Review article: Applications of Nano-composites in Industrial Systems

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ABSTRACT
A nano-composite is a multiphase solid material in which one of the phases has one, two, or three dimensions smaller than 100 nanometres, or structures having nano-scale repeat distances between the different phases that make up the material. Nano inorganic or organic powders or films with special physical properties are combined with polymers to form polymer nano-composites whose physical properties and mechanical performance significantly differ from those of the component materials. A primary purpose of producing polymer nano-composites is to impart the composites with multifunctional properties. There has been rapid development of multifunctional polymer nano-composites and a number of achievements have been reported. Due to their novel properties, multifunctional polymer nano-composites can be used in a broad range of applications from outer space to automobiles, and to address challenges in organic solar cells, and biological technologies.

Keywords: Nano-composite, nanometres, Nano-scale
1. Introduction

We are in the midst of a revolution that is transforming society, but because it is occurring at the atomic level, the average person might not even be aware of it. Through nanotechnology, mankind now has the ability to manipulate atoms to create materials and products that are changing the way we live our lives (Ash et al., 2004). Modern technology continuously needs new materials with special combinations of properties. Many efforts have been made in the last few decades using novel nanotechnology and nano-science knowledge in order to obtain nano-materials with determined functionality (Breuer and Sundarraraj, 2004). Micro and Nano systems have become an integral part of modern human living. They help people to improve safety, health and the quality of life (Gusev, 2001). Nano-composites are attractive to researchers both from the practical and theoretical points of view because of the combination of special properties (Biswas and Ray, 2001). A nano-composite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometres (nm), or structures having Nano-scale repeat distances between the different phases that make up the material (Jordan et. al., 2005). In general, the unique combination of the characteristics of nano-materials, such as size, mechanical properties, and low concentrations necessary to effect change in a polymer matrix, coupled with the advanced characterization and simulation techniques now available, have generated much interest in the field of nano-composites. In addition, many polymer nano-composites can be fabricated and processed in ways similar to that of conventional polymer composites, making them particularly attractive from a manufacturing point of view (Van Es, 2001).

2. Overview

The Nano era similar to the mid-industrial steel era, not only stands for great technical innovation but also indicates the future trends of existing technologies. It is believed that this period will dominate and transform the daily lives of people. The “Nano” is a unit of length defined as 10 to the power 9 of a metre. To give an idea of how small that is, the width of a human hair is 106 nm, and the size of an atom is 0.1 nm. Recently, the development of microscopes has enabled scientists to observe the structures of materials at the nano-scale and investigate their novel properties. In the early 1980s, IBM (Zurich) invented the scanning tunnelling microscope, which was the first instrument that could “see” atoms. In order to expand the types of materials that could be studied, scientists invented the atomic force microscope. Now, these instruments can be used to observe structures and the different properties of materials at the nanometre scale. Physics reveals big differences at the nanometre level compared to the normal scale world, and the properties observed on a microscopic scale are novel and important. For example, Quantum mechanical and thermodynamic properties have pushed forward the development of science and technology in the 20th century. Nanotechnology means the study and application of materials with structures between 1 and 100 nm in size, which, unlike bulk materials, it is possible to work with individual atoms and molecules and learn about the properties of an individual molecules. Also, atoms and molecules can be arranged together in well-defined ways to produce new materials with amazing characteristics. For example, nanotechnology has produced huge increases in
computer speed and storage capacity. That is why “Nano” has attracted much attention in the research fields of physics, chemistry, biology, and even engineering (Jordan et al., 2005). This word has entered the popular culture and can be found in television, films, and commercial advertisements. Politicians and leaders around the world have realized the importance and urgency of developing nano-science and nanotechnology, so countries have promoted research in these areas in their universities and laboratories. With the huge increase in funding, scientists are pursuing Nano research intensively and the rate of discovery is increasing dramatically (Gusev, 2001).

