Polymer Matrix Nano Composite Materials- A Critical Review

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Abstract— **Intention of this paper is to provide basic information associated with the research undergoing in the field of polymer matrix nano composites. It will provide the idea about the techniques involved in the fabrication, properties and characteristics of the nano composites. Also, it helps in understanding the area where this material is utilized and its merits and demerits.**

Keywords-**Nano materials, Nano composites, layered silicates.**

I. INTRODUCTION

Polymer composites are used in various applications such as automobiles, aerospace, sport goods, etc. Because of the tremendous advantages strong emphasize is given on the development of nano composite materials, which has atleast one dimension in the order of nano meters. The product is not necessarily nano scaled, but it can be micro called or macro scaled [1]. The field of nano composite material is one of the most developing and popular areas for the research and development activities involving most of the institutions and industries. Researchers in the area of biotechnology, electronics, automobile, aerospace and various other industries are having lots of interest in developing the nano sized materials. Other areas include nano sized polymer-based biomaterials, emulsion particles, imprint lithography, self-assembled polymer films, fuel cell electrode polymer bound catalysts, polymer blends and nano composites. In the field of nano composites, many topics exist including composite reinforcement, electro-optical properties, flame resistance, cosmetic applications, bactericidal properties, etc [3]. The meaning of the term nano technology is the manufacturing, processing and utilization of the materials, systems or devices of the order 0.1-100 nm.

Currently, some typical nano materials are under investigation such as nano particles, nano fibers, nano tubes, nano wires, and fullerenes. Generally, these materials are classified by their geometries broadly in three classes as particle, layered, and fibrous materials. Silica nano particle, Carbon black, polyhedral oligomeric sislesquioxanes (POSS) can be classified as nano particle reinforcing agents while nano fibers and carbon nano tubes are examples of fibrous materials [4]. If the filler has nano meter thickness and a high aspect ratio (30-1000) plate like structure it is classified as a layered nano materials such as organosilicate. [5]

Reinforcing efficiency increases in nano materials due to their high aspect ratios. Material properties depends on the nature of the components used (layered silicate or nano fiber, exchange capacity, and polymer matrix) and the method of preparation, significant differences. Size scale of nano composite component phases and the degree of mixing between the two phases determines its properties. Figure 1 shows three main types of composites for layered silicate materials. When the polymer is not able to penetrate between the silicate sheets, a phase-separated composite is obtained, and the properties remain in the same range as those for traditional micro composites. In an intercalated structure, where a single extended polymer chain can penetrate between the silicate layers, a well-ordered multilayer morphology results with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained. [6]
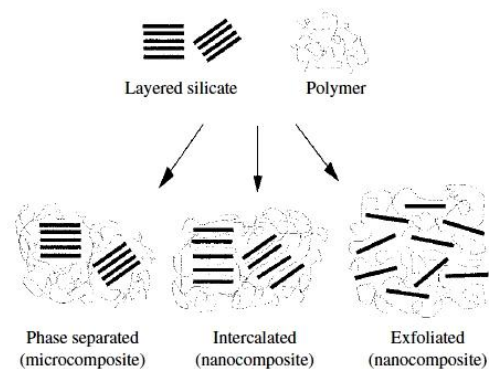

Fig. 1: Three main types of layered silicates [6]

In fibrous polymer nano composites (PNCs), dispersion of the nano particle and adhesion at the particle–matrix interface plays crucial role in determining the mechanical properties of the nano composite. Without proper dispersion the nano material will not offer improved mechanical properties over that of conventional composites. In poorly dispersed nano material the mechanical properties may degrade over the span of time. The properties of overall composite can be tailored by optimizing the interfacial bond between the particle and the matrix, similar to what is done in macro composite. Good adhesion at the interface will improve properties such as

interlaminar shear strength, delamination resistance, fatigue, and corrosion resistance. [7]

Research in nano composites is extremely broad which include the areas such as aerospace, automobile sector, electronics, data storage, communications, sporting materials, health, medicine, energy, national defense applications, etc. This review provides brief summary of processing, manufacturing, characterization, material properties, challenges, and applications of the polymer nano composites.

II. POLYMER NANO COMPOSITES

CONVENTIONAL MANUFACTURING TECHNIQUES

Properties of the nano composite materials shows improvement due to two principle factors first increased relative surface area and second quantum effects. Properties of some nano composites improvise because of interfacial interactions and for others it is due to quantum effects associated with nano sized structures. [8] Most important stage for manufacturing of nano phased polymer composite materials is the choice of a fabrication method. Some of the widely used methods for manufacturing of composite materials are wet lay-up, pultrasion, resin transfer moulding (RTM), vacuum assisted resin transfer moulding (VARTM), autoclave processing, resin film infusion (RFI), prepreg method, filament winding, fiber placement technology, etc [9]. Some of these methods are summarized here.

