modified, can be intercalated in a polymer matrix with outstanding property improvement. Toyota CRDL group utilised ammonium cation of ω-amino acids as a catalyst for the ring opening polymerisation of ε-caprolactum. The polymerisation of nylon-6 occurred in the presence of *Na*-montmorillonite after ε-caprolactum was intercalated into the gallery uniformly. This material contained only 4.2 Wt per cent clay and had a 50 per cent increase in the heat distortion temperature (HDT) of 80 °C, a 100 per cent increase in tensile modulus, and 20 per cent increase in impact strength[14,15]. The data are available on the improvement of properties over the neat nylon and conventional composite of nylon.[14, 15]

It has been reported that the presence of alkyl ammonium ions induces an increase in the amount of polymer in the inter layer and lowering of the reaction temperature[28]. Monomer intercalation method was also used by Cornell University group for the preparation of epoxy resin-clay composite[29-31]. In that case, diglycidyl ether of bisphenol A [Epon-828] was used as a matrix resin and poly-(ether amine) as a curing agent. Three types of clays were examined. From x-ray diffraction patterns, the Corndi University Group claimed that the formation of exfoliated clay-nano composite was dependent upon the nature of organophilic montmorillonites. Tensile strength and Young's modulus increased drastically for nano composites over the pristine polymer.

Poly(vinyl alcohol)-based nano composite has been tried by Strawhecker[20], et al. using montmorillonite as nanoscale filler. They emphasised the presence of new crystal phase of polyvinyl alcohol at the interface of montmorillonite. The hybrid polymer/silicate system had three-times higher Young's modulus as compared to the neat film. The hybrid film showed a reduction of about 60 per cent water permeability.

2.2 Monomer Modification Method

Modification of monomer has been tried to make it chemically compatible with clay to form polymer-clay nano composite. Acrylamide monomer has been modified to a water-soluble quaternary ammonium salt of *N*-[-3- (dimethylamino)propyl] acrylamide and reacted with hydrophilic *Na*-montmorillonite which gets ion-bounded to silicate layers. A number of acrylic resin-clay nano composites have been prepared by dispersing montmorillonite in an aqueous suspension of acrylic resin. An aqueous suspension of acrylic resin-clay nano composite exhibited the properties of a pseudo-plastic fluid with a clay content of above 3 per cent. The acrylic resin-clay nano composite films cross-linked by melamine are transparent. The gas permeability of the resulting films decreased to about 50 per cent with a monmorillonite addition of 3 per cent.

A polymethyl methacrylate-clay nano composite was synthesised using modified organophilic clay monomer modification by emulsion polymerisation[32]. Acrylic resin has been modified with ethyl acetate, acrylic acid, and acrylamide, and four types of nano composites have been prepared by dispersing montmorillonite in its aqueous suspension[33,34]. The resulting composite having 3 per cent montmorillonite and cross-linked with melamine was transparent and showed reduction in gas permeability of about 50 per cent.

2.3 Common Solvent Method

Common solvent method has been used to develop materials having low coefficient of thermal expansion, less moisture absorption, and dielectric coefficient. Polyimide-clay nano composites have been attempted using polyamic acid as precursor for polyimide with dodecyl ammonium ion as intercalating reagent, montmorillonite as clay, and dimethylacylamide (DMAC) as dispersing agents[35]. Ammonium ions with 10-12 carbon atoms were found suitable for organophilic montmorrilonite to be dispersed in DMAC. Longer carbon chain makes the organophilic montmorrilonite too hydrophobic. Dispersibility of organophilic montmorillonite was most important for the resulting composite. A montmorrilonite addition of 2 per cent brought the permeability of water vapours to a value less than one-half of the polyimide. However, the water adsorption at equilibrium was the same for with and without clay. Permeability of CO_2 was half in polyimide-clay composite as compared to polymer without clay[36].

