

Nanocomposites: Recent Development and Potential Automotive Applications

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ABSTRACT

Nanocomposites are relatively new material made with various polymers and nano-size inorganic or organic fillers. Nanocomposites have a number of advantages over conventional polymer composites, such as excellent mechanical properties, better durability, high smoothness, thermal stability and higher heat distortion temperature. The aim of this review focused on polymer-clay nanocomposites, carbon-nanotube/polymer composites, rubber nanocomposites and bionano-composites, including their manufacturing, processing, and characterization. The review also discussed the advantages, disadvantages of the nanocomposites and their current or potential applications in automotive industry.

INTRODUCTION

Over past decades, polymers have been successfully reinforced by inorganic fillers such as glass fibres, carbon fibres, talc, calcium carbonate, carbon black and some other organic fillers, like polystyrene, cellulosic fibres. The content of the filler is normally between 20 to 40% of a thermal plastic composite, and could be higher up to 60% in thermosetting composites. However, the mix of polymer matrix and fillers could not reach homogeneous on microscopic level and compromise the potential of the composites.

The first patent on nanocomposites was granted in 1950 (by National Lead Company (US 2,531,396) ¹, followed by the second patent issued in 1976 which was a Japanese Patent 109,998 assigned to Unitka. ² In 1980, the concept of molecular composites was proposed by Takayanagi et al.. ³ The idea is that if the filler is in molecular size, then the mechanical properties of the composite could be further improved. An example of such types is the nylon matrix containing 5 wt-% aramide fibers with the diameter of 30 nm.

Nanocomposites are defined as materials in which the polymer matrix (or continues phase) are incorporated with nanoparticulates (often referred to as *filler*) as

dispersed phase. The particles with small size in the range from a few to several tens of nanometers are called quasisize-zero-dimensional mesoscopic system, quantum dots, quantized or Qparticles, etc. ⁴ The nano-sized inclusions are defined as those that have at least one dimension in the range 1 to 100 nm (Figure 1). ⁵ Commonly used nanofillers are metal chalcogenides, carbon oxides, metal phosphates, clays and layered double hydroxides.

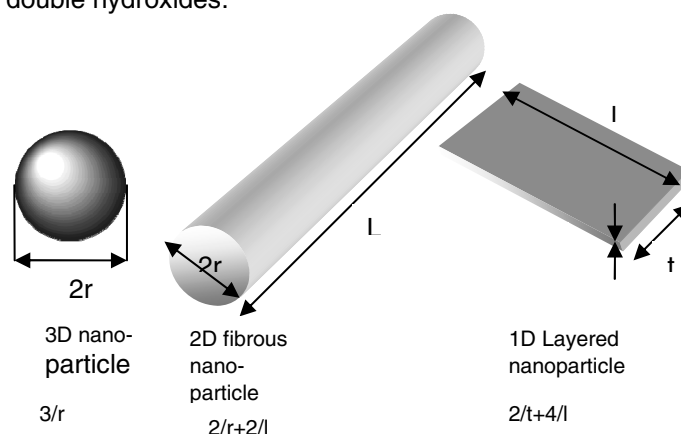


Figure 1. Nanoparticle geometries and their respective surface area to volume ratio

Nanocomposites have a number of advantages over conventional polymer composites, such as excellent mechanical properties, better durability, high smoothness, thermal stability and higher heat distortion temperature, improved resistance to gases, water, chemicals and hydrocarbons, better flame retardancy. ^{6,7,8} In addition, nanocomposites offer different surface appearance, electrical conductivity and optical clarity in comparison to conventional counterparts. The aspect ratio of nano-particles could be so high that the pinch of nano-particles can give a dramatic improvement to the composites with fewer drawbacks, such as brittleness, high density and loss of clarity, than those with the conventional reinforcements. Figure 2 illustrates the different size of the glass fiber and montmorillonite in nylon 6 composites. ^{3,9} Based on these unique properties, several applications such as in the automotive industry

particularly for the automotive outer body clear coat, and the bulk nano-structured materials, specifically polymer clay nanocomposites for noncritical automotive body parts, have been developed in the past decade.³

Supplier & Tradename	Matrix Resin	Nano-Filler	Target Market
Creanova (Vestamid)	Nylon 12	Nano-tubes	Electrically conductive
GE Plastics (Noryl GTX)	PPO/Nylon	Nano-tube	Automotive painted parts
Unitika	Nylon 6	Organo-clay	Multi-purpose
Hyperion	PETG, PBT PPS, PC, PP	Nano-tube	Electrically conductive
Nanocor (Imperm)	Nylon 6 PP Nylon MDX6	Organo-clay Organo-clay Organo-clay	Multi-purpose Molding PET beer bottles
Polymeric Supply	Unsaturated polyester	Organo-clay	Marine, transportation
RTP	Nylon 6, PP	Organo-clay	Multi-purpose, electrically conductive
Showa Denko (Systemer)	Nylon 6 Acetal	Clay, mica Clay, mica	Flame retardance Multi-purpose
Ube (Ecobesta)	Nylon 6, 12 Nylon 6, 66	Organo-clay Organo-clay	Multi-purpose Auto fuel systems

Source: Bins & Associates, Sheyboygan, Wis.