Wet lay-up is one of the simplest methods in which resin is applied only in the mould. It has some drawbacks such as presence of void in the final product which makes mechanical properties poor and non uniform [9].

Pultrasion is low cost continuous method with high production rate, but materials accumulating near the die can create jam. Void content can't be avoided due to the opening for fiber input [9].

Resin transfer moulding (RTM) is the closed mould process. Resin flow and fiber wet-out are critical issues in this process. Fiber wet-out depends on the fiber alignment and permeability of the preform. A fiber volume fraction of 55-60% can be achieved [10].

Vacuum assisted resin transfer moulding (VARTM) is only the modification of RTM which uses vacuum to make the parts. Some benefits of this process are low cost for production of high volume production, improvement in surface finish for larger parts and higher fiber volume fraction. If the resin viscosity is higher, it can restrict the flow of resin. Nano constituents can create the problem of altered resin viscosity and can cause dry spots over the entire volume of reinforcement [11].

Autoclave process can be used to manufacture complex parts of high quality composite materials. Both thermoset and thermoplastic composites can be manufactured with uniform thickness and minimum porosity. It is one of the most widely used methods in aerospace industry. Major problem associated with this process is the cost of fabrication [12].

Resin film infusion (RFI) is similar to RTM in which a thin film of solid resin is laid into the mould and preform is laid on the top of the resin film under heat and pressure. Resin impregnated woven fabric is used in the prepreg method with vacuum bagging and autoclave processing [9].

Resin impregnated fibers are wrapped over a mandrel at the same or different angles in filament winding method. It is a one of the most cost effective method for fabricating cylindrical and spherical parts. Viscosity related problems of resin can be eliminated by this method [13].

RTM, VARTM, RFI and filament winding method can be used to manufacture nano composite materials used in aerospace, automotive industries, gas barrier films, scratch resistant coating, flame retardant material, etc.

CHARACTERIZATION TECHNIQUES

Characterization methods are very important to determine and analyse the physical and chemical properties of polymer nano composites. Various techniques generally for characterization in polymer nano composites are wide angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) [14].

WAXD is the most commonly used method to investigate the nano composite structure and to study the kinetics of the polymer melt intercalation due to the easiness and availability and occasionally. Layered silicate nano composite material is characterized by the absence of intensity peaks in WAXD pattern. WAXD pattern concerning the mechanism of nano composite formation and their structure are tentative issues for making any conclusion [15].

SAXS is typically used to observe structures on the order of 10Å or larger, in the range of 0° or 0.5–5°.

SEM gives images of surface features associated with a sample. However, there are two other methods, scanning probe microscopy (SPM) and scanning tunneling microscopy (STM), which are indispensable in nano tube research. The SPM uses the interaction between a sharp tip and a surface to obtain an image. In STM, a sharp conducting tip is held sufficiently close to a surface (typically about 0.5 nm), such that electrons can 'tunnel' across the gap. This method provides surface structural and electronic information at atomic level. The invention of the STM inspired the development of other 'scanning probe' microscopes, such as the atomic force microscope (AFM). The AFM uses a sharp tip to scan across the sample. Raman spectroscopy has also proved a useful probe of carbon-based material properties [16].

TEM allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and views of the defective structure through direct visualization, in some cases of individual atoms. Therefore, TEM complements WAXD data [17].

TEM, AFM, and SEM, are also required to characterize nano particle, carbon nano fiber dispersion, or distribution. However, X-ray diffraction has found relatively limited success in CNT research. For thermal characterization and to study the cure behavior (typically for thermoset resin systems) of PNCs, the commonly used techniques are differential scanning calorimeter (DSC), thermo

gravimetric analysis (TGA), thermo mechanical analysis (TMA), Fourier-transform infrared (FTIR), dynamic modulus analysis (DMA), rheometer, etc [16].

III. NANO PLATELET PARTICLE COMPOSITES

Generally, there are two types of nano platelet particle composites, silicate clay minerals and graphite.

A. Silicate clay Minerals

Clay is of small inorganic particles without any definite composition or crystallinity. The clay mineral also called as phyllosilicate is usually of a layered type and a fraction of hydrous, magnesium, or aluminum silicates. Every clay mineral contains two types of sheets, tetrahedral (T) and octahedral (O) [18].

