

ANALYSING DIFFERENT NANO FILLER WITH POLYMER NANO COMPOSITES

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Abstract

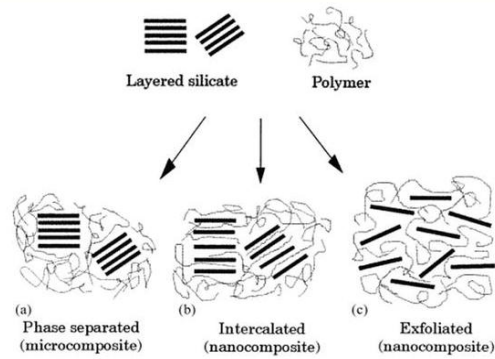
The development of polymer nanocomposites has been an area of high scientific and industrial interest in the recent years, due to several improvements achieved in these materials, as a result of the combination of a polymeric matrix and, usually, an inorganic nanomaterial. The improved performance of those materials can include mechanical strength, toughness and stiffness, electrical and thermal conductivity, superior flame retardancy and higher barrier to moisture and gases. Nanocomposites can also show unique design possibilities, which offer excellent advantages in creating functional materials with desired properties for specific applications. The possibility of using natural resources and the fact of being environmentally friendly have also offered new opportunities for applications. This chapter aims to review the main topics and recent progresses related to polymer nanocomposites, such as techniques of characterization, methods of production, structures, compatibilization and applications. First, the most important concepts about nanocomposites will be presented. Additionally, an approach on the different types of filler that can be used as reinforcement in polymeric matrices will be made. After that, sections about methods of production and structures of nanocomposites will be detailed. Finally, some properties and potential applications that have been achieved in polymer nanocomposites will be highlighted.

Keywords

Nano composites polymers nano fillers processing compatibilization morphology structures characterizations properties applications

Introduction

Polymer nanocomposites (PNCs) may be defined as a mixture of two or more materials, where the matrix is a polymer and the dispersed phase has at least one dimension smaller than 100 nm. In the last decades, it has been observed that the addition of low contents of these nano fillers into the polymer can lead to improvements in their mechanical, thermal, barrier and flammability properties, without affecting their processability. The ideal design of a nanocomposite involves individual nanoparticles homogeneously dispersed in a matrix polymer. The dispersion state of nanoparticles is the key challenge in order to obtain the full potential of properties enhancement. This uniform dispersion of nanofillers can lead to a large interfacial area between the constituents of the nanocomposites. The reinforcing effect of filler is attributed to several factors, such as properties of the polymer matrix, nature and type of nanofiller, concentration of polymer and filler, particle aspect ratio, particle size, particle orientation and particle distribution. Various types of nanoparticles, such as clays [3, 4], carbon nanotubes, graphene, nanocellulose and halloysite, have been used to obtain nanocomposites with different polymers.



Possible structures of polymer nanocomposites using layered nanoclays: (a) microcomposite, (b) intercalated nanocomposite and (c) exfoliated nanocomposite

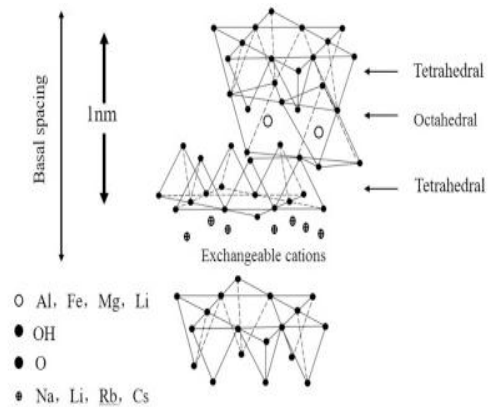
Nanoscale fillers and interfaces

Nanoscale fillers have various shapes and sizes; and they form ultra-large interfacial areas when bonded to polymer matrices. Since the properties of polymer nanocomposites are dependent on these factors, they will be first addressed in this section.

