

On Some Elementary Aspects Of Polymer Nanocomposites: A Mini Review

Sunil Bhat

Department Of Mechanical Engineering, RVITM, Bangalore, India

Abstract:

Materials at nanoscale are known to behave differently and advantageously than at micro and macro levels. As such, nanocomposites exhibit superior properties vis-a-vis conventional micro or macro filler composites in most of the engineering spectrums. Commonly used nanocomposites are Polymer matrix-based nanocomposites (or polymer nanocomposites) that are reinforced with nano fillers. This paper presents a brief review on various important aspects of polymer nanocomposites namely synthesis, properties, applications and limitations.

Keywords: Polymer; Filler; Polymer nanocomposite; Synthesis; Application; Limitations

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I. Introduction

Polymers have comparatively insufficient elastic modulus and strength. Therefore inorganic micro or macro size inclusions in the form of fibers, whiskers, platlets or particles are conventionally added to the polymer for improving its mechanical properties. In recent years, the inclusion size is allowed to reach up to the nano level. Materials at nano scale (between atomic and micro level) behave differently and are found to exhibit superior properties in mechanical, electrical, thermal, civil, chemical and magnetic spectrums vis-a-vis the properties at micro or macro levels. These enhanced properties at nano scale can be effectively utilized if the materials are implanted as fillers of nano size in the composite. So, the science of nanotechnology deals with functional materials containing nano filler particles in the range of less than 100 nano meters (nm) size. In other words when one of the constituents, usually the inorganic filler in a filler/matrix mixture, is nano sized, it is called as a nanocomposite. Nanocomposites definitely exhibit better and unique properties than conventional micro or macro filler composites. When the matrix in the nanocomposite is a polymer, it is known as the polymer nanocomposite.

II. Classification Of Nanocomposites

The nanocomposites are classified as follows:-

- a) Non polymer nanocomposites i.e. when the matrix of the nanocomposite is not a polymer. Various categories in non polymer nanocomposite are i) Metal/metal nanocomposite ii) Ceramic/metal nanocomposite and iii) Ceramic/ceramic nanocomposite.
- b) Polymer nanocomposites i.e. when the matrix of the composite is a polymer. Various categories in polymer nanocomposite are i) Inorganic (Filler)/polymer nanocomposite ii) Inorganic (Filler)/polymer hybrid nanocomposite iii) Polymer/polymer nanocomposite iv) Ceramic/polymer nanocomposite v) Layered silicate/polymer nanocomposite vi) Biocomposite etc. Broadly speaking, there are three major classifications of nanocomposite that are i) Ceramic matrix nanocomposite (CMNC) ii) Metal matrix nanocomposite (MMNC) and iii) Polymer matrix nanocomposite (PMNC) or in short polymer nanocomposite (PNC).

III. Ingredients Of Polymer Nanocomposite (PNC)

Commonly used polymers in PNC are Polyamide 6, Thermoplastic polyolefin, Epoxy, Polyisobutylene, Styrene, Polypropylene, Polyamides, Polyvinyl alcohol, Polylactic acid, Polyvinyl pyrrolidone, Polydimethyl siloxane, Natural rubber, Nylon 6 etc.

Commonly used fillers in PNC are Exfoliated nanoclay, Carbon nanotubes, Graphene and its oxides, Fibers, Metal oxides, Silica etc. Nano sized fillers are produced by methods namely i) Flame spray pyrolysis ii) Sol gel process iii) Precipitation method iv) Emulsion polymerisation v) Hydrothermal synthesis and vi) Chemical vapour deposition. In *flame spray pyrolysis*, the precursor solution (metal salt etc.) is subjected to combustion by a high temperature flame that leads to quick nucleation and growth of highly pure nanoparticles which then are collected on substrates or accumulated in a gas phase reactor. In *sol-gel process*, hydrolysis of metal alkoxides is carried out in the presence of water and alcohol to form a colloidal solution. Polycondensation then happens on its own resulting in a gel network. The solvent is removed and the remaining product is dried leading to nanoparticles

like xerogels or aerogels. In *precipitation method*, the solution containing the dissolved monomer of filler is agitated under desired pH and temperature to precipitate the nanoparticles. The precipitate is finally filtered, washed and dried. In *emulsion polymerisation*, initiators are employed to polymerize the monomers of filler, that are emulsified in water with surfactants, thereby resulting in nanoparticles of the filler. In *hydrothermal synthesis*, the mixture containing the filler reactants, placed in a sealed autoclave with water or solvent, is heated above the boiling point under pressure to trigger crystal growth of filler at nanoscale. In *chemical vapour deposition*, decomposition of gaseous precursor of filler at high temperature in the presence of a catalyst induces formation of filler nanoparticles. Some typical polymer matrix and nano fillers used in PNC along with the property improvement are displayed in Table 1. [1]