Table 1: Classification and example of clay minerals [5]

Structure type	Group	Mineral examples	Ideal composition	Basal spacing (Å)
2 : 1(TOT)	Smectite	Mont morillonite	$[(Al_{3.5-2.8}Mg_{0.5-0.2})(Si_8)O_{20}(OH)_4]\,Ex_{0.5-1.2}$	12.4–17
		Hectorite	$[(Mg_{5.5-4.8}Li_{0.5-1.2})(Si_8)O_{20}(OH)_4]\,Ex_{0.5-1.2}$	
		Saponite	$[(Mg_6)(Si_{7.5-6.8}Al_{0.5-1.2})O_{20}(OH)_4]\,Ex_{0.5-1.2}$	
2 : 1(TOT)	Illite	Illite	$[(Al_4)(Si_{7.5-6.5}Al_{0.5-1.5})O_{20}(OH)_4]K_{0.5-1.5}$	10
2 : 1(TOT)	Vermiculite	Vermiculite	$[(Al_4)(Si_{6.8-6.2}Al_{1.2-1.8})O_{20}(OH)_4]Ex_{1.2-1.8}$	9.3–14
1 : 1(TO)	Kaolin-serpentine	Kaolinite, dickite, nacrite	$Al_4Si_4O_{10}(OH)_8$	7.14

Properties of some of major clay minerals and its chemical compositions are listed in Table 1.

Hectorite, saponite, and montmorrillonite are the most commonly used smectite type layered silicates for the preparation of nano composites. Montmorrillonite (MMT) has the widest acceptability for use in polymers because of their high surface area, and surface reactivity. It is a hydrous aluminosilicate clay mineral with a 2:1 expanding layered crystal structure, with aluminum octahedron sandwiched between two layers of silicon tetrahedron [18].

B. Graphite Nano Platelet

Natural flake graphite (NFG) is composed of layered nano sheets, where carbon atoms positioned on the NFG layer are tightened by covalent bonds, while those positioned in adjacent planes are bound by much weaker van der Waals forces. The weak interplanar forces allow for certain atoms, molecules, and ions to intercalate into the interplanar spaces of the graphite. Interplanar spacing is thus increased. As it does not bear any net charge, intercalation of graphite cannot be carried out by ion exchange reactions into galleries like layered silicates [19].

Original graphite flakes with a thickness of 0.4-60µm may expand up to 2-20,000 µm in length which get separated to 1 nm thickness forming a high aspect ratio and high modulus graphite sheets. Improvement in physical and mechanical properties is obtained because of the dispersion

these nano sheets in the matrix. Expanded graphite (EG) can be produced by rapid heating of intercalation compound which made can be obtained from natural flake graphite (NFG).
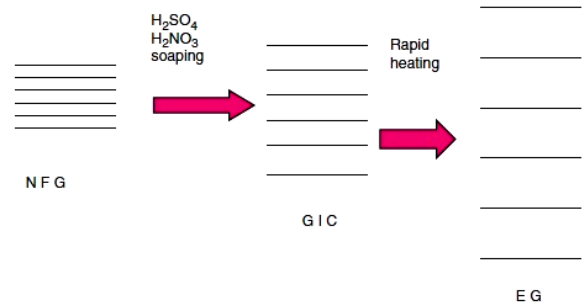

Fig. 2: Method of producing expanded graphite (EG) [19]

Preparation and Processing

Interaction mechanism of polymer and clay which is necessary for preparing polymer clay nano composites depends on the molecular weight, polarity, hydrophobicity, reactive groups of polymer and the solvent type. [18]

Some of the methods used for fabrication of are summarized here.

In situ intercalative polymerization

In this method, swelling of the layered silicate within the liquid monomer and the polymerization is initiated either by heat or radiation, by the diffusion of suitable initiator. Earlier this method is used to manufacture nylon-montmorrillonite and later it is applied for producing thermoplastics and thermoset clay nano composites [20].
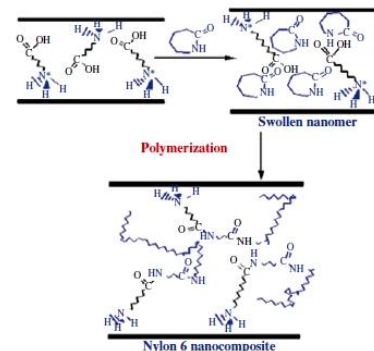

Fig. 3: Nylon-6 nano composite formed by in situ polymerization [20]

Exfoliation Adsorption

In this method, solvents such as water, chloroform, acetone, toluene in which the polymers and pre-polymers are readily soluble and silicate layers are swellable are used. The layered silicates can be easily dispersed in a sufficient amount of solvent. Then the polymer absorbs delaminated sheets and when the solvent is evaporated, the sheets reassemble, sandwiching the polymer to form. This method can be utilized to produce epoxy clay nano composites, but large amount of solvent in the resin is the biggest disadvantage [19].

