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Polymer-matrix Nanocomposites; Processing, Challenges, and Applications: An Overview

Jayant K. Jha[1*] **and A. V. Muley**[2]

[1]*PG Student, MPAE Division, NSIT, Delhi*
[2]*Faculty, MPAE Division, NSIT, Delhi*
E-mail[*]*: jayantjha90@gmail.com*

Abstract—*Polymer matrix nanocomposites (PMNCs) are advanced material with improved overall properties. PMNCs find applications in many fields. There is need to know about these new class of materials so as to take the advantages of their enhanced properties to its fullest. This paper gives brief review of the recent work in polymer nanocomposites. This is just an overview which provides an outline of the manufacturing techniques, their mechanical behavior, challenges posed during manufacturing and morphology of polymeric nanocomposites. This paper also discusses about number of composite systems having different nano-sized filler materials.*

1. INTRODUCTION

Polymer systems are advantagous over metal and ceramic system due to their lack of dificulty in manufacturing, lesser weight and ductility. As compared to metals and ceramics, polymer possess lower modulus and strength and to improve their mechanical properties polymers are embedded with the insertion of reinforcement like fibers, whiskers, platelets, or particles. By reinforcing fiberin polymer matrix we can achieve better material properties in comparison to single phase alone. Reinforcing polymers with fibers, whiskers and particulates, polymers properties can be enhanced while maintaining their low density and ductility. Improvement in polymer properties can be found even at comparatively low reinforcement. Development of Nanotechnology it has been possible to use nano-scale reinforcement in polymer matrix. A nanocomposite is a materialin which at least one of the elemental component is of nano-scale dimension i. e. 10^{-9} m level. Nano-compositescan be classified into three categories depending on their geometric configuration [10].

a) Intercalated nanocomposites: Intercalated nanocomposites are produced when polymer chain is induced in between of layered silicate structure or clay in a crystallographic regular pattern. In intercalated nanocomposites, silicate layer to polymer ratio is discarded. Properties of these type of composites typically approximated to those of ceramic materials [10].
b) Flocculated nanocomposites: These types of composites are nearly same as intercalated nanocomposites with one exception that silicate layers or clay are sometimes flocculated because of hydroxyl edge–edge interaction between the silicate layers [10].
c) Exfoliated nanocomposites: Exfoliated nano composite are different from intercalated nano composites, in which average distance between every clay layer in a continuous polymer matrix dependent on silicate layer loading. Concentration of clay in an exfoliated nanocomposite is considerably much lower compared to intercalated nanocomposite [10]. Please see **figure 1** in **table 1**.

Due to advancement in the field of nanotechnology, Nano reinforcementsare available in the form of fibers, whiskers and particulates. It is important to study the behaviour of PMNCs with objective that how the nano reinforcement size influences the material properties in comparison to micro level reinforcement. The different Innovate devices like Scanning tunneling microscope (STM), scanning probe microscopy (SPM) and Atomic Force Microscopy (AFM) helps in the research on Nanocomposites. These tools provides the material features at the atomic level. The material properties i. e. Young’s modulus, modulus of rigidity, thermal expansion of micro composites depends upon the properties of constituents, volume fraction, fiber shape, fiber orientations and matrix-fiber interface. But in the case of nanosized reinforcement these dependencies as in case of micro composites may not be similar [5]. The advances in the area of Nanotechnology help us to find the correlation between reinforcement size and properties of composites. But a definite conclusion in this regard is very far from satisfaction.

