E-ISSN: 2997-9382

SemantJournals

American Journal of Technology Advancement

https://semantjournals.org/index.php/AJTA

| Research Article

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Polymer Nanocomposites: Bridging the Gap Between Polymers and Nanoparticles

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Annotation

Polymer nanocomposite (PNC) represents a novel class of materials which has resulted from the combination of polymer polymer matrices with nanometer-sized particles. The mechanical property and robustness of the hybrid structure as well as the functional properties are superior to those of pure polymer composite. In this review, we also attempt to give an in-depth discussion of basic principles of PNCs such as classification and different types of PNCs, synthesis methods, analytical characterization techniques, and PNC properties (intrinsic). The PNCs are divided into three main types according to the geometric dimensions of the embedded nanofillers. The paper further addresses particular properties of each type of nanofiller and their further benefits and weaknesses on the global performance of resulting PNCs. The research analyses various approaches for the production of PNCs, such as melt mixing, in-situ polymerisation, and solution blending. Each approach has its own advantages and limitations. The text focuses on the characterization of PNCs, such as their shape, the structure of the inner core, and the phenolic matrix, as well as their physical properties, obtained using sophisticated diagnostic methods. interphase between the polymer matrix and the nanofillers. The paper deals with the study of the structural, mechanical, thermal, electrical, and functional properties of PNCs, and highlights the possibilities of Nanoparticulate filler to improve the functional properties of polymer composites. Particular importance of the nanoparticle/polymer matrix interface is stressed because it immobilizes the overall properties of polymer nanocomposites (PNCs). Special attention is given to the importance of achieving the homogeneous dispersion of the nanoparticles as well as to the modification of the interface bonding behavior. In a nutshell, this review serves as a tip of spear in summarizing the relentless progress of PNCs, and it sheds light on the strategic approaches toward the formulation and processing as well as the potential applications of PNCs. The contributions assembled here in this book certainly will serve as a good bibliographic reference for both academic researchers, industry researchers and research students working in the field related to polymer nanocomposite technology.

Keywords: Polymer nanocomposites, Nanofillers, Layered nanocomposites, Fibrous nanocomposites, Spherical nanocomposites, Interfacial interactions.

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Introduction

Rephrased Version:

The strength and durability of the polymers could be improved by incorporating particulate reinforcement of different sizes, which also allows to overcome intrinsic material weaknesses and to enlarge the use of these materials.

Overview:

The introduction of nanoscale additives into polymer systems has marked a breakthrough in the field of composite engineering, offering a remarkably successful alternative to the classical reinforcement strategies (Papageorgiou et al., 2017).

These fillers, which can be found in the nanometer scale, presenting from something so spherical shape to the long fibre, lamella, needle one with strong anisotropy.

Recent advances in nanoscience and nanotechnology have offered an opportunity to foster new classes of composite materials, generated by addition of inorganic nanofillers in polymer matrix. These systems, which are termed polymer nanocomposites, have novel functional and structural properties.

There are three principal classes of polymer nanocomposite based on the dimensionality of the nanoscale reinforcements: The second category of nanofillers are 2D materials (e.g., layered silicates, MXenes, and graphene derivatives) with a lamellar shape and few nanometer thickness as well as lateral size from to several micrometers (Li et al., 2018; Tu et al., 2018). Nanocomposites comprising such structures are typically called layered or lamellar nanocomposites.

Second where the fillers are two dimensional on the scale of a nanometer in two directions and the third direction is much larger, resulting in an elongated, one-dimensional shape. In this regard, the use of material such as carbon nanotubes (Nano Tube, CNTs), also nanofibers and halloysite nanotubes work as reinforcing agents and confer upon the polymer matrix excellent mechanical and functional enhancements (Fu et al., 2019; Idumah et al., 2019).

The third category is a subject-matter (e.g., nanocomposites with the nanosize fillers in three directions but in which the fillers are shaped isotropically, nearly spherical fillers). These fillers include for example silica nanoparticles, quantum dots, and other semiconductor nanoclusters. In Fig, an illustration of the various nanofillers geometries is provided.