Sheet-like nanoscale fillers

The first example of sheet-like nano-fillers often used in polymer nanocomposites is layered silicates belonging to the structural family known as the 2:1 phyllosilicates. Montmorillonite, hectorite and saponite etc. are the usually used layered silicates and their structure is presented in. Their crystal lattice is composed of two-dimensional layers. A central octahedral sheet of alumina or magnesia is fused into two external silica tetrahedron so that the oxygen ions of octahedral sheet pertain to tetrahedral sheets. The thickness of layers is ca. 1 nm and the lateral dimensions of the layers vary from several tens of nanometers to several micrometers and even larger. These layers will form stacks with van der Waals gaps between “interlayers” or “inter-galleries”. This kind of clay has a moderate cation exchange capacity and the

charge of the layer is not constant since it differentiates from one layer to another and thus a mean value over the whole crystal should be taken into account.



Structure

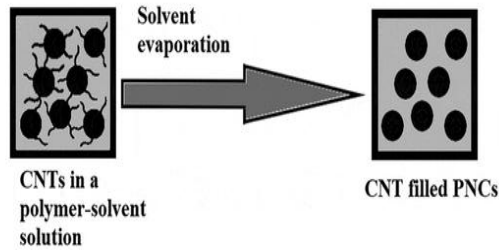
of commonly used phyllosilicates

PNCs incorporating nanofibre and/or nanotube filler

Carbon nanotubes (CNTs) and carbon nanofibres (CNFs) have emerged as the most sought-after fillers to fabricate high-performance PNCs owing to their excellent structural rigidity and thermal stability. The various methods used to fabricate PNCs with CNTs as filler include: (1) Solution mixing method, (2) Melt mixing method, (3) In-situ polymerization and (4) Electrospinning technique.

Solution processing or solution mixing is one of the convenient ways of fabricating CNT-filled PNCs. In this method, the CNTs are introduced into a suitable solvent and are thoroughly blended with the aid of high shear homogenization techniques or sonication method or magnetic/mechanical stirring. This results in homogeneous dispersion of CNTs within the polymeric material. This is followed by the dissolution of the polymer within the solution of solvent and CNT. The solvent is then removed either through evaporation or via coagulation to obtain the CNT-filled PNC.

Solution processing technique



Another method to fabricate CNT-filled PNCs is through melt processing or melt mixing. This method is widely used to produce CNT-filled thermoplastic-based PNCs owing to its highly economical process ability and conduciveness to be incorporated for large-scale production processes. In this method, CNTs are mixed with the thermoplastic matrix material in required weight percentage. The application of heat results in the formation of viscous liquid of thermoplastic matrix material. The viscous liquid is then made to enter the compounder or screw extruder with an attached high-shear mixer. This results in high shear mixing of the CNTs within the thermoplastic matrix and results in a uniform dispersion of the CNTs within the PNCs. Depicts a typical twin-screw extruder used in industries to disperse CNTs in a thermoplastic matrix. The extruded PNC can be then sent into an injection molding machine to obtain the desired end product with required geometrical shape.

PNCs incorporating spherical NPs as filler

NPs as fillers are widely used to fabricate high-performance PNCs as the processing of such PNCs is often easy and suitable for mass production. But, it is mandatory to achieve a uniform dispersion of the selected NPs within the polymeric matrices and often a challenge as the near spherical NPs tend to agglomerate owing to an increased surface forces of attraction. The available literature highlights three

methods to fabricate defect-free, good quality PNCs filled with NPs and those methods include direct mixing, in-situ polymerization and solution mixing techniques.

Direct mixing methods such as melt mixing, miscible solvent mixing and powder metallurgy techniques are effectively used to prepare PNCs filled with NPs. However, all such methods suffer a major drawback whenever large quantity of NPs are to be incorporated resulting in severe clustering/agglomeration of NPs within the polymeric matrix. Hence, it is needless to say that proper surface treatment of NPs is essential to process PNCs with uniformly dispersed NPs. In in-situ polymerization, the NPs are dispersed in a suitable monomer and the resultant solution is polymerized to obtain PNCs. In few of the published research, it is found that in-situ polymerization is not suitable for very small NPs measuring less than 10 nm.