2. COMPOSITE PROCESSING TECHNIQUES

Producing a good PMNCs sample is very much tedious job requires large amount of labor. Researchers have tried a variety of processing techniques to produce PMNCs, in which some are conventional as used for micro composites and others are unconventional. First step in preparing a polymer matixnano composite is to select the processing method. For processing of conventional composites wet lay up are the most simplest of all, other than wet lay updifferent processing techniques like pultrusion, resin transfer moulding (RTM), variation of RTM like vacuum boosted resin transfer moulding (VARTM), autoclave processing, resin film infusion (RFI), prepreg method, filament winding, fiber placement technology, melt mixing, in situ polymerization and recently developed process like electrospinning is been most widely used [2] and [30]. Wet lay-up is a straightforward process in which resin is directly applied into the mold. Material properties of the obtained composite is of very poor quality due to large number of void presents in the composite. Pultrusion process is a low-cost process having high production rate very much similar to extrusion but at the die interface materials gets piled up and creates a hurdle. If dies run with too much opening for fiber volume input voids can be created. Resin Transfer Moulding (RTM) is a closed mold operation in which fibers and resin are applied separately. In this process, dry fiber is placed into the mold then after that resin are poured in the mold. Here resin movement and fiber-resin interface interaction play a critical role. Motion of the resin in mold occurs in both direction i. e. along the plane as well as in transverse direction. Wetness of the fiber largely depends upon fiber composition and permeability of the resin perform. Theoretically, volume fraction of the fiber is of 55–60% The VARTM is avariation in the RTM, in which vacuum is used to draw resin in the mold. Autoclave is one of the promising technique which use combination pressure and temperature to process and manufacture different complex shapes of high-quality composite structures. Both thermoset and thermoplastic polymer can be processed with autoclave technique while maintaining homogeneous thickness and requisite amount of porosity. Another advancement of RTM process is Resin film infusion (RFI) in which a thin resin film or sheet isspread onto the mold and then perform is applied on top under heat and pressure. Filament winding consists of cloaking of resin impregnated fibersaround a rotating mandrel. It can be done at various angle to form a composite part. Filament winding and automated tape placement technique is used in a logical sequence for automation of fiber placement which over come many of the restrictions of manufacturing methods.

For processing of nanocomposite various methods are suggested but by most significant methods are Intercalation of polymer directly from solution, in situ polymerization, Melt intercalation, direct mixing of polymer and nano particulates, Template synthesis, and sol-gel process.

In intercalative process silicate layers is treated with some solvent like water, chloroform or tolueneto inflate and thenthoroughly mixed with polymer. Polymer chain displaces the solvent in layered silicate or solvent gets separated from the solution and resultant is obtained as Intercalated or exfoliated polymer nanocomposite [16]. Please see **figure 2** in **table 1**. In situ polymerization and direct mixing consists of mixing the polymer or monomer with reinforcement and polymerisation reaction occurs due to either by some external catalyst or photo polymerisation due to curing of ultrasonic waves. Melt intercalation process consist of heating polymer and silicate layer mixture up to softening point of the polymer. At softening point polymer chain diffuses with host clay or silicate layer. Template synthesis consisting of in situ mixing of aqueous polymer solution with silicate layer to form double layer hydroxide-based nanocomposites [16]. Sol-gel process includes hydrolysis and polycondensation reaction occurs between inorganic molecules and organic media. This reaction creates a 3-dimensional polymer consists of metal-oxygen bonds [1]. Vollenberg and Heikens [16]usedpolystyrene (PS), styrene–acrylonitrile copolymer (SAN), polycarbonate (PC) and polypropylene(PP) in their experimentations. They used reinforcement of alumina particulate 35 nm and 400 nm in size and glass particulate 4, 30, or 100 μm in size. Polymer matrix treated with polar solvent and further beads were mixed. Mixing process takes several hours. Mixture is then poured over the large surface mold to evaporate and dried under vacuum condition at 100^0 C for extended period of time. In this experimentation mixture contain 30% of volume fraction of the reinforcement particles. One of the key contention for preparation of good polymer matrix sample is dispersion of the nanoparticles in the host matrix. Yang et al. [17], prepared Nanocomposites sample using is situ polymerization. In this experimentation polyamide-6 as polymer matrix and silica reinforcement is mixed thoroughly and then dried for removal any water molecules. Further particles mixed with caproamide and suitable polymerisation initiator. Mixture polymerized under nitrogen and at high temperature. This technique is useful up till 50 nm in size only. Aggregation of the particles occur for smaller particle size around 12 nm shows by Reynaud et al [14]. Electrospined composite nanofiber along with nanoscale fillers infused into polymer matrix to form a composite solution. In electro spinning method of processing consists of three components a high voltage supplier, capillary tube consists of pipette or needle and a metal collecting screen. High voltage power supply is used to melt the polymer and using the pipette this is passed to metal collecting chamber. [2]. Please see **figure 3** in **table 1**. Due to development of Nano technology, Nano composite material have the plausibility to change the view as that of traditional composites being treated. One of the key concern in this regard is that if processing and commercialization for usage in real world scenario. Uniform dispersion of nano particles in polymer matrix is very much difficult as very high susceptibility of agglomeration of particle is there. Chemical instability is also another problem occurs while processing with traditional methods of processing. An agitation or use force, can be helpful to possiblysplit the agglomerate nano particle. Removal of gas in nanocomposite should be well taken care of while processing composite. Air entrapment can occur while pouring very high dense and viscous material in the mold. Air entrapment can initiate cracks and failure very easily at very low strain. Proper alignment of nanoparticles / nanoflakes in the polymer matrix can be very tough to achieve. These alignment issues are very critical for unidirectional properties, such as strength, modulus and toughness. Unlike the traditional micro composites, calculation of strength, composition, and functionality of the interfacial region in PMNCs is difficult. In addition to the composite integrity, the nature of the nanoparticle is also critical for improvement in properties. It is not possible to apply Molecular dynamics simulation (MD) and theoretical analysis to a real situation in PMNCs which are mainly based on certain assumptions. Many of the experiments have been conducted by composite enthusiast around the world to enhance the mechanical and tribological properties yet this area posits a challenge to whole composite community.