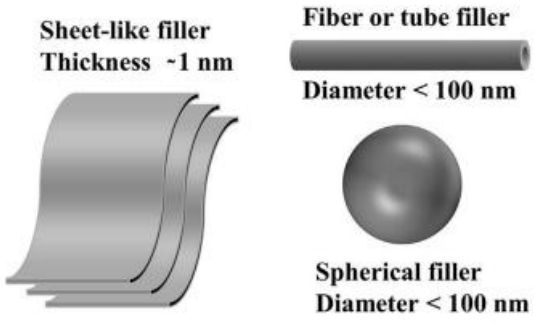

Figure 1. Illustration of some nanoscale fillers (Fu et al., 2019).

Uniform distribution of such nano-size additives homogeneous in all directions or anisotropic in nature which may have different properties in different directions will perhaps lead to a much higher ratio of contact surface to volume between these additives and polymers they get combined with. And in cases where the nano-size fillers are present in minute amounts the separation between the nano-elements effectively becomes in the order of molecular separation, in addition to the often large interfacial area. Thus the shape of the object is dictated by the properties at the nanoscale.

The remarkable mechanical and physical properties of PNC's as compared to the respective pristine polymer are mainly attributed to good interfacial compatibility between the polymer matrix and the incorporated nano-fillers. A representative case of such a measurable interfacial region is that provided by systems of spherical nanoparticles dispersed in polymer chains. The nanometer dimensions of these fillers lead to an unprecedentedly large interfacial area, leading to physical and mechanical properties which cannot be matched by conventional polymer composites. Tuning the properties of the nanofillers is also the basis to manage these interfacial characteristics towards enhanced properties and performances of the nanocomposites. These enhancements are mostly due to the high surface-to-volume of the interaction of the nanofillers and the polymer (Ferreira et al., 2016). For instance, the loading of the grafting polymer chains on the surfaces of the GNs was demonstrated to significantly enhance the interfacial shear strength and mode-II failure resistance in the graphene- based functional nanocomposites (Liu et al., 2016).

A number of excellent review articles reviewing different aspects of polymer nanocomposites have appeared. In their study, Guo et al. (2018) studied the fabrication processes of nanoclay/polymer nanocomposites. It was found that changing the processing protocol (e.g., type or processing parameters) would have a pronounced effect on the final morphology, mechanical behavior, and nanostructures of the clay or polymer nanocomposites. Tan and Thomas (2016) have reviewed the porosity of gas molecules in clay or polymer nanocomposites. Papageorgiou et al. (2017) in a review of the physical mechanical properties of graphene/ polymer nanocomposites concluded that good reinforcement could only be obtained at a very low weight percentage of graphene. It is because it is difficult to prepare the suitable dispersion at high contents of graphene.

In their study, Naz et al. Kim S. et al.(deg,2016) investigated the results of studies on the electrical and mechanical properties of polymer composites reinforced with graphite. They have also studied mixing various modifications of graphite in polymer matrices in creating polymer-carbon nanocomposites. A review was made on CNTs/polymer nanocomposites by Xue and Sun 2016. In their study, Chen et al. (2018) addressed the electrical percolation problem themselves. Liu et al. (2016) reviewed the studies on halloysite nanotube/polymer nanocomposites.

The basics aspects such as synthesis, analysis, and properties of different PNCs have been analyzed exhaustively in the present paper. An in depth review of the preparation, characterization and properties of polymer nanocomposites is presented in the paper. Various nano fillers are first added to the PMMA. The book gives a systematic description and study of production of PNCs based on various modalities, the study of the properties of PNCs produced with different methods, and the research of the structural and mechanical properties of the PNCs.