Melt Intercalation

In this method, layered silicate is mixed in the polymer matrix in the molten state and the solvent is not required. Thermoplastic polymer is mixed mechanically by conventional methods such as extrusion, injection moulding with organophillic clay at high very temperature. The polymer chains are then intercalated or exfoliated to form nano composites. It is one of the most suitable and frequently used methods for preparing thermoplastic nano composites [19].

C. Carbon Nano tube reinforced materials

Carbon nano tubes are graphite sheets rolled into seamless tubes and have diameters ranging from about a nano meter to tens of nano meters with lengths of up to centimetres. Use of carbon nano tubes is becoming very popular due to its high modulus and high electrical and thermal conductivity. It is used in lots of applications which require high conductivity and high strength, also it is used in energy storage and conversion devices, hydrogen storage tanks, sensors, nano sized semiconductor devices, etc.

Structure and Properties of CNTs

Basically there are two forms of carbon nano tubes, single wall carbon nano tube (SWNT) and multi wall carbon nano tube (MWNT) [21]. Schematic representation of both forms is shown in fig. 4.
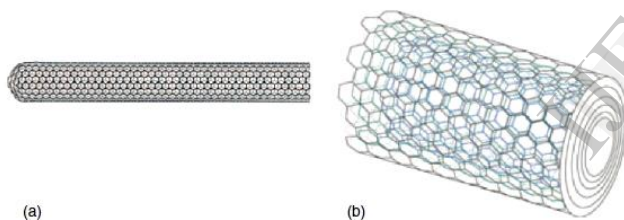

Fig. 4: Schematic representation of a) Single wall, b) Multi wall nano tube [22]

Nano tubes are available in three different morphologies: armchair, zigzag and chiral. The packing if the carbon hexagons in the graphite sheets define a chiral vector (m, n) and angle. These vectors and angles determine the morphology of the nano tube. When $\left(m - \frac{n}{3}\right)$ is an integer, the resulting structure is metallic; otherwise, it is a semiconducting nano tube. Electronics properties of an armchair nano tube are metallic; however, the electronic properties of zigzag and chiral nano tubes are semiconducting [22].
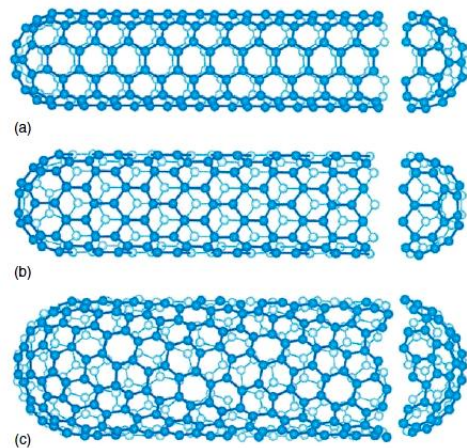

Fig. 5: Schematic of nano tube morphologies a) Armchair, b) Zigzag, c) Chiral [22]

Manufacturing techniques used for CNTs

Three main methods used generally for making nano tubes are direct current arc discharge, laser ablation and chemical vapour deposition (CVD).

In direct current arc discharge and laser ablation, the evaporation of solid carbon is used to condense carbon gas. The products of these methods are tangled and poorly oriented. In chemical vapour deposition (CVD) method, nano tubes are produced from the deposition of a continuously supplied carbon containing gas onto a substrate. High purity carbon nano tubes can be produced on larger volume scale because of the continuous supply of the gas [23].

Properties and Applications of CNTs

Nano tubes are generally used in thermoplastic due to the ease of processability. This allows fibers or films to be easily melt processed in to moulded parts. Nano tubes can toughen and stiffen amorphous brittle materials such as polymethyl methacrylate (PMMA). Most of the research has been carried out on thermoplastic materials, but some of the researchers are trying to investigate the possibility of its use in thermosets.

Nano tubes has a wide range of application including aerospace industry, automobile sector, bio medicines and bio medical sector, electronics and communications, defence related applications, etc. The application of carbon nano tubes is limited because of its very high cost of fabrication [23].

CONCLUSION

Study of various Polymer nano composite materials is carried out in this literature, which helps in understanding the physical, chemical and mechanical properties of these materials. Also, the study of various fabrication, manufacturing and processing techniques for these materials is carried out. Different characterization methods for polymer nano composite materials are also studied in this context.