2.4 Polymer Melt Intercalation Method

Polymer melt intercalation method had been evolved to overcome the difficulty of intercalation of nano material in polymers which do not possess any polar group in their backbone. Figure 2 presents the conceptual approach to the process. Clay having layered structure after modification is mixed at the requisite temperature where the polymer chains become mobile. The polymer chains enter the inter layer gap of the clay mineral. Layered clay is represented by the stacked structure and polymer chains by their typical isolated coiled structure. A nano composite is made by heating a mixture of a polymer (polypropylene) and an organophilic nano clay above the melting point of the polymer
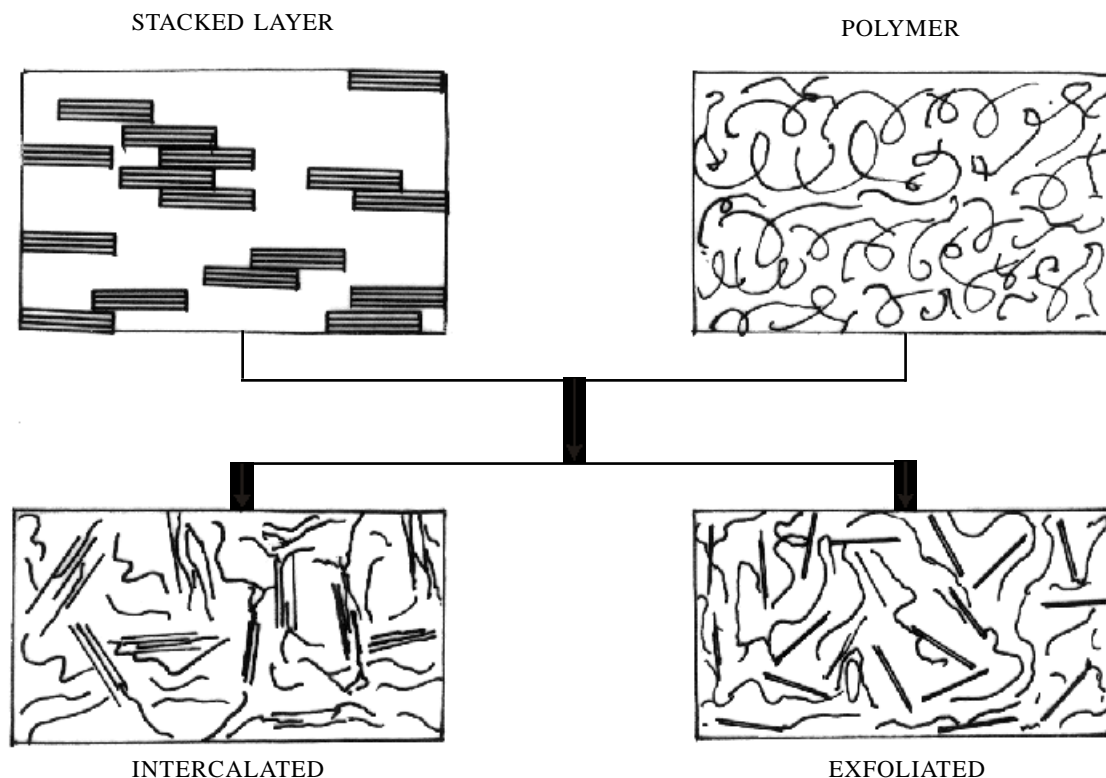
STACKED LAYER

POLYMER

INTERCALATED

EXFOLIATED

Figure 2. Schematic presentation of formation of nano composites having intercalated and exfoliated structures from polymer (organic) and clay (inorganic) interaction.

(polypropylene) and forcing the polymer chains into the clay galleries. Employing lattice-based statistical thermodynamics, Vaia and Giannelis[12] developed a model to explain polymer melt intercalation process in the clay.

Figure 3 shows that in general, an interplay of entropic and energetic factors determine the outcome of polymer intercalation. Here, three different interactions are considered, namely the polymer-surfactant interaction, the surfactant-surface interaction, and the polymer-surface interaction. The model indicates that the free energy, ΔG for complete exfoliation of the thermoset-nano composite is the sum of the terms contributed by the polymer matrix ($\Delta Gp = \Delta Hp - T\Delta Sp$) and clay ($\Delta Gc = \Delta Hc - T\Delta Sc$) and the total free energy change is $\Delta Gt = (\Delta Hp + \Delta Hc) - T(\Delta Sp + \Delta Sc)$, that is equal to $\Delta Gt = (\Delta Ht - T(\Delta St))$.

When monomer or polymer penetrates into the silicate layers, the entropy change is negative while expansion of gallery shows positive entropy change. The total entropy change determines whether or not exfoliation occurs. Depending upon the condition of fabrication of nano composites, various types of structures can be formed as a result of their interactions within the polymer matrix.

Exfoliated nano composites show greater phase homogeneity than the intercalated ones. In exfoliated state, almost each monolayer contributes fully to the interfacial interactions with the matrix. This structural distinction is the primary reason why the exfoliated clay is specially effective in improving the reinforcement and other properties.