1. Categorization of PNCs

According to their geometrical dimensions, PNCs are divided into three groups. The first one is a class of layered PNCs, two-dimensional nanoparticles with a thickness on the order of nanometers and a length from several nanometers to several hundred \sim 1000 nm. These PNCs are loaded with multilayer nanoclay, graphene or titanium carbide. The second type is PNC participants with nanosheets of two large dimensions plus one small areal dimension to form

nanometer-length fibers and tubes (Fu et al., 2019). These fibers and tubes are main fillers in the third group. Fibril and tubular nanofillers such as the carbon nanotubes, carbon and cellulose fibers, and halloysite, have been reported (Zhang et al., 2016). The third category comprises PNCs prepared with nanofillers wherein all the three dimensions are known to be in nanometer scales (Naz et al., 2016; Krishnaiah et al., 2017; Ladani et al., 2018). This group of PNCs predominantly uses the class of spherical fillers with isotropic three-dimensional dimensions, such as the quantum dots, NP clusters, as well as the spherical silica (Vengatesan and Mittal, 2016).

3. PNCs composed of inorganic metal-oxide nanoparticles

Some broader reviews have demonstrated the incorporation of inorganic nanoparticles into variety of polymer matrices because of their versatility, simple preparation, controllable properties of material and low cost. In particle-filled PNCs the continuous polymer phase is usually some form of chemical connectivity, e.g. covalent bounds or coordination interaction. If the polymer matrix contains metal-based nanoparticles, a polymeric layer is necessarily formed around the metal-fillers thus delimiting a well-defined interface between the polymer and the filler.

When metal oxides are created via oxide of the elemental metals, the crystal structures of the metal and oxide are very different and the electrical properties are also unique, ranging from conductor to semiconductive to insulator, depending on the composition. These oxides when present in the form of higher crystalline structure it contributes to enhance the mechanical strength of nanocomposite system (Saba et al., 2016). On the nanoscale, metal oxides exhibit quantized electronic states that modify the electron dynamics and modulate the band-gap of the material. Due to this, physicochemical, electronic and structural properties of metal oxide nanosparticles with PNCs are especially interesting.

Metal-oxide nanoparticles of high conductivity may be blended into a non-conductive polymeric matrix to yield a high-conductance PNC. The level of conductivity can be controlled by the quantity of conductive metal-oxide nanoparticles incorporated. The properties of the PNCs are therefore highly depending on parameters such as the number of metal-oxide particles, their shape, and their control over how evenly they are dispersed and attached to the selected polymeric matrix.

Salahuddin et al., an addition of a very minor weight fraction of 0.8% of zinc oxide nanoparticles and nanotubes led to a significant increase in mechanical properties of the epoxy polymer nanocomposites (PNCs) of the polymer. The tensile strength increased by 27%. Toughness was increased by 105% and the flexibility with 1 wt. ctrl of the above two nanoparticles was significantly increased. % of ZnO nanotubes and ZnO nanoparticles. However, Wong et al. (2016) reported that the UV absorption of the ZnO/DGEBA/micro-HGF composite was not seriously influenced.

Research by Wong et al. (2016) to the curing effects of EP matrix ZnO NPs which indicated that the addition of high volume percent of ZnO NPs caused steric affect that the negatively affects curing progress of PNCs. Furthermore, more than 3.5 weight % ZnO nanoparticles weakened the interaction of epoxy resin with the cross-linker causing degradation of the polymer nanocomposite properties. Both the size and the weight percentage addition of the NPs are relevant for the final properties of the PNCs.

Atta et al. (2017) adopted 3 wt% of 17 nm and 50 nm-sized TiO2 particles showed an improvement in tensile strength was observed in then the epoxy PNCs were used. Nevertheless, an increase in weight percentage of nanoparticles higher than this, did not lead to an additional improvement in flexural properties.

It has been also demonstrated that TiO2 nanoparticles work as catalyst and help the cure of epoxy in PNCs. In-situ synthesis reported the presence of perfect TiO2 nanoparticles addition in PNCs to withstand at high temperatures (Nayak and Ray, 2018; Parameswaranpillai et al., 2022).

