



Polymer Nanocomposites: Processing and Manufacturing

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| Abstract <p>This review discussed polymer nanocomposite manufacturing techniques including, In situ intercalative polymerization, Exfoliation-Adsorption, Melt Intercalation. In addition to presenting the scientific framework for the advances in polymer nanocomposite research, this review focuses on the scientific principles and mechanisms in relation to the methods of processing and manufacturing. Hence, this review offers a comprehensive discussion on processing and manufacturing concerns for polymer nanocomposites.</p> | Review Article <p>Received 4 Nov. 2012 Accepted 17 Feb. 2013 Published 30 Mar. 2013</p> Keywords: Clay Nanocomposites Exfoliation Intercalation |
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INTRODUCTION

In general, nanomaterials provide reinforcing efficiency because of their high aspect ratios [1]. The properties of a nanocomposite are greatly influenced by the size scale of its component phases and the degree of mixing between the two phases. Depending on the nature of the components used (layered silicate or nanofiber, cation exchange capacity, and polymer matrix) and the method of preparation, significant differences in composite properties may be obtained [2].

An improvement in a property arises when the length scale of the morphology (i.e., nano) and fundamental physics associated with a property coincide. Two principal factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area and quantum effects [3]. Some nanocomposites may show properties predominated by the interfacial interactions and others may exhibit the quantum effects associated with nanodimensional structures [4]. For manufacturing of nano-phased structural polymer composite material, the first step will be choice of a fabrication method. Some of the widely used methods for manufacturing conventional composite parts are wet lay-up, pultrusion, resin transfer molding (RTM), vacuum assisted resin transfer molding (VARTM), autoclave processing, resin film infusion (RFI), prepreg

method, filament winding, fiber placement technology, etc. [5].

For advanced structural applications, it is required to incorporate nano-reinforcements into macroscopic functions and validate them at the nanometric level. Recently, nanocomposites have been introduced in structural applications, such as automotive parts, gas barrier films, scratch-resistant coating, flame-retardant cables, etc. Also RTM, VARTM, RFI, and filament winding techniques can be used to manufacture nanocomposite parts for various applications including commercial aircraft structures for Boeing, Airbus, as well as many products in the industrial markets. Routine use of nanocomposites in automotive and aerospace industries is a long-term prospect as these are risk-averse sectors and extensive testing and characterization alone takes significant time[6]. But more emphasis should be given to technology development and for this issue participation from engineering communities are urgently needed. Hence, it will be easier to develop a product and bring out a product from the lab [6].

Preparation and Processing

For preparing polymer-clay nanocomposites, the interaction mechanism (pressure drop into the nano gallery, miscibility between polymer and clay, hydrogen bonding, electrostatic, coordination, etc.) of the polymer



and clay depends on the polarity, molecular weight, hydrophobicity, reactive groups, etc. of the polymer, and the type of solvent, i.e., water, polar, or nonpolar organic liquids and clay mineral type [7]. In this section some fabrication methodologies will be discussed, which have been developed with the layered silicates [8] and graphite nanoplatelet.

Nanoclay-reinforced Composites

In situ intercalative polymerization: Using this technique, polymer formation can occur in between the intercalated sheets. In situ polymerization is based on the following procedure: swelling of the layered silicate within the liquid monomer and the polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator, or by an organic initiator [9,10,8–11]. At first this approach was successfully applied in manufacturing of nylon–montmorillonite nanocomposite, and later it was extended to other thermoplastics [12]. This is a convenient method for thermoset–clay nanocomposites [13]. Messermith and Giannelis [14] have modified MMT by bis (2-hydroxyethyl) methyl hydrogenated tallow alkyl ammonium cation and they found the modified clay dispersed readily in diglycidyl ether of bisphenol A (DGEBA) by using this process. One obvious advantage of in situ polymerization is the tethering effect, which enables the nanoclay's surface organic chemical, such as 12-aminododecanoic acid (ADA), to link with nylon-6 polymer chains during polymerization.