Table 1. Partial Listing of Nanocomposites Suppliers.¹⁰

As listed in Table 1, nanocomposites have been based on a variety of resin matrices, including PP, TPO, EVA, acetal, polycarbonate, biodegradable polylactic acid (PLA).

The focus of this review is to highlight the recent development in polymeric nanocomposites field and potential automotive applications.

POLYMERIC NANOCOMPOSITES

POLYMER-CLAY NANOCOMPOSITES

Smectite clay minerals, especially montmorillonite (MMT), are commonly used as platelet-type filler (1-D nanoparticles) for molecular composites, since they are composed of several layers of silicates. These silicates are 1nm thick and have cross-sectional area of 100 nm²

or higher, which is very small compared to conventional fillers. MMT is the most common and ubiquitous clay mineral, and it is well known that it undergoes intercalation and swelling in the presence of water and organic cations.

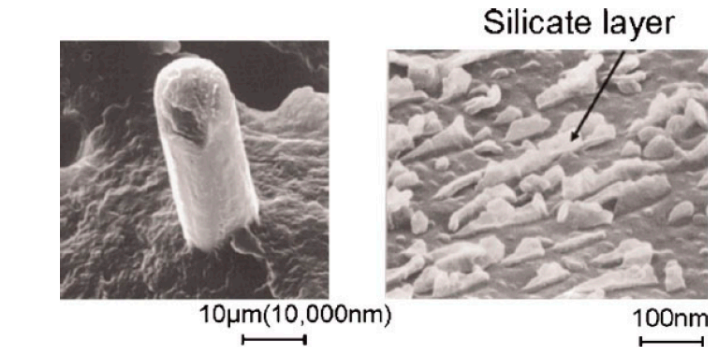


Figure 2. Comparison of size of glass fiber and montmorillonite in nylon 6 composites.^{3,9}

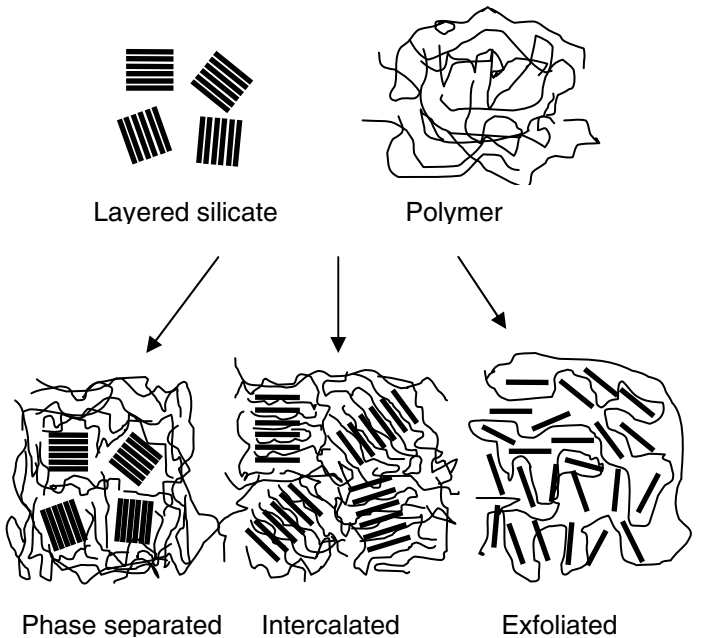


Figure 3. Dispersion schematic of organo-montmorillonite reinforced polymer nanocomposites.¹¹

If the polymer cannot intercalate between the silicate sheets, a conventional polymer composite is obtained. Intercalated structure is achieved when a single or more than one extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternating polymeric and silicate layers. The repetitive multilayer structure is well preserved. If the silicate layers are randomly and homogenously dispersed into the polymer matrix, an exfoliated morphology is obtained (see Figure 3).¹¹

Various techniques have been used in polymer nanocomposites characterization, including WAXD (wide angle X-ray Diffraction), SAXS (Small angle X-ray

scattering), SEM, TEM, and AFM. WAXD is most commonly used to identify the intercalated structure and nanocomposites structure. A complete exfoliation can be characterized by the absence of intensity peaks in the range of 2θ from 1.5° to 4° in the WAXD patterns, which corresponds to a d-spacing of at least 6 nm or demonstrates the expanded structure of the clay layers. TEM is also extensively used to observe the internal structure, spatial distribution; and often provides the information complementary to WAXD data.