2. Techniques for achieving homogeneous distribution of nanoparticles in polymer nanocomposites

Between the matrix and reinforcing phase in a polymeric matrix is necessary A strong bond to avoid large agglomeration or cluster of the latter. Investigators stress surface characterisation of nanoparticles for the homogeneous dispersion in a matrix. For example, where a particle surface is highly water attractant, modifying the surface properties to be water repellent may be desirable. Surface modification is required to prepare a uniform distribution of nanoparticles in polymer matrix. Most of the polymeric matrices are more hydrophobic, whereas inorganic nano-fillers tend to be more hydrophilic in nature. Surface modification methods have been also developed to decrease hydrophilicity and to increase hydrophobicity of inorganic nano-fraud, which makes them compatible with the matrix materials (Müller et al., 2017; Chen et al., 2022).

Inorganic nanoparticles can be physically modified on their surfaces and chemically modified, which may be done physically or be by reaction. These are brought about by a range of physical forces- hydrogen bonding, van der Waals and electrostatic attractions to initiate connections between polymeric matrix material and nanoparticle fillers. This is accomplished through the use of inorganic nanoparticles coated by either a low molecular weight surfactant or a high molecular weight polymer. Surface forces are developed between the surfactant and the nanoparticles, which facilitates the clinging of the polar groups of the surfactant on the nanoparticle surface when they are treated with the surfactant. The interaction forms ionic binding and the surface potential of the modified NP decreases. The modified nanoparticles have lower surface energy and have less chance to form the aggregates (Gu et al., 2016; Yao et al., 2017; Hiremath et al., 2021).

Encapsulation is a physical method for the surface modification of NPs. This can be via the utilization of pre-formed polymer materials or the growth of a polymeric encapsulation material directly on the nanoparticles using in-situ techniques. The hyperdispersant material, which is rich in functional molecules including hydroxyl, carboxyl, carbonyls, and nitro, also contributes to a high level of chemical bonding to the NP and the polymeric material. Encapsulation by forming a polymer coating at the same place can yield a uniform coverage of the nanoparticle (Bachar, “Time-resolved spectroscopic studies of coaxial stabilization and aggregation of colloidal CdSe/ZnS quantum dots in polymer matrices,” 2022).

A polymeric shell is formed around the NPs, through a solution, or emulsion polymerization. Emulsion polymerization is based on the monomer adsorbing at the NP and the formation of an adsorbed layer. The second polymerization step occurs within the adsorbed layer and generates a compact polymeric shell around the NP, preparing the particle for drug loading (Khan et al., 2016; Morsi et al., 2016; Liang et al., 2017).

A drawback of these physical techniques is, however, that the adhesion of the polymeric coatings to the particle surface is not as strong as the one of covalently chemically bound particles. The researchers suggest that covalent bonds between the NP and the matrix can be formed by chemical reactions occurring at the presence of modifiers. One accepted method includes using a coupling agent solution to improve the spreading and adherence capacity of the NPs to the matrix (shutterstock-378495400_Solverdy et al., 2010; Kumar et al., 2017).

Polymer grafting techniques have now been found that enable the circumventing of these limitation(s) and the preparation of such a new amphiphile of increased hydrophilicity and lipophilicity. This alteration improves the distribution ability of the nanoparticles in the polymeric material. The "grafting to" route is decorating the surface of particles with functional

monomers and polymerizing them achieving homogeneously covered nanoparticles (Tong et al., 2018).

Ultrasonication is an approach for achieving homogeneous dispersion of nanoparticles in a matrix. It consists of energy transference via cavitation, affecting physical and chemical bonds between particles and with other molecules. These radicals cause the nanoclay surface interaction in the reinforced clay composites by breaking the carbon bonds between them owing to this energy (Tomić et al., 2016). This makes the uniform distribution of nano-clay possible, and also improves the wettability of the filler phase by the matrix phase. Mechanical alloying can change the shape of particles and can produce nanoparticles, it can improve contact surface to make uniform dispersion and production compatible with the material. High-energy ball milling is a method of reducing the particle size of particles into near-ultrafine ranges (50 nm and below). This can be done by using high energy for particle pulverisation (Mehrizi et al., 2016). Surfactants are introduced in this process to inhibit particles from aggregation. Steric blocking is formed, and thus the boundary particles on the surface which are important for nanocomposites have good inhibited rigidity. Surfactant is used to prevent the aggregation of NPs and also to make them compatible with the material (Iqbal et al., 2016).