2.1 Classification of Nano-materials and Nanostructures

The main classification of nano-materials can be described as the following: carbon-based materials, nano-composites, metals and alloys, nano-polymers, and nano-ceramics. Carbon-based materials refer to carbon black, fullerenes, single-walled or multiwalled carbon nano-tubes (CNT), and other carbides. Carbon nano-tubes (shown in Figure 1), discovered in 1991 by S. Iijima, are hollow cylinders made of sheets of graphite (Ash et al., 2004). The dimensions are variable, and one nano-tube can also exist within another nanotube, which leads to the formation of multiwalled carbon nano-tubes. Carbon nano-tubes have amazing mechanical properties due to the strength of the sp2 carbon-carbon bonds. The Young’s modulus and the rate of change of stress with applied strain represent the stiffness of a material. The Young’s modulus of the best nano-tubes can reach 1000 GPa, which is approximately five times higher than the Gpa of steel. The tensile strength can be as high as 63 Gpa, and this value is around 50 times higher than steel. Depending on the graphite arrangement around the tube, carbon nano-tubes exhibit varying electrical properties and can be insulating, semiconducting, or conducting. Also, carbon nano-tubes are an interesting media for electrical energy storage due to their large surface area, and they are still being investigated as a hydrogen storage medium (Mishra et al., 2005). Organic-inorganic nano-composites are a fast-growing area of current material research. Significant effort is directed at developing synthetic approaches and controlling their nano-scale structures. The properties of nano-composite materials are determined not only by the properties of their individual components but also depend on their morphology and interfacial characteristics. The rapid growth of research into nano-composites has already generated many exciting new materials showing novel properties. It is also possible to discover new properties that are still unknown in the parent constituent materials. Metal and alloy nano-materials generally include gold, silver, magnetic iron-based alloys, and magnesium-based alloys. Gold and silver nano-particles can be easily prepared, and they are promising probes for biomedical applications. Unlike other fluorescent probes such as organic dyes, gold and silver nano-particles do not burn out after long exposure to light. Gold nano-particles have already been used as ultrasensitive fluorescent probes to detect cancer biomarkers in human blood. Iron, cobalt, and their alloys are classes of magnetic nano-particles whose magnetic performance can be modified by controlling the method of synthesis and the chemical structure of the materials. In most cases, the magnetic particles ranging from 1 to 100 nm in size may display super paramagnetism.
Fig. 1. Electron micrographs of microtubules of graphitic carbon (Parallel dark lines correspond to the (002) lattice images of graphite). A cross section of each tubule is illustrated, (a) Tube consisting of five graphitic sheets, diameter 6.7 nm. (b) Two-sheet tube, diameter 5.5 nm. (c) Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm) (Mishra et al., 2005).

Polymers are large molecules (macromolecules) composed of repeating structural units typically connected by covalent chemical bonds. They are widely used in our lives and play an important role in industry. The Nobel Prize in Chemistry in 2000 was awarded for the discovery and development of conductive polymers. In the future, one can use such new exciting materials based on conductive polymer technology. In nanostructured polymers, the attractive force between polymer chains plays an important role in determining their properties. When inorganic or organic nano-materials are dispersed in the polymers, the nanostructures of polymers can be modified and the desired properties can be obtained. The nano-ceramics considered in this study are oxide and non-oxide ceramic materials. Since nanocrystalline materials contain a very large fraction of atoms at the grain boundaries, they can exhibit novel properties. One important class of nano-ceramics is semiconducting materials such as ZnO, ZnS, and CdS; they are synthesized by different methods, and the scientist can control their size and shape easily. They show quantum confinement behaviour in the 1-20 nm size range. For such materials, the focus is on the production and application of ultrathin layers, fabrication, and molecular architecture (Shelley et al., 2001). A nanostructure is defined as an object of intermediate size between molecular and microscopic (micrometre-sized) structures. Based on the different shapes, generally they can be classified into nano-particles, nano-fibres, nano-flakes, nano-rods, nano-films, and nano-cluster types and typical photographs are shown in Figure (2). Materials with different nanostructures can obviously have different properties, so one of the tasks scientists face is to find the relationship between the properties and the structure. It is known that the structure of materials will determine their properties, and the properties of materials can reveal their structure. Thus, it is necessary to focus on exploring size-controllable and shape-controllable nano-materials (Shelley et al., 2001).
2.2 Nano-materials from Academia to Industry