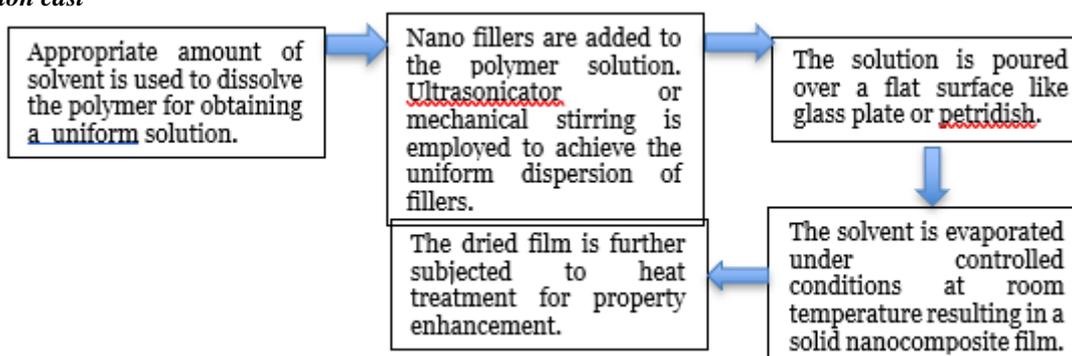
Table 1. Commercial polymer matrix, nano fillers and applications of PNC's

Polymer matrix	Nano filler	Property improvement	Application
Polyamide 6	Exfoliated clay	High stiffness	Automotive parts
Thermoplastic polyolefin	Exfoliated clay	High stiffness and strength	Automotive parts
Epoxy	Carbon nanotubes	High stiffness and strength	Sports equipment
Polyisobutylene	Exfoliated clay	Reduced permeability	Sports and automotive equipment
Natural rubber	Silver	Improved antimicrobiality	Medical equipment

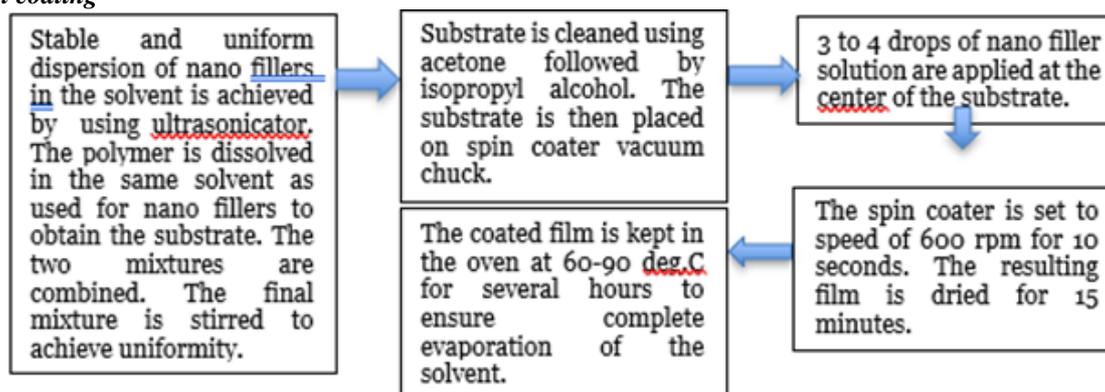
IV. Synthesis Of PNC's [2]

The following methods are employed to obtain the PNC's. The solvents commonly used in synthesis processes are Dimethyl formamide (DMF), Cyclopentanone, Chloroform etc. The amount of solvent is of the order of 10 ml and the weight range of nanoparticles typically lies between 0.05 to 0.15 mg.