Sumita[31,32], *et al.* reported dramatic improvement in the yield stress (30 %) and Young's modulus (170 %) in nano clay-filled polypropylene compared to mica-filled polypropylene[32]. Innovation was required however for the preparation of a clay-polypropylene nano composite because of low polarity of polypropylene. A method of mechanical shear was adopted to separate out stacked layer structure of the clay. However, the chemical treatment of the clay by dimethyl-octadecyl ammonium chloride before mixing
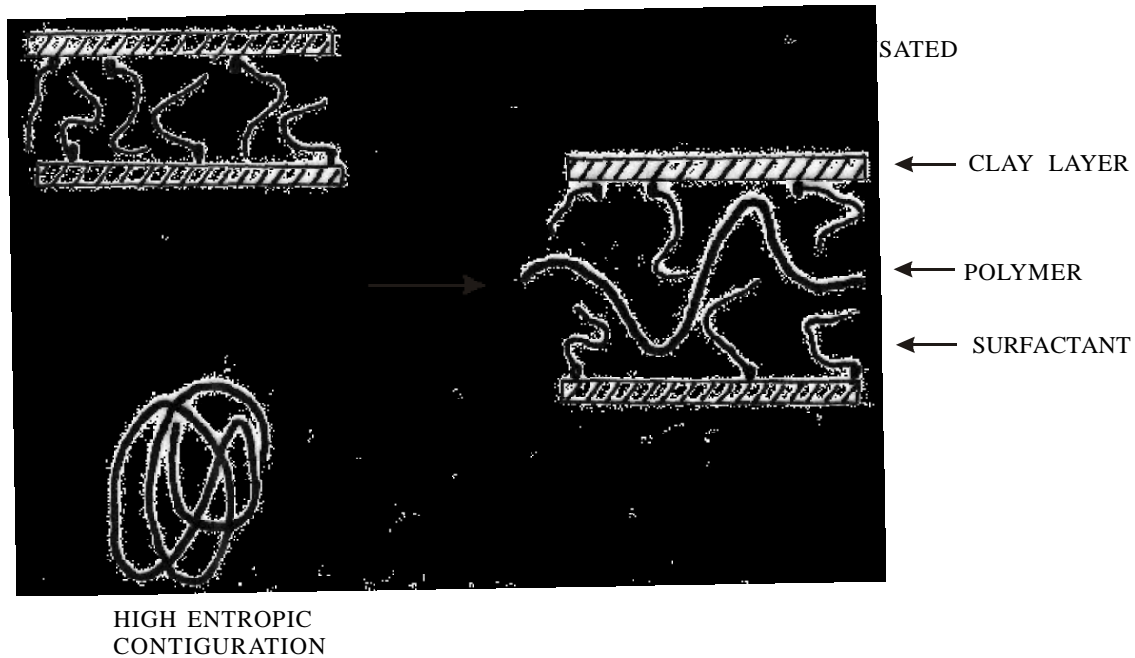
SATED

← CLAY LAYER

← POLYMER

← SURFACTANT

HIGH ENTROPIC
CONTIGURATION

Figure 3. Thermodynamic considerations in terms of entropic and enthalpic cosideration for the formation of polymer-clay nano composites.

facilitated the formation of polypropylene-clay nano composites. Improvements in mechanical properties of polypropylene have been achieved, in general, by melt-mixing with particulate (talc, mica, clay) and fibrous (glass, jute, aramid, carbon fibres) additives[34-39]. Ou[38], *et al*. filled nylon–6 with 50 nm silica particles and reported increase in tensile strength (15 %), strain to failure (150 %), Youngs modulus (23 %), and impact strength (78 %) with only 5 Wt per cent nano particles[38].

2.5 Co-vulcanisation Method

Carbon black has been used in reinforcement of vulcanised rubber as well as other polymeric products but these often decrease the processability of rubber compounds at high volume loading. Minerals, on the other hand, have a variety of shapes suitable for reinforcement, such as needles and sheets, but these have poor interaction with rubber. Attempts have been made to disperse montmorillonite in rubber, a highly hydrophobic material. Montmorillonite cation exchange with amine-treated butadiene-acrylamide oligomer in a solvent mixture of *N–N*-dimethyl sulphoxide, ethanol, and water have been used to blend with nitrile-butadiene rubber (NBR) by roll-mixing and the rubber vulcanised with sulphur.

The transmission electron microscope (TEM) evaluation indicated well dispersed silicate layers in the rubber matrix. The tensile stress at 100 per cent of this rubber-clay nano composite containing 10 parts per 100 parts of rubber (phr) of montmorillonite (MMT) was found to be equal to that of rubber containing 40 phr of carbon black. The permeability of water and hydrogen decreased by 70 per cent by adding 3.9 volume per cent montmorillonite. In a rubbery polyurethane elastomer, Petrovic and Zhang[39] found a sixfold increase in the elongation-to-break and a threefold increase in the Young's modulus was achieved with 40 per cent Wt 12 nm silica compared to a micrometer-sized filler that embrittled the polymer. Nano composites showed no reduction in transparency even at these relatively high loadings unlike the micrometre-sized filled systems.

3. STRUCTURAL CHARACTERISATION

The strength of interaction between the polymer and the layered clay, as well as the size and rigidity of these inorganic particles, has been shown to influence the extent of property enhancement. Also, the distribution, conformation, and orientation of the layered nano materials in the matrix are crucial in dictating structure-property relationship. These

morphological features are normally determined by an array of instrumental techniques.

X-ray and electron microscopy have been used extensively to determine the size, shape, and the changes in crystal structure of nano materials as well as their distribution in the matrix. Diffraction and scattering provide qualitative structural details for these systems. In addition to rapid characterisation of layer separation, powder diffraction provides information on layer order, size distribution, and atomic arrangements of the constitutions. Differential scanning calorimetric (DSC) investigations and mechanical properties are the other important parameters that provide invaluable help in evaluating the nano composites.

The most commonly utilised layered silicates for the preparation of nano composites are the smectites which possess the same structural characteristics, as is known for minerals like talc and mica. Their crystal structure is characterised by a 0.96 nm thick silicate layer consisting of two silicate tetrahedral sheets fused to an edge-shared octahedral sheet of alumina or magnesia (Fig. 1).