The general meaning of synthesis and assembly of nano-materials is to create engineering materials with novel properties through the preparation of material at the nano-scale level. In fact, nano-materials have already existed before the advanced microscope was invented. The problem is that scientists cannot observe their nanometre structures directly at the moment. Research in nano-materials and their novel properties is motivated by understanding how to control the building blocks and enhance the properties at the microscale. For example, scientists can increase the magnetic storage ability, catalytic enhancement, electronic or optical performance, hardness, and ductility by controlling the size and method of assembly of the building blocks. The most frequent techniques used in the laboratory to synthesize nano-materials include chemical vapour deposition, physical vapour deposition, the sol-gel technique, and precipitation from vapour and supersaturated liquids. These techniques have been applied in industry for the preparation of nano-products ranging from electronics to drug delivery systems. There are several reviews of the synthesis and assembly of nano-materials (Mishra et al., 2005; Tidjani, 2005). In the global market for nano-materials, conventional materials such as SiO2, TiO2, Fe2O3, and ZnO are the main products that make the greatest initial commercial impact. The reason is that these nano-ceramics can be easily synthesized and the cost of production is lower. In future, the possibility of incorporating “smart” features in nano-materials should be explored. Smart materials can also be termed as intelligent materials. Such materials have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, light, magnetic fields, or electric fields. Smart materials including piezoelectrics, electrostrictions, magnetostrictors and shape memory alloys, all perform sensing and actuating functions. It is believed that smart materials containing nanostructures will dominate our lives (Schmidt, 2001).
3. Nano-composites

Composite materials (or composites for short) are combined from two or more constituent materials that have significantly different physical or chemical properties. The constituent materials will remain separate and distinct at the microscopic level within the finished structure. Generally, two categories of constituent materials, matrix and reinforcement, exist in the composite. The matrix materials maintain the relative positions of the reinforcement materials by surrounding and supporting them, and conversely the reinforcements impart their special mechanical or physical properties to enhance the matrix properties. Thus, the composite will have the properties of both the matrix and the reinforcement, but the properties of a composite are distinct from those of the constituent materials. As an analogy, thousands of years ago, people used straw to reinforce mud in brick making to increase the strength of the brick. According to the type of matrix, nano-composites can be classified into ceramic matrix nano-composites, metal matrix nano-composites, and polymer matrix nano-composites. In ceramic matrix nano-composites, the main volume is occupied by ceramics including oxides, nitrides, borides, and silicides. In most cases, a metal as the second component is combined into the ceramic matrix nano-composites. Ideally, Ku et al., (2004) stated that the metal and the ceramic matrix are finely dispersed in each other to form a nano-composite that has improved nano-scopic properties, including optical, electrical, and magnetic properties. In metal matrix nano-composites, ceramics are often used as reinforcement and matrices are based on most engineering metals, including aluminium, magnesium, zinc, copper, titanium, nickel, cobalt, and iron. Depending on the properties of the matrix metal or alloy and of the reinforcing phase, the metal matrix nano-composites can have the features of low density, increased specific strength and stiffness, increased high-temperature performance limits, and improved wear-abrasion resistance. Compared with polymer matrix composites, metal matrix composites can offer a higher modulus of elasticity, ductility, and resistance to elevated temperatures. However, they are more difficult to process and are more expensive. Polymer composites are generally made of fibre and matrix. Usually glass, but sometimes Kevlar, carbon fibre, or polyethylene is used as the fibre. The matrix usually refers to a thermoset such as an epoxy resin, polydicyclopentadiene, or a polyimide. The fibre is embedded in the matrix so as to increase the strength of the matrix. Such fibre-reinforced composites are strong and light, and they can be even stronger than steel, but weigh much less. This means that composites can be widely used in industry for their high strength-to-weight ratio. For example, a reinforced polymer composite is used in the automotive industry to make automobiles lighter (Simonsen and Palaniyandi, 2004).