Another popular method to disperse metal-oxide NPs within the polymeric matrix is the sol-gel technique. This method combines in-situ formation of the required NPs followed by in-situ polymerization to fabricate particle-filled PNCs. This method is also widely used to homogeneously disperse different inorganic NPs in various organic polymer matrices to fabricate hybrid PNCs. Sol-gel technique has enabled the dispersion of very tiny particles whose dimensions are extremely less than the polymer chain length. But, this method suffers from a major disadvantage in that the choice of polymer material used in this method is strictly limited to alcohol and/or water soluble resins, which are able to bind with the hydroxyl groups of the organic phase through the generation of a hydrogen

bond. Another hindrance in this technique is its effect on the formation of the particle (inorganic) network structure, which possess a challenge in the employment of control over the size and dispersion of the particle fillers in hybrid PNCs.

In order to overcome the above-mentioned limitations, a novel method has been proposed to synthesize hybrid PNCs called the site selective molecular hybrid method. This method is widely used to disperse fine silica particles in a silane modified polymer matrix. In this technique, polymerization of an alkoxy siloxane compound is ensued to produce polyalkoxy siloxane having a functional group similar to glycidyl group. With the aid of this glycidyl-like group, the introduction of the polyalkoxy siloxane in the required positions of the polymer is carried out. A sol-gel hardening reaction is produced at the site of introduction of polyalkoxy siloxane to produce very fine silica as the formation of siloxane bond is cut-short by the polymer. The major advantage of this new method is the erudite control over the structure enabling the generation of application specific materials.

Inorganic metal-oxide NPs as fillers in PNCs

Incorporation of inorganic nano-scaled particles in various polymeric matrices has gained widespread attention owing to the ease of handling and manufacturing, tailorability of material properties and economic viability. Usually in particle-filled PNCs, the continuous polymeric phase is attached to the NPs via a covalent or coordination bond. When metal-based NPs are incorporated in PNCs, a polymeric film is produced on the surface of metal NPs and this condition allows for the generation of a unique interphase between

the polymer and the particle. Metal-oxides derived out of pure metals exhibit different structural geometries in comparison with their base metal and also possess unique metallic, semiconducting or insulating characteristics. Metal-oxides possessing a bulk crystal structure impart the PNCs of the required structural rigidity. Due to the nanoscopic scale, most metal-oxides possess discrete energy levels leading to the transport of electrons, which result in a change in electron band-gap. Thus, metal-oxide-filled PNCs exhibit some unique electronic, chemical and physical properties. The incorporation of highly conductive metal-oxide NPs within the non-conducting polymer matrix can result in a PNC with enhanced conductivity, which can be tailored by changing the loading of the conductive metal-oxide NPs. Hence, most of the properties of the PNCs depend upon the metal-oxide particle loading, its geometry and its adhesion and dispersion within the selected polymeric matrix.

In one of the researches comparing the effect of zinc oxide (ZnO) NPs and nanotubes dispersed in epoxy composites, it is found that the addition of as low as 0.8% ZnO has remarkably improved the mechanical properties of the epoxy PNCs. The tensile strength improved by 27% and toughness was increased by 105% compared with neat epoxy. Greater flexibility of the PNCs was found for ZnO nanotube addition of 1 wt.% and ZnO NP addition of 0.8 wt.%. Another published work highlighted the effect of obtaining NP dispersion through chemical route and aims to investigate the interfacial bonding, resistance to UV absorption and the solvent effect on the dispersion of NPs. The research group fabricated ZnO NP (in varied wt.%) -filled epoxy PNCs by

dissolving ZnO in two different solvents, viz., isopropyl alcohol and ethanol, and then this was mixed with epoxy resin and glass fibre-reinforced epoxy PNCs were fabricated through hand layup route. It was reported that isopropyl alcohol blending had a positive effect on the dispersion of ZnO NPs, mechanical and UV absorbability properties of the PNCs.

It is known that surface treatment of NPs helps in reducing their surface energy and allowing for uniform dispersion of treated NPs uniformly within the matrix material. Such well-dispersed NPs eventually promote attractive mechanical, thermal and electrical properties in a PNCs. However, one of the research highlights that silane surfactant treatment of ZnO NPs had no effect for UV absorption in ZnO/DGEBA/micro-HGF composite. Some of the published work studied the effect of ZnO NP on the curing behavior of the epoxy resin, and it was reported that high volume percent addition of ZnO NPs-induced steric hindrance, which adversely affected the curing behavior of epoxy PNCs. Also, it is highlighted that addition of more than 3.5 wt.% of ZnO NPs resulted in the reduced reaction of epoxy resin and the cross-linker that will adversely affect the PNC properties.