To date, several synthetic polymers have been utilized to prepare nanocomposites. Below are some typical ones:

Nylon 6-clay nanocomposites

In order to well-disperse clay layers into polymer (e.g., nylon) matrix, it is very important to ensure the compatibility between polymer and clay. Since most polyolefins and polyamide (nylon) are hydrophobic in nature, it is an often practice to render clay organophilic or hydrophobic via a pretreatment. Organo-clay can be formed from normally hydrophilic clay by the treatment of amino acids, organic ammonium salts, or tetra organic phosphonium solution.^{3,12-14}

The typical methods for preparing nylon 6 clay nanocomposites are as follows:

- In situ polymerization;
- Solution induced intercalation;
- Melt processing;

By in situ polymerization method, an organic compound (e.g., Amino acid (AA) hydrogen chloride with 2 to 18 numbers of carbon) was used to conduct ion-exchange of the clay in an attempt to promote the intercalation of monomer into the silicate layers, as illustrated in Figure 4.¹⁵ With the aid of initiator and/or the catalyst, polymerization of the monomer is propagated, thus allowing clay layers to be dispersed into polymer matrix. Normally, polymerization methods are limited to the manufacturers producing nylon/clay nanocomposites in a large quantity.

By solution induced intercalation method, polymer is prepared in an organic solvent, then the clay is dispersed in the obtained polymer solution and subsequently either the solvent is evaporated or the polymer precipitated. However, this method tends to create poor clay dispersion and other problems, such as the high costs and a large amount of solvents required to achieve appreciable filler dispersion, phase separation problem and environmental and safety concerns. Solvent route technique is promising in the case of water-soluble polymers for obvious reasons.

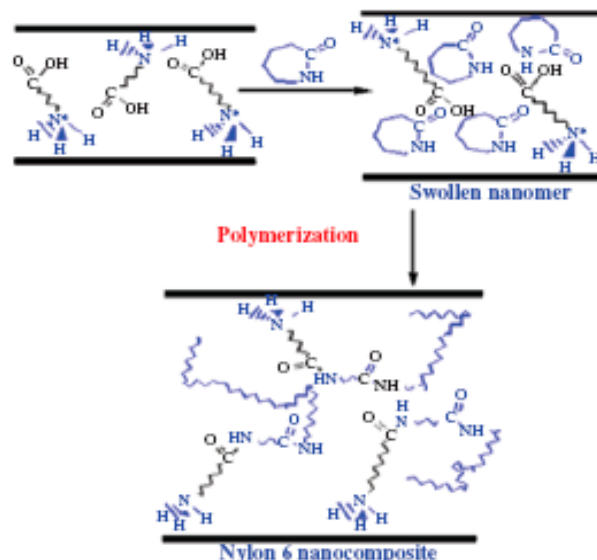


Figure 4. Nylon-6 nanocomposite formed through in situ polymerization with ADA–MMT (amino-dodecanoic acid treated montmorillonite).¹⁵

In the third technique, polymer or nylon 6 is mechanically mixed by conventional methods such as extrusion and injection moulding of clay/polymer blends at an elevated temperature.¹⁶ The silicates layers are directly dispersed into the polymers during the melt. In order to use this method, the silicates surface has to be pre-treated through the organo-modification. In 1991, Maxfield et al. obtained a composite by blending organo clay and nylon 6 with shear stress over 10 s^{-1} .¹⁷ The processes are schematically presented in Figure 5.³

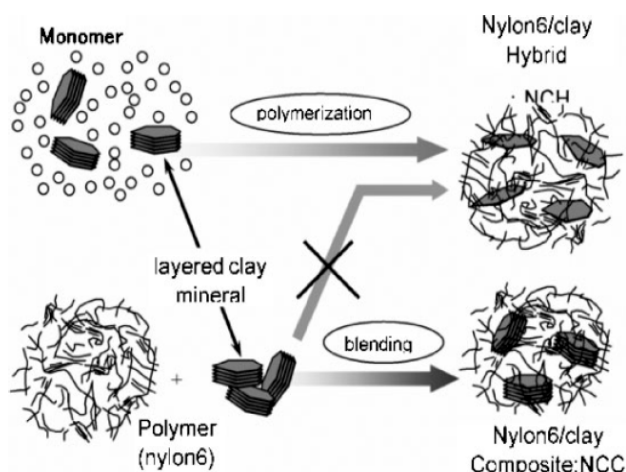


Figure 5. Conceptual picture of preparation of NCH.³

Table 2 shows the mechanical properties of NCH (nylon clay hybrid) against those of nylon 6 (1013B). NCH is superior to nylon 6 in terms of its strength and elasticity modulus. However, its impact strength is below that of nylon 6.