3.1 Polymer Nano-Composites

Polymer-based materials are by far the most widely commercialized class of Nano-composites and global revenues were approximately US$223 million in 2009. The incorporation of nano-materials can improve the properties of a polymer such as its tensile strength, Young’s modulus, impact and scratch resistance, electrical and thermal conductivity, thermal stability and fire resistance. Presently, minerals and CNTs are the most frequently used
nano-materials and one of the first commercial applications was by Toyota who used a nano-clay/nylon-6 polymer nano-composite in an engine component. In the late 1980s, Toyota Central Research Labs collaborated with Ube Industries, a Japanese resin supplier, to produce a new composite polymer consisting of nylon-6 interspersed with layers of montmorillonite, naturally occurring silicate clay. The clay greatly improved the mechanical and thermal properties of the nylon and Toyota subsequently used the material for a timing belt cover, capitalising on its enhanced heat resistance and dimensional stability. Since then, several vehicle manufacturers have employed clay/polymer nano-composites in components such as rocker-box covers, body panels and bumpers; the latter being 60 per cent lighter and far more resistant to denting and scratching than conventional parts. The cargo bed in GM’s 2005 model Hummer used about 3 kg of moulded nano-clay / polypropylene nano-composite parts for its trim, Centre bridge sail panel and box rail protector. Polymer barrier technology is also benefiting from nano-composites. Nylon-nano-clay composites are being used in beverage bottles and for food packaging (Fischer, 2003). The addition of clays can reduce gas/vapour permeation very significantly, as the clay platelets form a “tortuous path” and so inhibit migration through the material, yielding significant improvements to the shelf life. An example of a commercial barrier nano-composite is Imperm, which consists of MXD6 nylon and nano-clay, dispersed by a proprietary process and produced by Nanocor. It offers superior barrier properties to MDX6 as shown in Table 1 and is used in multi-layer polyethylene terephthalate (PET) bottles.

Table 1 Barrier properties of imperm nano-composite compared to MDX6 nylon

<table>
<thead>
<tr>
<th>Property</th>
<th>MXD6</th>
<th>Imperm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water vapour transmission rate</td>
<td>1.36</td>
<td>0.58</td>
</tr>
<tr>
<td>(g mm/m² day)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ transmission rate</td>
<td>0.30</td>
<td>0.15</td>
</tr>
<tr>
<td>(cc mm/m² day atm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen transmission rate</td>
<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>(cc mm/m² day atm)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CNT-based nano-composites are finding growing uses in industries ranging from sports and leisure to electronics, automotive and defence. CNTs are particularly attractive due to their excellent physical properties which frequently exceed those of the best conventional materials as shown in Table 2 and are now being incorporated into a wide range of polymers (Chan et al., 2002).
Table 2 Physical properties of single-walled CNTs (SWCNTs) and comparison with conventional materials

<table>
<thead>
<tr>
<th>Property</th>
<th>SWCNT</th>
<th>Stainless steel</th>
<th>Kevlar</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus (TPa)</td>
<td>1-5</td>
<td>0.186-0.214</td>
<td>0.06-0.18</td>
<td>-</td>
</tr>
<tr>
<td>Tensile strength (GPa)</td>
<td>~13-53</td>
<td>0.38-1.55</td>
<td>3.6-3.8</td>
<td>-</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>16</td>
<td>15-50</td>
<td>~2</td>
<td>-</td>
</tr>
<tr>
<td>Specific strength (tensile strength/density) (KN mKg(^{-1}))</td>
<td>Up to 48,000</td>
<td>154</td>
<td>2,510</td>
<td>-</td>
</tr>
<tr>
<td>Thermal conductivity (W m(^{-1}).K(^{-1}))</td>
<td>3,500-6,000</td>
<td>-</td>
<td>-</td>
<td>385</td>
</tr>
<tr>
<td>Electrical conductivity (Sm(^{-1}))</td>
<td>&gt;107</td>
<td>-</td>
<td>-</td>
<td>5.69 x 10(^7)</td>
</tr>
<tr>
<td>Current carrying capacity (A cm(^{-2}))</td>
<td>4 times;109</td>
<td>-</td>
<td>-</td>
<td>106</td>
</tr>
</tbody>
</table>