Depending upon a particular silicate, the lateral dimensions of the layers vary from 20 nm for laponite to tens of microns for vermiculite. The isomorphous substitute within the silicate layers generate a negative charge in the layers (eg Approx–100 meq/100 g for hectorile). This layer charge is counterbalanced by hydrated alkali metal and alkali earth cations in the gallery. Exchange of the interlayer cation is relatively facile, allowing for the synthesis of numerous derivatives of the layered silicates with polymers. Intercalated nano composites contain self-assembled, well ordered multilayered structures where the extended polymer chains are inserted into the gallery space (2–3 nm) between the parallel individual silicate layers. The exfoliated or delaminated nano composites are formed when the individual silicate layers are no longer close enough to interact with gallery cations of the adjacent layers. Both of these hybrid structures can co-exists in the polymer matrix. This mixed morphology is very common for the composites based on smectite silicates and clay minerals.

X-ray diffraction shows no indication of the incorporated material if the resulting nano composite structure has exfoliated structure. Figures 4 (a) and 4 (b) show x-ray diffraction patterns of three pristine organo-montmorillonites with different *d-spacing* for each clay [Fig. 4(a)] used for the preparation of glassy epoxy-montmorillonite nano composites. Figure 4(b) shows the x-ray pattern of the resulting glassy epoxy-montmorillonite nano composites. The diffraction pattern of the composite does not reveal the presence of clay due its the exfoliation of the clay layers. It is reported that the intercalated structures give rise to x-ray diffraction peaks of the clay material.

X-ray diffraction studies can also be exploited for the quantitation of *d*-spacing resulting from the chemical treatment of the pristine clay as well as after the incorporation within the matrix[39-42]. X-ray diffraction has also been used to study the polymerisation process of formation of nano composites. Figure 5 shows changes in the x-ray patterns during the formation of nylon-mica composites at different time intervals. The resulting nano composites do not show the presence of synthetic silica. Although WAXD offers a convenient method to determine the interlayer spacing of the silicate layers in the original layered silicate and in the intercalated nano composites, little can be extracted about the spatial distribution of the silicate layers or any structural non-homogeneities in the nano composites. Additionally, some layered silicates do not exhibit well defined basal reflections.

TEM has been used to directly view the hybrid structure for the formed nano composite with the emphasis on the dispersion of the nano clay fillers in the polymer matrix. TEM allows a qualitative understanding of the internal structural, spatial distribution of the various phases, and views of the defects in the structure directly.TEM observations reveal co-existence of nano clay material in the intercalated and the exfoliated states. Intercalated layers or structures are referred to as where the inorganic layers maintain the parallel registry of pristine clay material and are separated by ultrathin polymeric films[43-46].
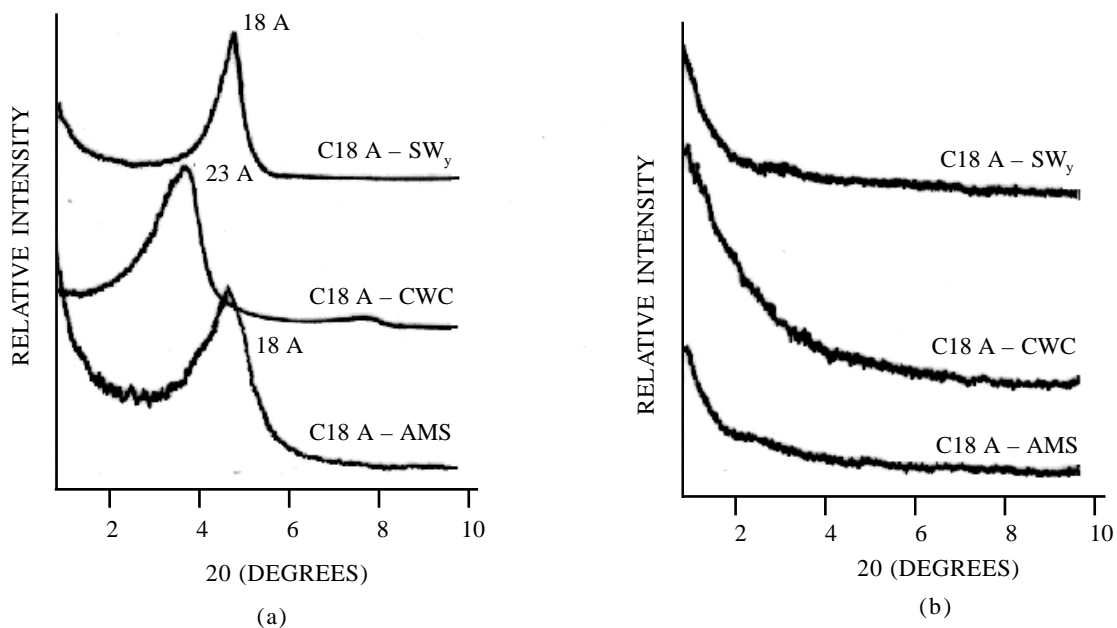
Figure 4. (a) X-ray profiles of three clays and (b) the resulting nano composites devoid of pristine reflections.