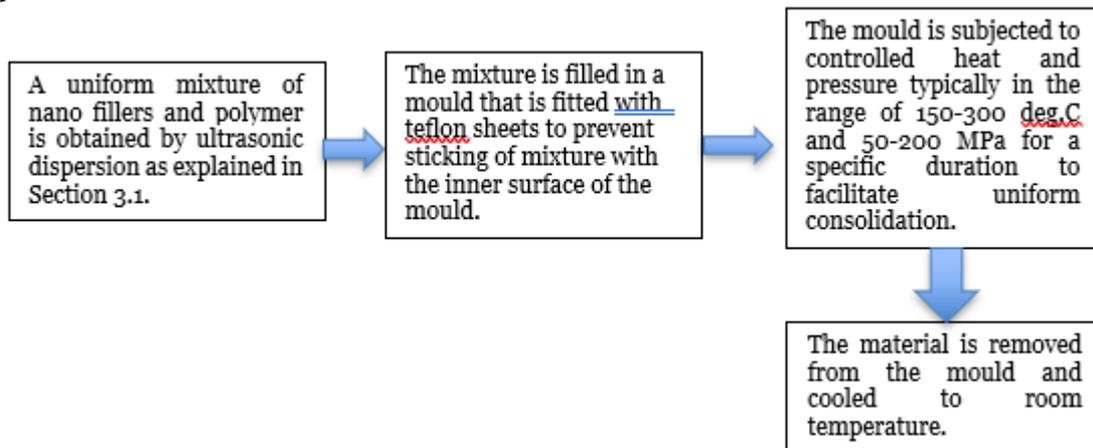
Solution cast



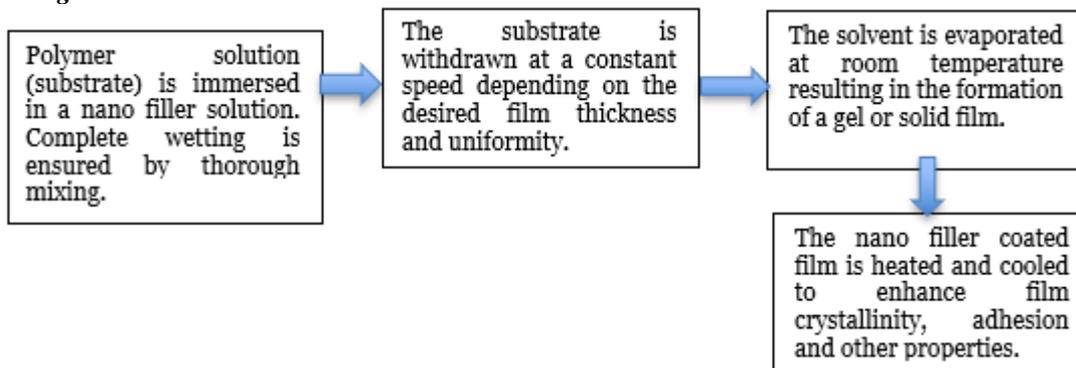
Spin coating



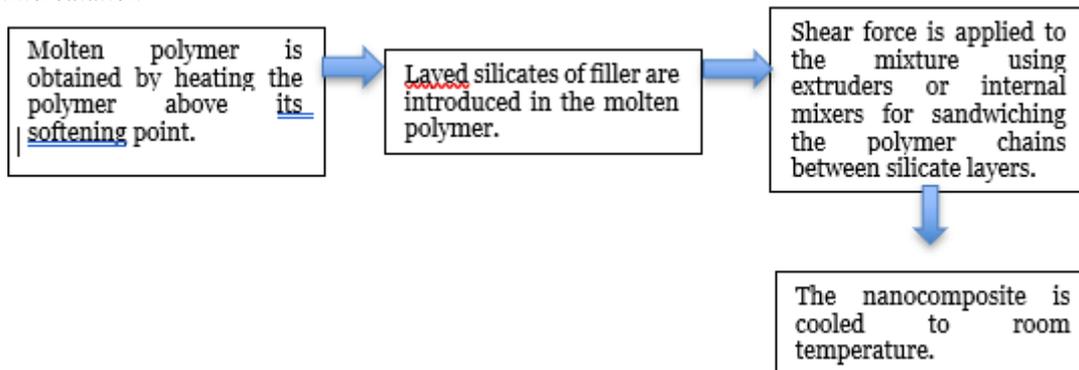
Hot press



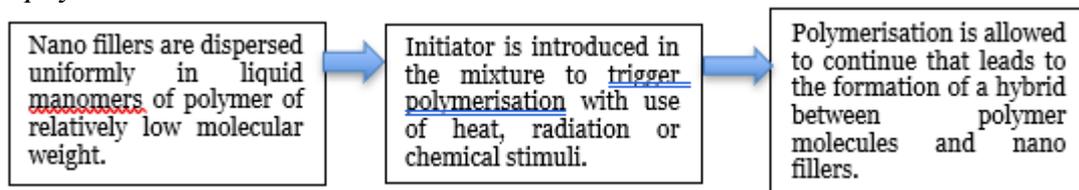
Dip coating



Melt intercalation



In-situ polymerisation



V. Properties Of PNC's [3]

Mechanical properties

These properties depend on the type of nano filler used. *Nano clay* has a layered structure with typical thickness of 1 nm. If properly exfoliated, clay assumes the shape of platlets having a very high aspect ratio (Average length of 100-120 nm is reported). High aspect ratio (Length/Thickness) of the nano filler contributes to high strength and increased modulus of elasticity values of PNC which are certainly higher than those of a

conventional composite. Increase in nano filler content further contributes to enhancement in properties of PNC. But excessive nano filler mass eventually results in agglomeration and poor dispersion of nano fillers that is detrimental to PNC properties. The yield strength of organic nano clay/Nylon 6 PNC with nano clay content of 16% is found to be of the order of 84 MPa. The corresponding value of neat polymer, Nylon 6, with zero filler is 64 MPa whereas the value of a conventional micro glass fiber/Nylon 6 composite with glass fiber of 5% is 72 MPa. In the category of *nano tube* fillers, carbon nano tubes (CNT) possess very high mechanical properties. It is found that in CNT/Polystyrene nanocomposite, addition of CNT of weight of 1% results in substantial 25% jump in tensile strength and 36-42% increase in elastic stiffness. In the case of *spherical fillers*, the nanocomposite strength is found to increase with decreasing nano filler size without changing the weight of the nano filler. Since small nano filler particles have higher total surface area for a given volume fraction, the strength increases with increase in surface area. Stress transfer from the polymer matrix to fillers, in service conditions, takes place via filler-matrix interface. Higher surface area of nano filler and hence higher contact or interfacial area between polymer and nano filler enhances the efficiency of stress transfer. These properties are relatively inferior in conventional composites in which the surface area of fillers is less than that in nanocomposites.