3. The effect of nanoparticles on the physical characteristics of PNCs

Polymer nanocomposites (PNC) the most promising materials in most advanced technologies like aerospace, automotive industries, biomedical implants and energy storage. To direct the optimization of such composites for enhanced performance and sustainability, it is necessary to understand how nanoscale additives such as the SAPC affect the mechanics of the composite. A number of theoretical models have also been developed to account for dynamic behaviour of the polymer matrix and nanoparticles/fillers, which is one of the most important mechanismsthat controls the mechanical properties in PNCs. It is largely possible to the favorable design of nano-scale reinforcements, matrix phase constituent elements and modifiers constituting construction of strong interface zone and therefore rational mechanical performance of multiphase composite structure. The importance of the interphase for PNCs is also highly relevant in terms of microstructural characterization and stress distribution at several length scales (Maghsoudlou et al., 2019).

and the miscibility of the two phases, as well as the compatibility of the components as those of the composite material. When the nanoparticles agglomerate/aggregate and adhesive forces among particles are stronger and dominated, this will decrease the interface area, and, hence, the structure of the material could negatively affected (Machrafi, Aisati, Zargari, Mohsennia, & Machrafi, 2016; Bazrgari, Rashidi, Morsali, & Oladegaragoze, 2018). Their morphology and alignment are strongly correlated with the degree of aggregation of the particles. The efficient stress transfer between the ductile matrix and stiff nanofillers is closely related to the interfacial interaction between the two materials during mechanical stretching. The contacting area is influenced by the size of filler particles and the filler percent (Sharifzadeh et al., 2020). Smaller particles at the same loading, corresponding to an increase in the effective interface, lead to a higher nanocomposite strength (Li et al., 2018; Razavi et al., 2018). Accordingly, the focus on the size of the nanoparticles is of utmost importance (Ashraf et al., 2018).

These parameters as well as the interphase thickness and a diameter of the constituting particle(s) dominate the tensile strength of the composites. The good adhesion between the nanofillers and the polymer matrix could also lead to their good loading ability and the low failing of the material. Interface thickness is attributed to the adsorption of high molecular weight chains on the SURFACE (S) of nanoparticles and it is related with nanoparticle loading ratios (Msekh et al., 2018). If on the other hand, at the generation of the exhausting exhaust gas, the above mentioned floc is permitted to accumulate so high that the interphase between the exhaust gases separated from each other may become moderate and thin then a tensile strength which can be still lower

than the minimal required volume is made available. Furthermore, large particles have very dense interphases leading to a slow but very dense interphase. Thus, it is crucial for the tensile properties of the two to match the size of filler. Utilization of fine particles and stimulating the thicker interphase layers might be a novel way to enhance the mechanical properties also the long-term stability of polymer filled nanocomposites (Sharifzadeh & Cheraghi, 2021).

9. Conclusion

The properties of the polymer nanocomposite depend on the preparation method and on which type of nanoparticles are used as fillers. PNCs containing laponite-based PNCs have been prepared using different synthesis approaches, including in-situ intercalative polymerization, exfoliation-adsorption, template synthesis and melt intercalation (Cho et al. Melt blending, solution blending, electro spinning and in situ polymerization are the methods to prepare PNCs with nanotubes. In these cases, with the use of the nano-particles as a filler, it is desirable to use the in-situ polymerization, the solution mixing and the direct mixing methods. A uniform dispersion of NPs is important for the manufacture of high quality PNCs. The modification of NP surface could decrease the NP surface energy and restrain the NP aggregation in polymer. This homogeneous dispersion enhances the stiffness of the matrix material and the mechanical and thermal properties of the PNCs. The hybridization of multi-types of nanoparticles could be investigated, and the total effects would be analyzed. Further experimental studies are necessary to tackle any environmental concerns associated with NPs.

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