Thermal properties have been evaluated through DSC and mechanical properties using uniaxial tensile testing machines[47,48]. Dynamic mechanical analyser (DMA), has been used to study temperature dependence of storage modulus of nano composites. Studies indicate that addition of co-polymer has a strong effect on the elastic properties of the corresponding matrix. On the other hand, the Tan δ peaks for the
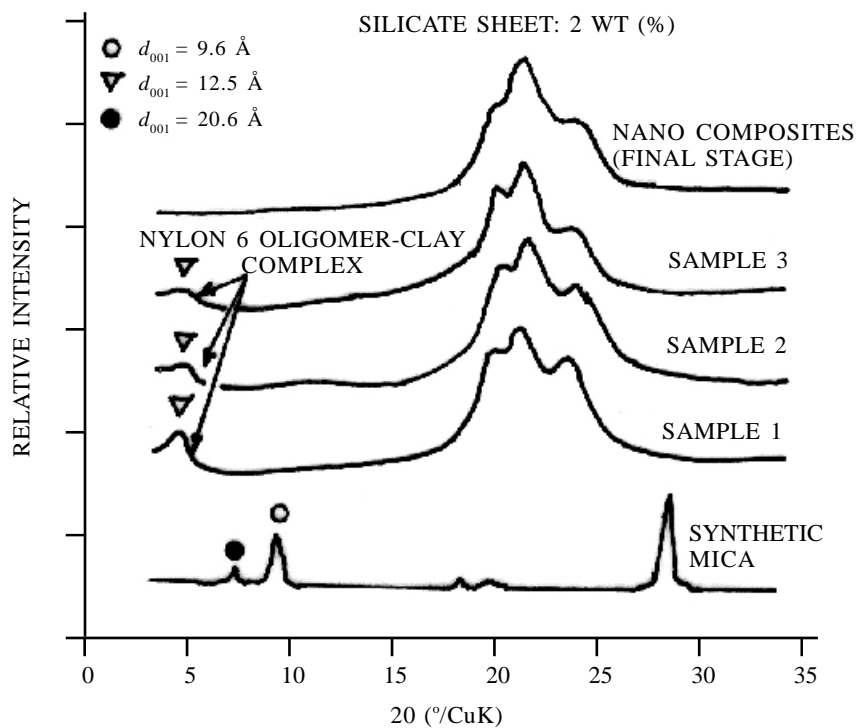

Figure 5. Changes in the X-ray patterns during polymerisation of the nano composites. X-ray profile of incorporated synthetic mica does not show up in the composite.

nano composites are shifted towards lower temperatures than for the corresponding clay-free blends. Effects of size of nano composites and compatibliser on the morphology and the mechanical properties are also reported[49,50].

The tensile modulus of polymeric material has shown to be remarkably improved in the nano composites. In general, the extent of improvement of the modulus depends upon the average length of the dispersed clay particles and the extent of dispersion. The stiffness is also dependent on the matrix molecular weight at a given concentration of nano particles. Similar trends wrt the level of organo-clay content and molecular weight are evident in the yield strength. The difference in strength improvement wrt molecular weight is very prominent at the higher clay contents. The increase in strength relative to the virgin matrix for the high molecular weight composite is nearly double to that of the low molecular weight composite. The difference between MMT and elongation-at-break for the different matrices indicate that ductility of the matrix gradually decreases with increasing clay content[51,52].

4. MODELS DESCRIBING PROPERTY ENHANCEMENT FOR NANO COMPOSITES

Several models have been proposed for predicting the behaviour of polymer composites with layered clay. The most extensively cited model is of barrier properties but some models for physical properties also exist.

4.1 Mechanical Properties

The increase in tensile modulus of polymeric material (N6-NC) has been attributed to the strong interaction between matrix and silicate layers via formation of hydrogen bonds.

The dramatic improvements in mechanical properties in nano-filled polymers challenge the existing theories of mechanical reinforcement. The plausible explanation for such improvement is in addressing the presence of a large volume fraction of an interphase zone that has properties different from the bulk polymer. The interphase zone is defined as the region surrounding such particles where the polymer chain dynamics may be altered due to an intimate contact with the nano particles (resulting in restricted or enhanced mobility), and these immediate layers, ie far-field influence on the surrounding matrix because of relatively large volume fraction of interfacial polymer in even moderately-filled nano composites, this interphase zone could occupy a considerable volume fraction in a composite. It has been observed that some particular fibre/matrix combination yields an unusual crystalline morphology near the surface of the reinforcing fibres.

Recently, structural properties of nano composites based on nylon-11 and nylon-12 have been compared with nylon-6 and found that crystallisation occures around the clay material[53]. This transcrystalline structure occurs as a result of dense nucleation of the thermoplastic matrix along with the surface of the reinforcing fibres. However, it is reported that some fibres produce transcrystallisation in one form of a thermoplastics matrix and no transcrystallisation in another form of the matrix. It appears that transcrystallisation is a system's property and is not an inherent property either of fibres or of thermoplastics.