The size along with the wt.% addition of the NPs incorporated also has a bearing on the final properties of the PNCs. In one of the works (Al-Turaif, 2010), it is found that the incorporation of 17 nm and 50 nm sized TiO₂ at 3 wt.% addition resulted in improved tensile strength of epoxy PNCs, whereas for 200-nm-sized TiO₂, the improvement in tensile strength was observed at 5 wt.% addition of TiO₂ NP. In the same work, it is also highlighted that improvement in flexural properties of epoxy PNCs is found at as less as 1 wt.%

addition of TiO₂ and further increment in wt.% addition of NPs did not yield any increment in flexural properties. In contrast to ZnO NPs, it is found that TiO₂ NPs act as catalysts and facilitate curing in epoxy PNCs. Yet another work involving in-situ synthesis of epoxy/TiO₂ PNCs indicate that the addition of TiO₂ NPs improved the thermal resistance of the PNCs by reducing the glass transition temperature of the epoxy PNCs. The work also suggests that higher loading of TiO₂ resulted in the reduction of mechanical properties owing to severe agglomeration of NPs. The addition of TiO₂ NP in epoxy polymer matrix improved the hygrothermal behavior of epoxy PNCs for as low as 0.1 wt.% addition of TiO₂ NPs.

Effect of size and dispersion of NPs in PNCs

An NP is a scientific term coined to classify such small particles which cannot be deciphered through naked eyes and are known to possess at least one dimension which is less than 100 nm. A more stringent definition defines NPs as such particles whose properties are dependent directly on their size. This definition restricts the size of the NP to be smaller than 10–20 nm. As stated in the aforesaid paragraphs, the size and dispersion of the NPs play a significant role in determining the final properties of the PNCs. This is because of the pronounced increment in surface properties with the reduction in particle size. As the particle size reduces, the surface-to-volume ratio increases. This implies that whenever a material is composed of nano-scaled particles, the surface area of such material increases and such nano-sized materials have a greater number of surface particles. This can be explained through the consideration of a typical case, wherein a 10 nm particle

possesses nearly 20% of its particles at its surface as opposed to a 3 nm particle, which has almost 50% of its particles at the surface. This property of the nanomaterials renders them highly reactive. Most of the materials, which are chemically inert in their bulk form, are often found to be severely reactive when they are brought down to nanoscale form. When nanomaterials are incorporated in polymeric matrices, such surface properties largely influence the interfacial properties between the matrix and the reinforcing NPs, tendency of the formation of aggregates/agglomeration of NPs within the matrix and finally leads to the enhancement or reduction in the material property of the PNC. It is found that the high surface area of the NPs results in setting up of an intense Vander Waal's forces of attraction between the particles which result in agglomeration of NPs. Such agglomeration has a negative impact on the mechanical properties of the PNCs as the material is devoid of active interphases due to lack of interfacial area.

In order to realize the nano-effect of NPs on the final properties of the PNCs, it is also mandatory to ensure a uniform dispersion of NPs within the selected polymeric matrices as such dispersion has an impact on the polymer chain structure. The uniform dispersion of the NPs in the polymer matrix is controlled by various factors such as inter phases between the polymer and NP, size of NPs and the weight/volume percent of NPs in the polymeric matrix. Researchers have also studied the influence of shape of NPs on the interfacial reactions in a PNC. The shapes of the NPs are found to bear a direct relation with the surface area to volume ratio and thus influence their

interaction with the polymeric matrix material.