Fig.3. Molecular Structural Schematic of a CNT
Figures 3, 4 and 5 show the molecular structure of a CNT, a scanning electron micrograph (SEM) of CNT bundles and the raw material, respectively. In many cases, the aim is to increase the electrical conductivity of the composite and examples of products which exploit this property are automotive fuel lines, fuel pumps, filter housings and the O-rings in fuel system connectors, where the CNTs are used as an alternative to carbon black. Less than 5 per cent of CNTs by weight imparts the same level of conductivity as 10-15 percent carbon black, yet the physical properties are improved. Another automotive application is electrostatic paint spraying. Plastic body panels need to be conductive so that the paint is applied evenly and again CNTs are starting to be used as an alternative to carbon black or costly primers. The advantage is that the low CNT loading required to achieve the necessary conductivity is such that the polymer retains half of its original elongation at break rather than the 3-4 per cent preserved when carbon black is used. This is vital to ensure that the panel retains its toughness at low temperatures and does not crack or shatter. Further, because the CNTs are so small and used at such low loadings, a class surface finish is achieved. The high electrical conductivity of CNT-based polymer nano-composites is also being exploited by the electronics industry, particularly to minimize the possibility of damage caused by electrostatic build-up or discharge.
These materials are finding growing uses in Joint Electron Device Engineering Council integrated circuit (IC) trays as seen in Figure (5), wafer carriers and IC test and burn sockets due to their high conductivities combined with superior physical properties. They are often replacing carbon black-filled polymers in these components. An example of a material used in this industry is the Plasticyl range of CNT/thermoplastic nano-composites produced by Nanocyl.

The aim of a 42-month, €3.75 million, and EU-funded research programme is to develop materials and components which exploit the thermal properties of polymer nano-composites. Dubbed “Thermonano” (low-temperature heat exchangers based on thermally conducting polymer nano-composites), this will investigate the role of polymers (nylon, PET, polyvinylidene fluoride, etc.), filled with nano-materials such as CNTs, carbon fibres, metal coated nano-particles and graphite nano-particles, for use as heat exchanger materials. Some anticipated applications include seawater-cooled intercoolers on large marine diesel engines and power plants where polymers would provide a cheaper alternative to copper alloys, heat recovery systems from combustion flue gases, operating below 300 °C where commercial metal-based systems lose cost-effectiveness and in the chemical and process industries where harsh or corrosive environments prevail. The aim is to reduce total system costs by around 20 percent. The project involves four research establishments and five companies from six European countries (Denault and Labrecque, 2004). Table 3 listed the improved physical properties of a CNT-epoxy nano-composite.

<table>
<thead>
<tr>
<th>Property</th>
<th>Improvement over neat epoxy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression strength</td>
<td>+39</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>+42</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>+16</td>
</tr>
<tr>
<td>Impact strength</td>
<td>+31</td>
</tr>
<tr>
<td>Vibration damping factor</td>
<td>+44</td>
</tr>
</tbody>
</table>

3.1.1 Polymer Nano-Composite Materials

These applications have been made possible by the recent and now ready availability of suitable nano-materials. Many mineral, chemical and specialist nanomaterial companies produce montmorillonite clays and CNTs are now being manufactured on an industrial scale. Several plants in Europe and the Far East now have annual capacities of several hundred tons.
In 2010 Bayer opened a plant in Leverkusen, Germany, with a capacity of 200 metric tons/year and in 2009 Californian CNT manufacturer Nano Technology brought a 500 ton/year facility online in China. Chinese production is growing very rapidly and the country is already a major CNT producer. Just a few years ago, CNTs were priced at over US$1,000/g but today prices start at few hundred dollars per kilogram and will certainly continue to fall as consumption and production levels increase. However, incorporating nano-materials, particularly CNTs, into resin or other matrices is no simple matter and issues such as phase separation, aggregation, poor dispersion and poor adhesion to the host material have to be overcome. Accordingly, there has been much research into the development of efficient surface treatment and functionalisation techniques. The two broad approaches are covalent functionalisation with amino (NH$_2$) or carboxyl (COOH$_2$) groups through reactions onto the p-conjugated skeleton of the CNTs and non-covalent adsorption or wrapping of various molecules on the side walls of CNTs. Some companies have developed proprietary chemistries. For example, Zyvex uses a novel technology based on rigid conjugated polymers, whereby the major interaction between the polymer backbone and the nanotube surface occurs through non-covalent p-p (“aromatic”) interactions.