Modelling the interphase zone is difficult as imperfect bonding, mechanical stresses, and chemical interactions can play a decisive role in determining its behaviour. Enhancement of properties appears to be a general phenomenon related to the nanoscale dispersion of material, but the degree of property enhancement is not universal for all polymers. Unusual crystallisation behaviour of organo-clay reinforced poly (L-lactic acid) composite has been reported. The overall bulk crystallisation rate was increased in the intercalated system and somewhat retarded in the exfoliated system. The overall per cent crystallinity and the size of crystalline domain decreased by the addition of organo-clay and found to be the lowest in the fully exfoliated case[54].

Enhanced toughness in nano composits has also been predicted to result from a critical interparticle spacing. Wu[55] hypothesised that if adjoing particles stress fields overlap, there exists a critical ligament

thickness that will result in toughening of the matrixdue to stress field interaction[55]. This concept has since been used to describe the changes in mechanical properties in rubber-filled epoxy, nano silica-filled nylon-6, and nano silica-filled PMMA-HEMA[8,13,14]. Toughness is thus achieved when a large volume of the bulk comopsite has its stress altered by the filler, favouring more energy absorbing-yielding mechanism.

4.2 Barrier Properties

4.2.1 *Neilsen Model*

Improved barrier properties in a polymer-clay nano composite have been related to increase in path-length for permeate due to the tortuous path imposed by the high aspect ratio clay. Neilson proposed an equation relating various parameters of polymer-clay to the permeability.

$$Pf/Pu = V_p/1 + (L/2 \ W)V_f$$

where Pf is the permeability of the polymer-clay composite, Pu is the permeability of the polymer, V_p is the volume fractions of the polymer, V_f is the volume fractions of the filler, L is the average length of the face of the filler, and W is the average thickness of the filler.

Neilsen proposed a simple two-dimensional model that assumes perfect registry of the clay plates/ flakes parallel to the surface of the film, which
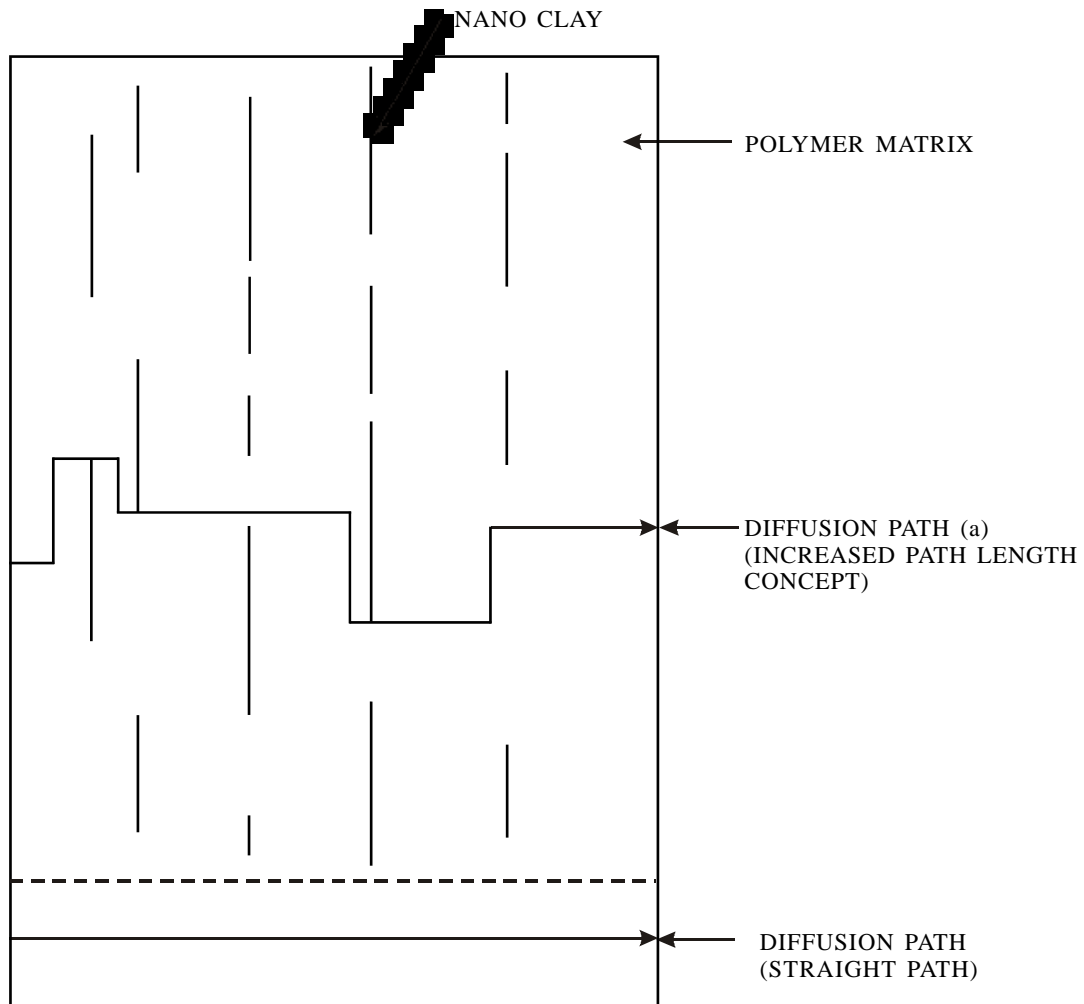