Exfoliation-Adsorption:

This is based on a solvent system in which the polymer or prepolymer is soluble and the silicate layers are swellable. The layered silicates, owing to the weak forces that stack the layers together, can be easily dispersed in an adequate solvent such as water, acetone, chloroform, or toluene. The polymer then adsorbs on to the delaminated sheets and when the solvent is evaporated, the sheets reassemble, sandwiching the polymer to form. This strategy can be used to synthesize epoxy–clay nanocomposites [16], but removal of solvent is a critical issue here. Moreover, there is a disadvantage in using a large amount of solvent in the resin system [17]. This process also includes the emulsion polymerization

where the layered silicate is dispersed in the aqueous solution [8]. The Toyota Research Group has been the first to use this method to produce polyimide (PI) nanocomposites [10,18].

Melt Intercalation:

In this technique, no solvent is required [19,20,8,21] and the layered silicate is mixed within the polymer matrix in the molten state. A thermoplastic polymer is mechanically mixed by conventional methods such as extrusion and injection molding [17] with organophilic clay at an elevated temperature. The polymer chains are then intercalated or exfoliated to form nanocomposites. This is a popular method for preparing thermo plastic nanocomposites. The polymers, which are not suitable for adsorption or in situ polymerization, can be processed using this technique [22].

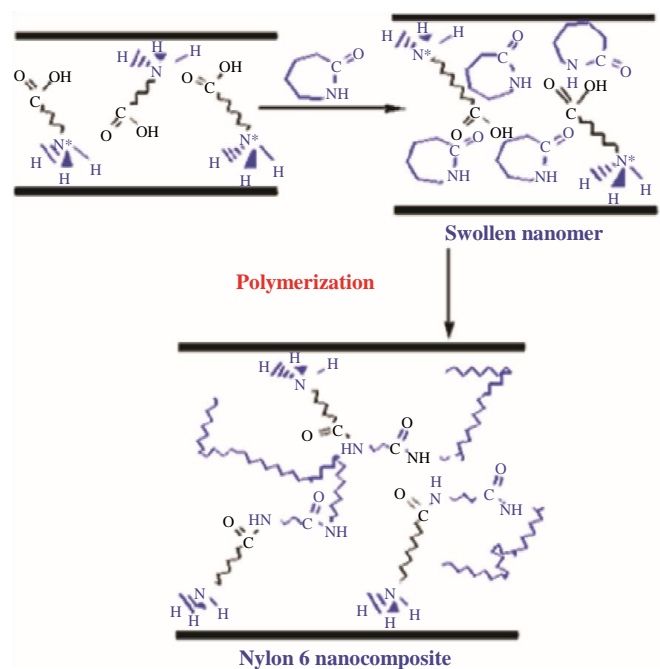


Figure 1. Nylon-6 nanocomposite formed through in situ polymerization with ADA–MMT [15] with permission.

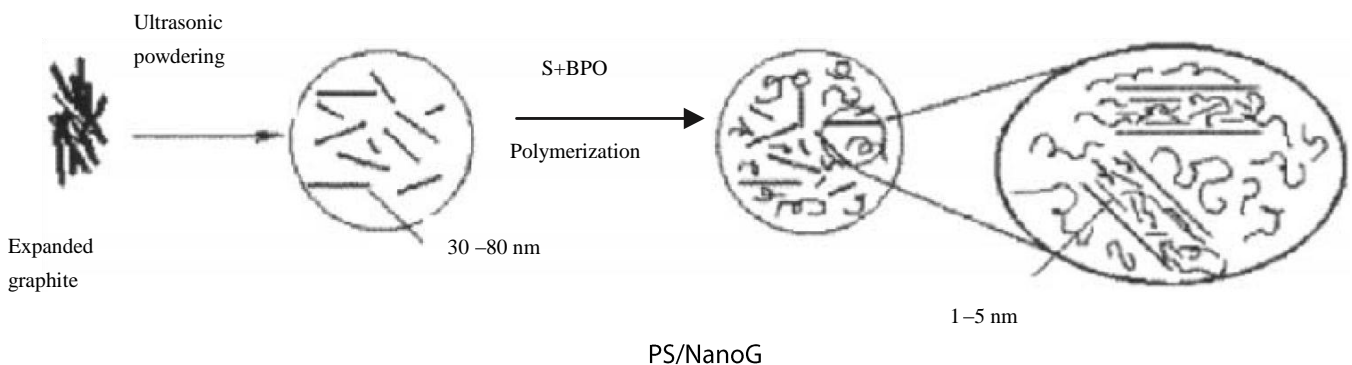


Figure 2. Schematic illustration of the process for the formation of nanocomposites of polystyrene-nano graphite (Reproduced from [29]. 2005 Elsevier)