Although these form a weaker bond than covalent interactions, their sum creates a large net stabilising energy that results in stable systems. Likewise, dispersing clay nano-particles into polymers requires specialised techniques, the most common being solution induced intercalation, in-situ polymerisation and melt processing using clays with appropriate surface treatments. Some manufacturers now produce chemically functionalized CNTs for incorporation into composites while others offer nano-composite polymer master batches typically containing 10-20 percent CNTs by weight. These are based on a variety of polymers including acrylonitrile butadiene styrene, polycarbonate, polystyrene, polybutylene terephthalate and polyamide. Similarly, master batches containing dispersed nano-clays are commercially available. Thus, an effective material supply chain now exists (Helbert et al., 1996).

3.2 Ceramic Nano-Composites

Ceramics stand, in principle at least, to benefit from the incorporation of nano-materials, most notably CNTs. While strong and hard, most ceramics have low fracture toughness and are therefore brittle. Despite the availability of ceramics toughened with carbon and silicon carbide (SiC) fibres (ceramic matrix composites), prevailing research aims to develop CNT-based ceramic nano-composites with improved properties.

Nano-tube reinforcements promise to increase the fracture toughness of the material by absorbing energy through their highly elastic behaviour during deformation. However, fabrication difficulties have limited the development of these materials and a major problem is obtaining a uniform dispersion of CNTs in the matrix. Damage or destruction of the nanotubes often occurs because of the high temperatures and highly reactive environments associated with many ceramic production methods. Nevertheless, some progress has been made and as with the early days of polymer nano-composite technology, a significant element of the research effort concerns manufacturing techniques. A group from the University of California,
Davis, has produced a ceramic (alumina) CNT nano-composite by combining SWCNTs with alumina nano-powders using a novel powder preparation and consolidation technique. The result is a composite with improved thermal, electrical and mechanical properties. It is highly thermally anisotropic with a thermal conductivity ratio of 3:1 in the aligned plane and the electrical conductivity is 13 orders of magnitude higher than that of pure alumina. Most significantly, the fracture toughness is three times that of alumina. More recently, a group from Tohoku University have developed an improved method for incorporating the CNTs into an alumina ceramic, based on treating multiwalled carbon nano-tubes (MWCNTs) with an acid. This process can diminish the phase segregation of the nano-tubes and render the composites highly homogeneous. The addition of 0.9 percent acid-treated MWCNTs by volume yields a material with a fracture toughness of 5.90 ± 0.27 MPam1/2, which exceeds that of pure alumina (3.5MPam1/2), and with an increased bending strength of 27 percent. A group from the Chinese Qingdao University of Science and Technology recently reported an MWCNT/zirconia ceramic nano-composite produced by a spark plasma sintering process which has a fracture toughness 18 percent higher than pure zirconia. With the aid of government funding, US nano-material specialist Nano Labs has developed a high toughness boron carbide (B4C) composite containing CNTs, produced by a hot pressing/sintering technique. This was designed for lightweight ballistic armour for military aircraft and a 4-5 percent CNT loading led to a fracture toughness of 5MPam1/2, compared to 3MPam1/2 for standard B4C. The material is now available from the company. However, none of these results have yielded materials with a fracture toughnesses approaching those of SiC fibre-reinforced composites (2.0MPam1/2) so it will clearly be some time before structural ceramic nano-composites become widely available (Silberglitt, 2004).