Figure 6. Schematic presentation of Neilsons barrier model for diffusion, depicting increased path length concept (a) and a straight path that the diffusing molecule would travel in absence of nano clay.

helps in enhancing the barrier resistance of the composite. Figure 6 illustrates the conceptual aspects of the resistance offered due to the increased path length. The model predicts that the relative permeability would strongly depend on the function of the aspect ratio at a given loading for all permeants. The relative permeability should not be affected by parameters such as humidity or temperature. The experimental data on a number of systems show that this simple model appears to predict the permeability behaviour of systems reasonably well at very low loading of clay (< 1 Wt %) but at higher clay loadings, the data deviate substantially from the model.

Work conducted on the permeability of O_2, CO_2 and H_2O across polyimide composites revealed that the aspect ratios of 87, 83, and 132 of the filled material would satisfy the Neilson model[56]. The model, though provides a first approximation estimate of permeability to a satisfactory level, but the experimental data deviated for different humidity, particularly at higher loading of clay. Permeability of ethyl acetate[57,58] on the polyimide composites showed that the humidity affected the permeability. At higher humidity (50 % RH), the permeability was low (p 0.09) than at zero humidity (p = 0.19). Whereas the permeability of pure polyimide increased with measured RH (from 1.24 to 2.89), the permeability of the nano composite went down. This behaviour could not be explained by the simple tortuous path model.

4.2.2 *Conceptual Model*

A conceptual model has been put forward which deals with various physical interactions between organic and inorganic, as well as chemical interactions between the polymer and the clay. This model is a modification of tortuous path model and incorporates a constrained polymer and clay structure-modifier regions. The model proposes a three-region domain around the clay plates immersed in the polymer matrix region.

The first region is assumed to be around the surface of the clay occupied by the compatibliser and is about 1-2 nm thick.

The second region, termed as the constrained polymer region, is less well defined and may extend to 50–100 nm away from the surfaces. The size of this region is determined by a host of variables including, the type of bonding between the surface modifier and the polymer, the strength of interaction between polymer, and the extent of nucleation imparted by the clay. The type of interaction could be the direct chemical bonding and/or a combination of Vander Wall attraction and hydrogen bonding. A polymer that has strong intermolecular forces will have a large constrained region as compared to a polymer with weak intermolecular forces. The presence of nano size material may also lead to localised nucleation of the domain. The ability of the clay to impart a nanophase structure to the composite will have a profound effect on both the permeability and physical properties of the polymer.

The third and final region proposed is the unconstrained polymer which is not directly affected by the clay. The properties of this third region will be largely those of the pristine polymer. There is substantial experimental evidence that the three regions exist as revealed by x-ray studies[59].

The physical proportion of these regions, namely the clay, clay-compatibiliser domains, and constrained polymer, will be different from those of the pure polymer. With respect to permeability, the diffusion coefficients in these three regions and their relative volume fractions will be the most important parameters.

This conceptual model also discusses the situations where the magnitude of diffusion coefficients as well as the volume fractions differ in these regions and their relative bearing on the permeation properties of the nano composite.

The conceptual model predicts that the observed permeation can be lower or higher than that predicted by the simple tortuous path model, depending on the relative diffusion coefficients of the phrases. The permeability of a given nano composite can be quite different for different permeants. Nematic *phrases* will predominate at or above 5 Wt per cent loading of clay in most of the polymers. The aspect ratio of the mineral only may not always
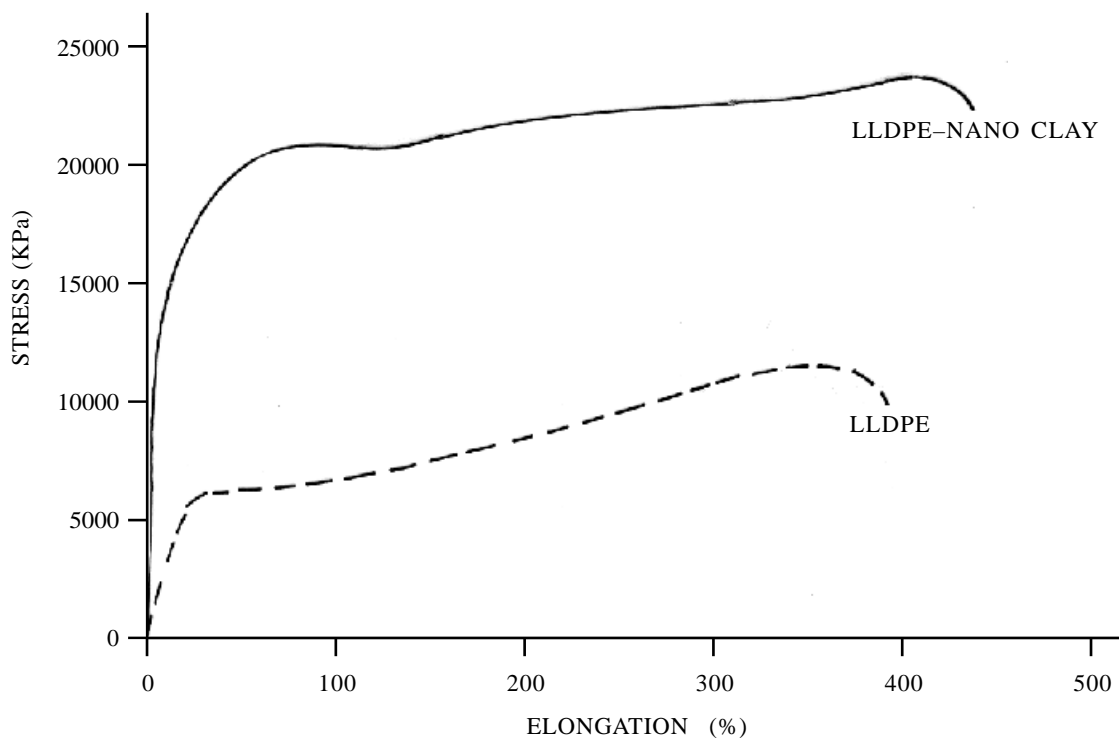
Figure 7. Stress-strain curve for LLDPE and DRDE developed LLDPE nano clay composite.