3. MECHANICAL PROPERTIES OF THE POLYMER NANO COMPOSITES

Most paramount importance of adding reinforcement to polymer matrix is to enhance the mechanical properties. Proper selection of processing technique has some influence on the properties. Vollenberg and Heiken [16] observed that modulus increased with decrease in size of inclusion in Polystyrene, Polycarbonate and Polypropylene. However, these effects were observed in microscopic level. Similar observation was found that by Chan et al as referenced in [5] where $CaCO_3$ was used as nano particle in polypropylene matrix. Please see **figure 4** in **table 1**. Polyamide – 6 nanocomposites with silica reinforcement as experimented by Reynaud et al [14] observed that the yield stress increases with increase in filler content. In this experimentation, yield stress increases slightly with decrease in reinforcement size. Please see **figure 5** in **table 1**.

4. TRIBOLOGICAL PROPERTIES OF POLYMER NANO COMPOSITES

The wear in polymeric composites can be described in various ways but abrasion, adhesion and fatigue are generally most recognised as basic assumption in wear rate [1]. Abrasive wears as scratch, cut marks and scar marks characterises the abrasive wear at abrasive surfaces. In adhesive wear formation of wear occurs at the junction of interacting polymer interface. The kinematic law of friction will govern the wear rate. In fatigue wear, repeated plastic deformation will induce the wear. It is a multistage wear process. Short carbon fibers are currently used to enhance wear characteristics in poly ether ether ketone (PEEK) based nanocomposites. Due to reinforcement of carbon fiber, composites show high wear resistance at elevated temperature under water lubrication [4]. In polyolefin-based nanocomposites where multiwalled carbon nanotubes are used to enhance the wear resistant properties of the composites. Polyoxymethylene polymer have wide use in tribological application due to self-lubricating properties. Further various reinforcement like graphite, Al_2O_3, carbon fibers are being used to enhance tribological properties [4]. Tribological properties of composites are closely related to mechanical and thermal properties of the composites [29]. Chen et al [29] experimented the tribological properties in polyimide matrix nano composites in which reinforcement was amine functionalized graphene (AFG). In this experimentation they found that friction behaviour shows two zones 1. Run in period 2. Stable period. Due to roughness in mating part, friction coefficient is remarkably high while in stable period shows stability. **Figure 6** shows friction coefficient comparison between pure polyimide polymer and AFG induced composites whereas in**figure 6** shows about wear rate and friction coefficient at different volume fractions. Please see **figure 6** and **figure 7** in **table 1**.

Kurdi et al [31] presented the effect of TiO_2 nanofiller on the poly ether ether ketone (PEEK) composites using pin on disk test. They concluded that PEEK based composites gives better wear resistance in dry condition compared to aqueous condition. PEEK based composites gives best tribological properties at 5% nanofiller materials[31].

5. APPLICATION

Sreenivasulu et al [22] highlighted graphene reinforced polymer composite has some of application in microelectronics industry, development of LED, electro chromatic gadgets can be possible with these types of composites. Fischer (2003) as referencedin [13]reported the coating application of nanocomposites. Permeability of the polymernanocomposites coatings with water vapor sharply decreased in comparison with non-modified coating. This can be explained by the facts due to presence of strong methylene – clay bonding. High degree of uniformity in clay dispersion in the composite leads to transparent coating [13]. Inorganic reinforcement with organic matrix composites shows their application in hard coating on lenses. Such composites typically made up of organoalkoxysilanes and other alkoxides. Combination of nanoparticles with epoxy silanes (act as cross-linking agent) promotes abrasion resistance with transparency and having low surface energy. Carbon nanofiber (CNF) reinforced composites possess great mechanical properties, like high toughness, stiffness, strength while maintaining low strength to weight ratio. Hence, these composites posit good structural application such as aerospace structures, ultra light thin walled structure for use in space program. Nanocomposites offers better mechanical properties, thermal, electrical and barrier properties. Nano composites possess better application scope over micro composites Layered silicate nano composites having 2 – 5% weight fraction similar mechanical properties which was found in micro composites with 30 – 40% weight fraction. These characteristics creates numerous potential application some of the application are as follows:

- Automotive parts which can sustain at high temperature.
- Construction sector due high strength to weight ratio.