Expanded Graphite-reinforced Composites

An expanded graphite (EG) preparation method has been reported in different literatures [23,24]. Concentrated sulfuric acid and concentrated nitric acid (industrial grade) were used as chemical oxidizers to prepare the EG [25]. Chung [26] mentioned intercalation of NFG using an intercalating agent. For an intercalated compound (GIC), the stacking could be of the form $-C-C-I-C-C-I-C-C-I-C-C-$, where C is a carbon layer and I an intercalated layer. Pan et al. [27] used intercalation polymerization to prepare nylon-6-EG nanocomposites. Shen et al. [28] developed a process to prepare EG by solution intercalation. Chen et al. [28] sonicated the expanded graphite to make graphite nanosheets (thickness of 30–80nm) and dispersed in a polystyrene matrix via in situ polymerization. They achieved excellent conducting property through this method (Figure 2).

Exfoliation

Exfoliation of nanoclay-reinforced composites:

Exfoliated nanocomposites have higher phase homogeneity than the intercalated counterpart. Hence the exfoliated structure is more desirable in enhancing the properties of nanocomposites [29]. Some factors (i.e., length and number of modifier chain, structure of clay, curing agent, curing conditions: temperature and time, viscosity, functionality of resin matrix, etc.) need to be considered to process the exfoliated thermoset polymer-nanoclay nanocomposites.

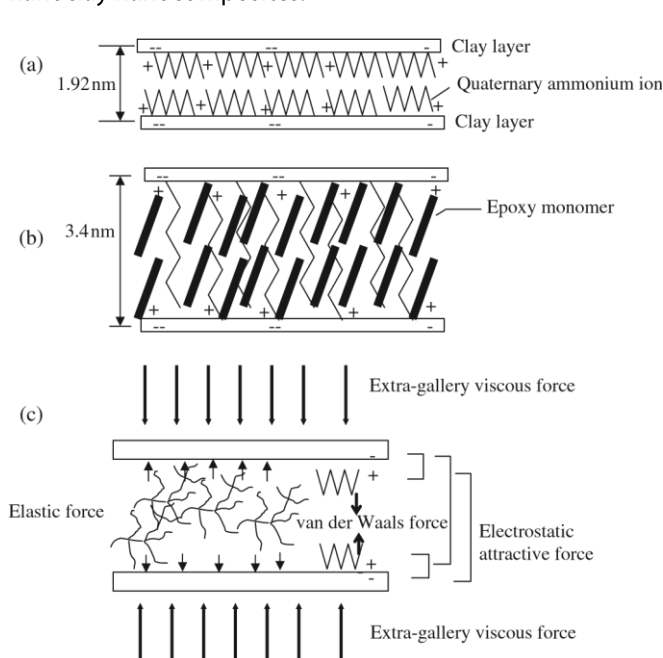


Figure 3. Schematic illustrations of the forces acting on a pair of clay layers for intercalation and exfoliation (Reproduced from [34]; 2005 American Chemical Society)

Typically, these factors should be considered before polymer network formation and matrix gelation, in order to achieve a high degree of exfoliation [30,31,32]. Therefore, it is a technical challenge to achieve full exfoliation of clay, due to the large lateral dimensions of the layers (1mm or larger), high intrinsic viscosity of the

resin, and strong tendency of clay platelets to agglomerate [33]. Park and Jana [34] hypothesized that the elastic force developed in the clay galleries during epoxy curing is responsible for exfoliation. They explained that (Figure 3) the sum of the viscous force and attractive forces arising due to electrostatic attraction and van der Waals force work against exfoliation, while elastic force due to conformational entropy work for clay layer separation. If the elastic force overcomes the attractive forces and viscous force, exfoliation of clay occurs [34]. In an uncured system, exfoliation is not expected, because the magnitude of the entropic force is small for separating the clay layers[34]. As shown schematically in Figure 8[35], the inner layers have a higher ionic bonding energy than the surface layers [35]; hence, the separation of the clay layers from the tactoid structures begins with the outermost clay layers. Full exfoliation results if all layers are separated from all tactoids [34]. Jiankun et al. [36] have found a few factors that promote the exfoliating ability, such as catalytic effect during cross-linking, penetrating ability of curing agent to clay, long alkyl-chain of the organocation, etc. Besides these they presented a thermodynamic analysis of exfoliation[31,37,38], which is determined by the change of free energy(rG) of the system during the curing process. They suggested that, when $rG \frac{1}{4} rH Tr S < 0$, the exfoliation can occur [32]; where rH is the change of enthalpy and rS is the change of entropy.