Thermal stability

Both intercalated and exfoliated PNC's display greater thermal stability as compared to pure polymer or corresponding composite counterparts. This is caused by reduction in permeability/diffusivity of oxygen and other degraded volatile products due to homogeneously distributed nano filler with high aspect ratio. PNC's also display increased resistance to char formation. The thermal stability of PNC's consistently improves as the nano filler content goes up. All these observations are confirmed in bio-degradable polycaprolactone nanocomposite filled with layered nano filler silicates of montmorillonite.

Gas barrier and magnetic properties

Thin PNC's films, prepared by exfoliation process, contain high aspect ratio layered silicates that are capable of reducing gas permeability. Relative permeability is found to decrease with increase in nano filler volume fraction.

PNC films are usually weakly ferri-magnetic at room temperature. But typical superparamagnetic behaviours at high magnetic fields i.e. no hysteresis, almost immeasurable coercivity and remanence with non saturation is seen in some PNC's.

Dimensional stability and electrical conductivity

Dimensional stability of PNC's is a critical issue in many applications. Addition of low content of nano fillers in polymers significantly reduces the coefficient of thermal expansion thereby improving the dimensional stability of PNC. This is because the coefficient of thermal expansion of nano fillers is much lower than that of polymer matrix. Low coefficient of thermal expansion of PNC is desirable for cryogenic engineering applications as well.

High aspect ratio and high conductivity of carbon nano tubes make them excellent fillers for making conducting PNC's. When the volume fraction of nano fillers exceeds the percolation threshold at which there is a continuous conducting path, the PNC becomes conducting. As discussed in Section 4.1, with long thin nano fillers, the contact area between nano filler and polymer increases causing conduction of PNC at much lower filler loading.