- Aerospace application due low coefficient of thermal expansion
- Electrical parts and Microelectronics.
- Packaging due to good barrier properties (containers and wrapping films)

Silberglitt (2004) as referenced in [13] tells us that growth of nanocomposites can approach two possible ways**a high-growth path** under which nanocomposites materials are persuasively applied throughout camaraderie or**a low-growth path** in which gradual growth occurs in the specific application areas. **See figure 8 in table 1.**

6. DISCUSSION

Nano composites with nano level reinforcement usually have different properties as compared to micro composites. Specific causes of this differentiation need to be well understood well. Some of the researcher tried to explain but satisfactory answer remains unanswered which can be universally applied. Michler et al [20] tried to explain the physics and mechanics of nanovoids and nanoparticle with different combination of polymers by assuming the shape of nanofoam which is difficult to produce. Reynaud et al [15] find the evidence of reinforcement size effect on reinforcement dispersion in polymer nanocomposites. This result intimate us for the possible existence of an optimal size configuration of the reinforcement but further experimentation is need to be carried out for confirmation. Vollenberg and Heikens tried to explain the particle size effect on the young modulus. They concluded that solidification of the polymer composites may be activated locally. Zhao et al [18] introduced simulation method for calculation of different physical properties of the polymer nanocomposites. They also discussed about molecular dynamics simulation technique for finding profile of the nano reinforcement. Akila et al [21] and Faud et al [25] prepared polypropylene polymer matrix composites with the help of compatibilizer, this promotes better intercalation and improves mechanical properties**.**

7. CONCLUSION

Considering the beginning of nano composites compelling research is required to point out exact behaviour of nano composites. Development of mathematical model for understanding polymer-reinforcement interface is the key issue. Further development of mathematical model will be such that it can be useful for mechanical performance optimization. We have seen in the preceding sections that smaller sized inclusion enhances the overall properties of the nano composite.

Table 1

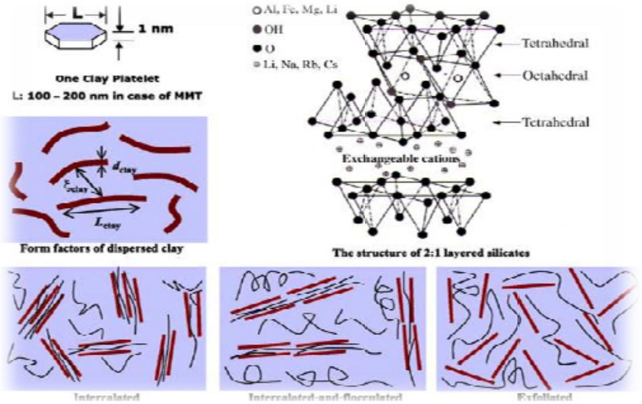

Figure 1 – Types of Nano Composites [10].

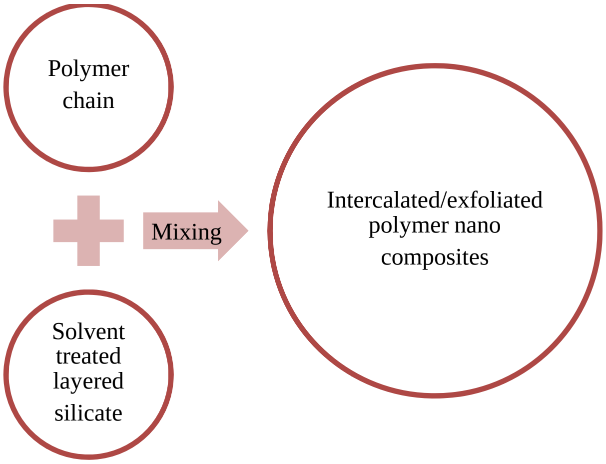

Figure 2 – Intercalative Process.