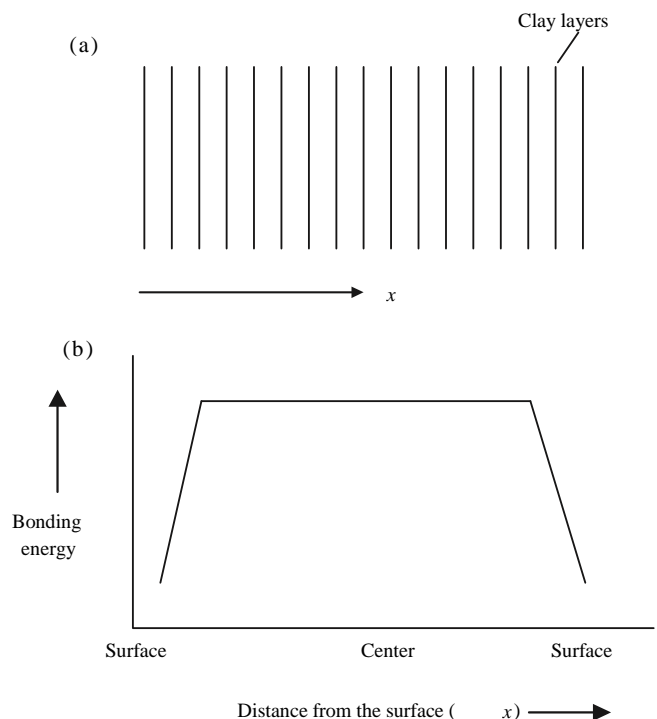


Figure 4. Schematic diagram showing the relationship between the ionic bonding energy and the location of the layers in the tactoid. (a) Tactoid and (b) Variation of bonding energy along the thickness of the tactoid [35] (2005 American Chemical Society)

Tolle and Anderson [39] investigated the sensitivity of exfoliation for processing. They found that both at lower temperatures for isothermal cure and at higher heating rate for nonisothermal cure cause an inhibition of exfoliated morphology. Messerith and Giannelis [14] prepared exfoliated layered silicate epoxy nanocomposites from diglycidyl ether of bisphenol A (DGEBA) and anadic methylan hydride-curing agent and found that the dynamic storage modulus improved. Kormannetal.[30] investigated the effect of three different curing agents upon the organoclay exfoliation in the DGEBA-based system. In their work, exfoliation of organoclay occurred in cycloaliphatic diamine-cured DGEBA nanocomposites only at higher temperatures. The speed of diffusion of curin gagents and increased curing temperatures also influenced the degree of exfoliation [30,29,39,40]. Lan et al. [13–41] reported that the balancing of intra and extra gallery polymerization rates is a primary concern to obtain exfoliated thermoset/layered silicate nanocomposites. Pinnavaiaetal.[42] achieved exfoliated morphologies in epoxy resins by gradual diffusion of monomeric epoxy in to the gallery. They suggest that faster intragallery polymerization produced exfoliated structures by pushing out the individual clay layers from the tactoids [34,42]. Wang et al. [43] mentioned that the relative curing speed between the interlayer and extra layer is the most important factor for clay exfoliation. Messerith and Giannelis [14] used anhydride species curing agents to prepare exfoliated nanocomposites, whereas the use of amine curing agents allowed them to prepare only intercalated composites. Lan et al. [13–41] used amine-curing agents and they achieved exfoliation only at an appropriate temperature, when the curing speed of the interlayer and extra layer is almost the same. Exfoliated nanocomposites have been prepared by preaging of an intercalated epoxy/layered silicate prepolymer mixture before curing and it showed enhancement of toughness[44]. Vaiaetal.[20] mentioned that, the degree of exfoliation can be improved by the use of conventional shear devices such as extruders, mixers, sonicators etc. Park and Jana [34] observed that hydroxylated quaternary ammonium ions and quaternary ammonium ions with nonpolar functional groups produced exfoliated structures. High levels of exfoliation and dispersion of the silicate clay layers in the epoxy matrix gave improved dynamic modulus using a three-roll mill as a means of applying external shearing forces [45]. Improved impact, flexural, and tensile properties have been achieved from exfoliated epoxy nanocomposites by using ball milling [46]. A combination of both usinghighershearforcesandimprovedcuretemperatureduringthecuringprocessorthe use of swelling agents [47], are the effective issues for exfoliation.