VI. Application Of PNC's [4-6]

Light weight PNC's used in reducing the weight of the vehicles result in the improved vehicle fuel efficiency and performance. Use of PNC's improves the strength, impact resistance and durability of automotive and aerospace parts. PNC's can be added to paints, batteries, fuel cells, tires, mirror and windows of the vehicle for property improvement. PNC's have efficient heat dissipation characteristics and improved thermal and ablative capabilities that is imperative for high speed aircrafts and space vehicles. Light weight of sports equipment, like tennis rackets and hockey sticks etc., is also achieved with the use of PNC's.

Mechanical strength and durability of concrete structures is improved by the use of PNC's. PNC coatings and sealants enhance the life of buildings and related infrastructure. PNC's also contribute in strengthening and rehabilitation of existing buildings, development of better concrete, cement, asphalt etc.

Controlled and targeted release of therapeutic agents is aided by PNC's that increases the treatment efficiency. Tissue regeneration for cell growth and repair is also promoted by PNC's. PNC's are suitable for use in implants and prosthesis materials for patients due to good mechanical and compatibility properties. PNC's greatly enhance the mechanical stability and robustness of implants that is a vital requirement for biomedical applications necessitating durable materials. Some PNC's have good anti-microbial properties too that is conducive to faster recovery from wounds.

Use of PNC's is foreseen in flexible electronic sensors due to electromagnetic shielding. PNC's improve the performance and longevity of batteries and super capacitors. Their use results in excellent properties of transistors, memory devices, light emitting diodes, touch screens, sensors etc. Heat management in electronic devices, to prevent their overheating, is also improved with the use of PNC's.

PNC's can be introduced in materials meant for protective gear and armour of defence personnel. Their use results in high fatigue and fracture resistance, enhanced ballistic properties and reduction in brittleness of military equipment, armament and armour. PNC's improve the protection against electromagnetic radiation. Sensitivity and functionality of several detection systems is also increased by the use of PNC's.

PNC's augment the efficiency of separation process that is important in industrial applications. They aid in capturing and neutralising pollutants in air and water sources. PNC's can be employed as membranes and adsorbents for removing contaminants and heavy metals from water. They also adsorb and degrade hazardous gases by photocatalysis or chemical processes.

VII. Limitations Of PNC's [7]

Excessive use of nano fillers like carbon nanotubes and graphene, that have high surface area, results in agglomeration of nano fillers during PNC synthesis. This in turn leads to poor dispersion of nano fillers in the polymer matrix causing degradation in PNC properties, although methods like ultrasonification, high shear mixing and use of surfactants tend to address the problem of agglomeration and poor dispersion to some extent. Incompatibility between nano fillers and the polymer is another problem that results in weak interfacial adhesion and bonding between the two. This causes limited mechanical properties and reduced stress transfer when the PNC is subjected to service loads.

Addition of nano fillers to polymer adversely changes the rheological properties of the mixture that makes the synthesis of PNC's more difficult. Moreover, large scale production of bigger sized PNC's for industrial applications also presents a lot of challenges due to the scalability issues.

Defects like voids, cracks and agglomerates reduce the mechanical integrity of PNC's. These defects act as crack initiation sites for failure under applied stress in real life applications.

PNC's exhibit degradation in properties under high temperature environment. Also, small size and high reactivity of nano fillers raise concerns about their potential toxicity and environmental impact. Nano fillers can migrate from the PNC posing risk to human health and eco system.

Production of high quality PNC's by complex synthesis techniques is costly. Importantly, long term behaviour of PNC's like aging and degradation in performance over extended period of time is not fully understood. This limited knowledge poses challenges in prediction of life span and viability of PNC's.

VIII. Conclusion

PNC's show a lot of promise and potential for use in many engineering fields. But their extensive applications are hampered by their limitations. Interdisciplinary research and developmental efforts are needed to address the issues of PNC's like poor nano filler dispersion and agglomeration, reduced compatibility and limited interfacial bonding between polymer and nano filler, problems in synthesis and assessment of environmental and health impacts etc. Resolving these problems shall pave the way for large scale implementation of PNC's in industries related to automotive, aerospace, defence, electronics and packaging etc.

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