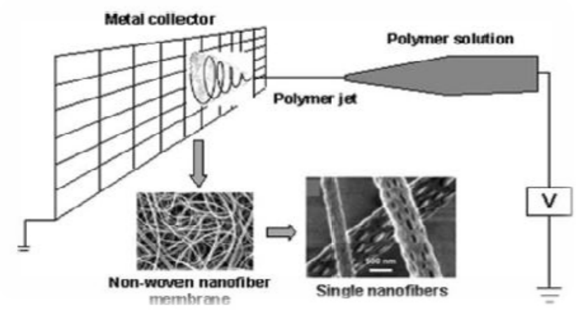

Figure 3 – Poly nanofiber from electrospinning[2].

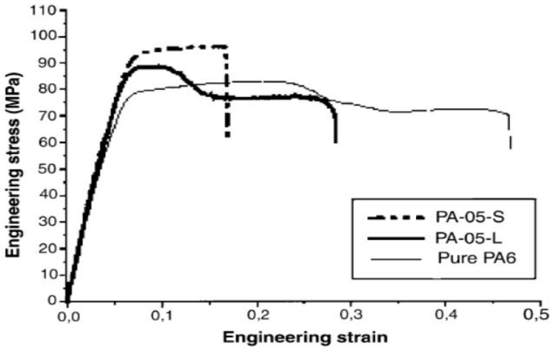

Figure 4 – Polypropylene with $CaCO_3$ as reference in [5].

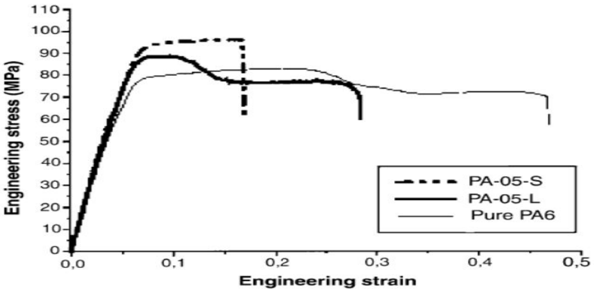

Figure 5 – Polyamide-6 with small (S) and Large (L) inclusion [14].

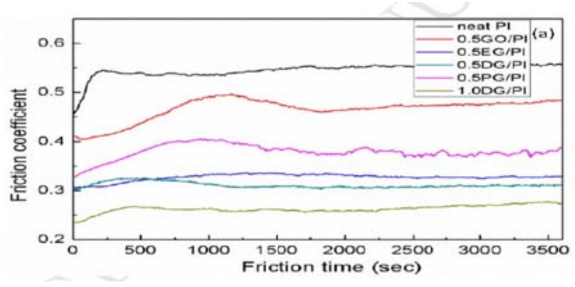

Figure – 6 Friction Coefficient and friction time for AFG/PI composites [29]

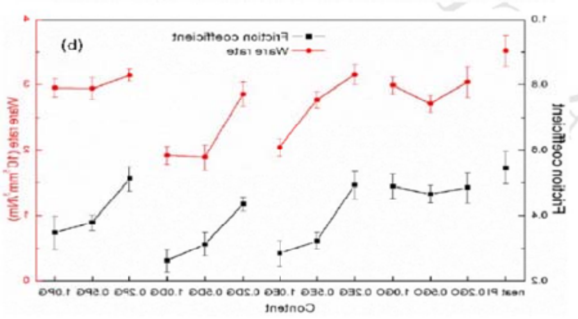

Figure 7 – Wear rate and friction Coefficient in AFG/PI Composites [29]

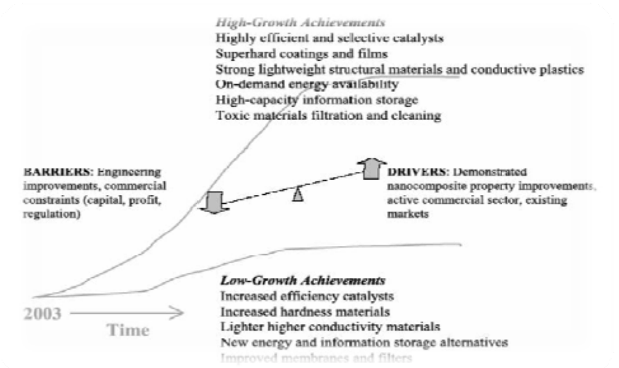

Figure 8 - Possible Growth Path (Silberglit, 2004) as referenced in [13]

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