predict the permeability correctly for a given polymer.

Recently, Chauhan,[60] et al. developed a nano clay-based photodegradable polyethylene films by incorporating modified semectonic clay. These films show improved mechanical properties as compared to the virgin polyethylene films. The films get mineralised after 48 h of exposure to UV radiation under standard ASTM conditions.

Figure 7 shows the stress-strain curve (average of 5 curves) for control LLDPE films (broken lines) and the composite films having 1 per cent nano clay. The nature of the curve at the initial portion indicates that films having nano clay became stiffer for low level of deformations and take up higher load before deformation sets in. The magnitude of the stress build up increased at least three-folds in the case of composite films, and the area under the stress-strain curve registered at least a four-fold increase. The composite films also showed better oxygen barrier properties (3.03 x 10^{-12}) as compared to unfilled polyethylene (2.11 x 10^{-11}).

It is reported that nano particles enhance biodegradability of biodegradable polymers[61]. In the present case, it has been demonstrated that incorporation of nano clay enhanced the photodegradability of the developed polyethylene nano composites. The improvement in other properties are listed[60].

5. APPLICATIONS

The subject of nano composites is of great vitality and offers immense opportunity because a variety of compounds can be synthesised by combining a wide variety of host materials as well as polymers. The resulting nano composites have many superior functional properties than the original material without compromising the original characteristics.

Over the past decade, the utility of inorganic nano particles as additives to enhance polymer performance has been established. The enhancement appears to be a general phenomenon related to the nanoscale dispersion of layers, however, the degree of property enhancement differs from polymer to

polymer. Nano composites have been put to use for various applications like replacement as engine cover, timing belt cover, oil reservoir tank, and fuel hose in the automobile field. The nano composites show very high tensile modulus, without affecting adversely the other mechanical behaviours, therefore, the opportunities in the Defence sector are enormous where energy absorbing systems are needed, and high material-to-weight ratio, vis-à-vis material toughness, are required.

Hybrid organic-inorganic materials based on Rubrene and Tetracene nanocrystals have been developed for chemical and biological sensors. Some of the organic-inorganic hybrid nano materials have excellent laser efficiency and good photoreceptivity. Self-extingushing flammability for polycaprolactone layered silicate composites, aliphatic polyimide layered silicate nano composites, and polyethylene layered silicate nano composites has been developed[65]. The nano composites have superior self-extinguishing as well as reduced flammability properties. The heat-release rates of thermoset polymer-based materials are reduced by 60 per cent when intercalated with 2-6 per cent silicate clays. A highly loaded thermoplastic melamine formaldehyde nano composite coating has been designed to impart very high gas barrier properties to PET films and articles.

Nano composites can be converted to films, while with conventional composites, it is not possible. These films show highly improved properties in terms of oxygen, air, and water-permeation resistance. Polymer nano composites have excellent barrier properties against oxygen, nitrogen, carbon dioxide, water vapour, gasoline, etc, compared to the pristine polymer matrix.

Nano composites can be processed into fibres by conventional spinning methods. When being melt-spun, these closely maintain the cross-sectional shape of the nozzle.

These hybrid nano composites have good dimensional stability, as the expansion coefficients are lower than those of pristine polymers, both above and below the glass transition temperature (T_g). Almost all nano composites exhibit exceptional chemical stability and solvent resistance.

These have similar, and sometimes superior, transparency to neat polymers. Nano composites register improved mechanical behaviour for tensile, flexural, and compressional stresses[62-64]. Consolidated nano structures, employing both ceramic and metallic materials, are considered important in creating new generations of ultra-high strength, tough structural materials, new type of ferromagnets, strong and ductile materials, and new biomedical prosthetics.

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