REFERENCES

[1] Hussain, F., Okamoto, M., and Gorga, R. E., (2006), "Polymer matrix nano composites- Processing, manufacturing and application- An overview", Journal of Composite Materials, Vol.14, No. 17, pp. 1511-1575.

[2] Paul, D. R. and Robeson, L. M., (2008), "Polymer nano technology: nano composites", Polymer, 49, pp. 3187-3204.

[3] Thostenson, E. T., Li, C. and Chou, T. W., (2005), "Nano composites in context", Composites Science and Technology, 65, pp. 491-516.

[4] Schmidt, D., Shah, D. and Giannelis, E. P., (2002), "New Advances in Polymer/Layered Silicate Nano composites", Current Opinion in Solid State and Materials Science, 6(3), pp. 205–212.

[5] Alexandre, M. and Dubois, P., (2000), "Polymer-layered Silicate Nano composites: Preparation, Properties and uses of a new class of materials", Material Science Engineering, 28, pp. 1–63.

[6] Park, C., Park, O., Lim, J. and Kim, H., (2001), "The Fabrication of Syndiotactic Polystyrene/Organophilic Clay Nano composites and Their Properties", Polymer, 42, pp. 7465–7475.

[7] Gorga, R.E. and Cohen, R.E., (2004), "Toughness Enhancements in Polymer (methyl methacrylate) by Addition of Oriented Multiwall Carbon Nanotube", Journal of Polymer Science, Polymer Physics, 42(14), pp. 2690–2702.

[8] Christopher, O. O., and Lerner, M., (2001), "Nano composites and intercalation compound", Encyclopedia of Physical Science and Technology, Vol. 10, 3rd edition.

[9] Mazumdar, S. K., (2002), "Composites Manufacturing, Materials, Product and Process Engineering", CRC Press Taylor and Francis, ISBN 0-8493-0585-3.

[10] Octeau, M. A., Yousefpour, A. and Hojjati, M., (2004), "Procedure Manual for using Resin Transfer Molding (RTM) Manufacturing Set-up", LM-AMTC-0025.

[11] Hussain F., Derrick, D., Haque, A. and Shamsuzzoha, A. M., (2005), "S2 Glass/Vinyl Ester Polymer Nanocomposites: Manufacturing, Structures, Thermal and Mechanical Properties", Journal of Advanced Materials, 37(1), pp. 16–27.

[12] Chen, J. and Tanguay, M., (2004), "Autoclave processing in the Aerospace Manufacturing Technology Center (AMTC)", Internal Technical Paper for AMTC, NRC.

[13] Mahfuz, H., Baseer, M. A. and Zeelani, S., (2005), "Fabrication, Characterization and Mechanical Properties of Nano Phased Carbon Prepag Laminates" SAMPE Journal, 41(2).

[14] Giannelis, E.P., (1996), "Polymer Layered Silicates Nano composites", Advanced Materials, 8, pp. 29–35.

[15] Yano, K., Usuki, A., Okada, A. and Kurauchi, T., (1991), "Synthesis and Properties of Polyimide-Clay Hybrid", Polymer Preparation (Jpn), 32(1): 65.

[16] Meyyappan, M., (2004), "Carbon Nanotubes, Science and Application", CRC Press, Taylor & Francis.

[17] Chen, T. K., Tien, Y. I. and Wei, K. H., (1999), "Synthesis and Characterization of Novel Segmented Polyurethane/Clay Nano composites via Poly (ε-caprolactone)/Clay", Journal of Polymer Science, 37(13), pp. 2225–2233.

[18] Scott, M. A., Carrado, K. A. and Dutta, P. K., (2004), "Hand Book of Layered Materials", CRC Press, Taylor & Francis.

[19] Ray, S. S. and Okamoto, M., (2003), "Polymer/layered Silicate Nano composite: A Review from Preparation to Processing", Progress in Polymer Science, 28, pp. 1539–1641.

[20] Kawasumi, M., Hasegawan, M., Usuki, A. and Okada, A., (1997), "Preparation and Mechanical Properties of Polypropylene–Clay Hybrids", Macromolecules, 30, pp. 6333–6338.

[21] Jin, L., Bower, C. and Zhou, O., (1998), "Alignment of Carbon Nanotubes in a Polymer Matrix by Mechanical Stretching", Applied Physics Letters, 73(9), pp. 1197–1199.

[22] Dresselhaus, M. S., Dresselhaus, G. and Eklund P. C., (1996), "Science of Fullerences and Carbon Nano tubes", Academic Press, London.

[23] Liu, J., Fan, S. and Dai, H., (2004), "Recent Advances in Methods of Forming Carbon Nano tubes", MRS Bulletin, pp. 244–250.