Methods to obtain uniform dispersion of NPs in PNCs

In order to extract maximum out of the reinforcing NPs, it is all the more important to ensure that the selected NPs are uniformly dispersed within the polymeric matrix and a strong interfacial adhesion between the matrix and the reinforcing phase is established. The attainment of these conditions has always posed a challenge in the fabrication of PNCs due to the tendency of the NPs to form into aggregates/clusters/agglomerates due to the strong force of attraction between the particles. Researchers emphasize that the knowledge of the surface characteristics of the NPs is a must to overcome the problem of uniform dispersion of the same within the selected matrix. For instance, if the NP surface exhibits greater affinity to moisture and such a particle is to be incorporated as a filler in a nonpolar polymeric matrix, then it is highly advisable to convert the surface properties of the NP to render it hydrophobic. Hence, surface modification of the nano-fillers is carried out to ensure a uniform dispersion of the NPs within the polymeric matrix. Most of the polymeric matrices demonstrate a greater degree of hydrophobicity, while the inorganic nano-fillers are generally hydrophilic. Thus, the surface modification techniques are aimed to decrease the hydrophilicity and increase the hydrophobicity of the inorganic nano-fillers so that they become compatible with the matrix material.

Influence of NPs on the mechanical properties of PNCs

PNCs, in recent years, have evolved as multi-functional materials catering to the need of high-technological applications

such as aerospace, automobile, biomedical devices, electronic and energy storage applications. In order to enhance the reliability of PNCs in various applications, it is all the more important to understand the influence of NPs on the mechanical properties of the composite. Several researchers have put forward theories which throw light upon the synergies between the polymeric matrix material and the chemistry and/or geometry of the NPs along with interfacial interactions between the filler and the matrix that by and large influence the mechanical properties of the PNCs. It is well understood that the nano-scale filler particles, the polymer matrix material and additional substitute materials that are added to obtain a healthy inter phase play a crucial role in the evolution of the final mechanical property of the multiphase material. It is also important to understand the interaction mechanism between various phases in the PNCs that give rise to novel microstructures and the multilevel complex stress transfer between such phases (Crosby & Lee, 2007). Out of several mechanisms that influence the final mechanical property of the composite, one mechanism that has a strong bearing on the mechanical property is the particle-to-particle interaction within the selected polymeric matrix. The tendency of the NPs to form as agglomerated clusters/aggregates due to increased surface area and the subsequent development of a strong interactive forces of attraction between the particles tend to negatively influence the mechanical properties of the PNCs by imposing restriction on the effective interfacial area. Such agglomeration is also dependent on the orientation and shape of the NPs. An effective stress transformation mechanism from the brittle matrix to strong NPs can

be set up in a PNCs provided there is a big interfacial area to sustain the applied loads. Published reports indicate that the interfacial area depends on the density and size of the nano-scaled fillers. The reduction in the size and density of the nano-fillers results in the creation of larger interfacial area and thus helps in the improvement of the final mechanical properties of the PNCs. Thus, the size of the NP is also an important parameter, which needs due consideration for the improvement in material's mechanical properties. Along with the particle size, it is also seen that the inter phase thickness plays a crucial role in determining the tensile properties of the composite mater. This is because, the bonding between the NPs and the matrix is stiff in the interfacial region and this stiff bonding will enable the PNCs to withstand loads and retard the possibility of failure. Some of the published work -highlight the fact that this crucial interface thickness is related to the quantity of the adsorbed polymer chains of high molar mass onto the surfaces of NPs and this condition can be tailored by varying the loading. It is reported that small-sized NP producing a thin and weak inter phase is not beneficial for the improvement in the tensile strength of the composite material. This is also true for a large-sized NP producing a thicker inter phase. Hence, one cannot negate that both particle size and inter phase thickness should be synergized for an optimum tensile strength of the material. In order to obtain a greater reinforcing effect and thereby an improved mechanical property, it is essential to incorporate smaller NPs with thicker inter phases.

Conclusion

Polymer nano composites filler excellent opportunities towards explore new

functional beyond those of conventional materials. The field of nano composites has been one of the most promising and emerging research areas. They find special attention due to the unique properties such as light weight, ease of production and edibility. A deterring feature of polymer nano-composites is the small size of the fillers leads to an enormous increase in interfacial area as compared to traditional composites. The interfacial area creates a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings of the nano filler. Interfacial structure is known to be different from bulk structure, and in polymers with nanoparticles possessing high surface areas, most parts of the polymers are present near the interfaces, in spite of the small weight fraction of the filler. This is one of the reasons why the nature of reinforcement is different in nano composites. The crucial parameters which determine the effects of fillers on the properties of composites are filler size, shape and aspect ratio and filler-matrix interactions.

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