For the fabrication of thermoplastic polymer nanocomposites, Dennis etal. [19] found that increasing the mean residence time in the extruder generally promotes exfoliation, but excessive shear intensity or back mixing causes poor delamination and dispersion. Ahnet al.[48] prepared the exfoliated polypropylene–clay nanocomposites underanelectric field (with a function of

generator and high voltage amplifier). Silicate layer exfoliation in polyolefins such as PP and polyethylene is achieved by the introduction of small amounts of polar groups to nonpolar polyolefins [12,49–50]. The degree of delamination and dispersion of the layered silicates have been achieved in polyamide 6 by melt compounding [19] using an extruder.

Complete exfoliation (single platelet dispersion) is a very difficult issue, but all researchers easily say 'exfoliation' and 'exfoliated structure of the dispersed clays'. At this point, the meaning of full exfoliation has to be taken into consideration. For example, exfoliation due to 'parallel stacking or layer registry of the nanoclay is disrupted'. Nano clay has a terminal hydroxylated edge group. Therefore, the edge–edge interaction of the silicates takes place and then the flocculated structure is developed at high clay content loading (2 wt% corresponding to about 0.75 vol.%). To achieve the finer dispersion (near to exfoliation), the volume fraction of clay must be less than 1/(aspect ratio). Most of the nanocomposite researchers believe that the preparation of a completely exfoliated structure is the ultimate goal for better properties. However, these significant improvements are not observed in every nanocomposite system, including systems where the silicate layers are nearly exfoliated [51].

Exfoliation of graphite-reinforced composites:

Exfoliated graphite consists of a large number of delaminated graphite sheets [52,53]. Du et al. [54] prepared expandable polyaniline/graphite nanocomposites by chemical and physical treatments, especially by microwave irradiation. Instead of the usual $\text{HNO}_3\text{--H}_2\text{SO}_4$ route [54], they prepared the nanocomposites through the $\text{H}_2\text{O}_2\text{--H}_2\text{SO}_4$ route to avoid the evolution of poisonous NO_x . 1–2 wt% of EG were fabricated using epoxy resin (DGEBA) by sonication, shear, and a combination of sonication and shear mixing methods [45]. Shioyama [54] reported improved exfoliation at weight fractions of graphite below 1 wt% through polymerization with vaporized monomers such as styrene and isoprene. Fukushima and Drazal[53] used O_2 plasma treated graphite nanoplate let in an acrylamide/benzenesolution. After applying heat treatment (80C for 5h) they produced grafted graphite; which was used as reinforcement in an epoxy matrix with a high aspect ratio and better thermal and mechanical properties. For better exfoliation Cho et al. [56] pulverized EG nanoplatelets after heat treatment (900C) using ultrasonication, ball-milling, and vibratory ball-milling techniques to fabricate the phenylethynyl-terminated polyimide (PETI)-5/E Gcomposites. Li et al. proposed [57] UV/ozone treatment on expanded graphite at room temperature and atmospheric pressure. After ultrasonication they achieved uniform dispersion and interfacial adhesion of EG with the epoxy matrix. Improved mechanical and electrical properties were achieved using this technique.

In the case of graphite, the term 'complete exfoliation' has no exact meaning. It does not mean a single layer

sheet as in the case of polymer–clay nanocomposites; it may mean a separated graphite flake which is completely delaminated layer by layer. The EG is somewhat partially exfoliated graphite, because the graphite sheets are interlinked with each other [58]. But in polymer–EG nanocomposites, it is impossible to completely delaminate the carbon layer, because EG is fragile and breaks down during processing of the mixture of EG and polymer [29]. Each graphite layer is theoretically separated by a 3.354\AA space. Chen et al. [29] conducted research on graphite nanosheets of 50 nm thickness. They [59] tried to get one-layer carbon film, which is not related to the field of polymer nanocomposite. Thostenson et al. [60] gave a summary of the properties between exfoliated graphite platelets and exfoliated clay platelets from different literatures [1,58,61].

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