3.3 Metal Matrix Nano-Composites

Metal matrix composites such as aluminium and magnesium reinforced with continuous carbon, SiC or boron fibres are used in aerospace and other applications due to their low weight and excellent physical properties. There is much interest in producing similar composites that incorporate nano-particles and CNTs for structural applications, as these materials have the potential to yield greater improvements than micron-sized reinforcements. Metal matrix nano-composites have been studied for around a decade but work is still at a relatively early stage. The ultimate aim is to develop improved materials for uses in the defence, aerospace and automotive industries but as with their ceramic and polymer counterparts, processing techniques critically govern the properties of a metal matrix nano-composite. Accordingly, the processes seek to achieve homogeneous dispersion of the CNTs throughout the matrix, high interfacial bond strength between them and the matrix and maintain the structural stability of the nano-tubes. Some of the most widely studied processes include powder metallurgy (sintering, pressing, etc.), melting/solidification, thermal spraying, electrochemical deposition and a number of minor methods such as sputtering and vapour deposition. Some results of recent studies are shown in Table 4. It appears that the more novel fabrication techniques are most successful in improving the mechanical properties of the materials because of improved dispersion and interface bonding. Although the mechanical and thermal properties of a composite are related to the volume fraction of the reinforcement, there
is no direct correlation between the CNT content and the mechanical properties of materials described in the recent literature. This is due to the presence of defects induced by the various different processing techniques. Uniform dispersion of the CNTs has been the main challenge in producing CNT-reinforced composites, be they polymer, ceramic or metal. This is because CNTs have a very large surface area, which leads to the formation of clusters via van der Waals forces. Hence, a homogeneous distribution of the reinforcement is essential. Clustering leads to the concentration of reinforcement at certain points which can lead to a worsening of certain mechanical properties, as shown by research into the problem. As with ceramics, more development is required before metal nano-composites become a commercial reality (Biswa and Ray, 2001).

### Table 4 Results of recent metal matrix nano-composite developments

<table>
<thead>
<tr>
<th>Material</th>
<th>CNT content (%)</th>
<th>Manufacturing Technique</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-CNT</td>
<td>5</td>
<td>-</td>
<td>129 percent increase in tensile strength</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>Plasma spraying</td>
<td>~40 percent increase in elastic modulus</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>Nano-dispersion</td>
<td>350 percent increase in compressive yield strength</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>CVD plus sintering</td>
<td>184 percent increase in tensile strength</td>
</tr>
<tr>
<td>Cu-CNT</td>
<td>10</td>
<td>Spark plasma sintering</td>
<td>79 percent increase in hardness</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Cold rolling</td>
<td>8 percent increase in tensile strength and 128 percent increase in elastic modulus</td>
</tr>
<tr>
<td></td>
<td>9-12(Ni coted CNTs)</td>
<td>-</td>
<td>80-100 percent increase in hardness</td>
</tr>
<tr>
<td>Ni-CNT</td>
<td>2</td>
<td>Electrode less deposition</td>
<td>44 percent increase in hardness</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Electro deposition</td>
<td>320 percent increase in tensile strength for SWCNTs and 270 percent for MWCNTs</td>
</tr>
<tr>
<td>Mg-CNT</td>
<td>0.55(Ni coated CNTs)</td>
<td>Melting and casting</td>
<td>150 percent increase in tensile strength</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>casting</td>
<td>15 percent increase in yield strength</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>casting</td>
<td>36 percent increase in compressive strength</td>
</tr>
<tr>
<td>Ti-CNT</td>
<td></td>
<td>Powder metallurgy</td>
<td>450 percent increase in hardness and 65 percent increase in elastic modulus</td>
</tr>
<tr>
<td>Tin solder-CNT</td>
<td>0.04</td>
<td>Sintering and extrusion</td>
<td>31 percent increase in tensile strength</td>
</tr>
<tr>
<td>Ag-CNT</td>
<td>9</td>
<td>Compacted, sintered and repressed</td>
<td>27 percent increase in hardness</td>
</tr>
</tbody>
</table>
3.4 Applications in Electronic Components

The applications so far considered principally concern structural uses but nano-composites also offer promise to yield a range of new and improved electronic devices. Researchers at Georgia Tech have developed a new technique for creating films of barium titanate (BT) nano-particles in a polymer matrix that could allow the fabrication of improved capacitors. By using tailored organic phosphonic acids to encapsulate and modify the surface of the nano-particles, the group was able to overcome the particle dispersion problem to create uniform nano-composites. The particles, with diameters of 30-120 nm, were dispersed in Viton and polycarbonate matrices and the materials were able to store twice as much energy as conventional devices. The researchers have also produced nano-composites from benzocyclobutene (BCB) and BT nanoparticles which showed k-values of 50 and a capacitance density of 19 nFcm^-2 which was achieved for a 50 percent BT loading. The dielectric breakdown strength could be maintained at 1.65 MVcm^-1, which is even higher than that of some polymers themselves. It is suggested that high-k BT/BCB nano-composites could be used as gate dielectric insulators in organic field-effect transistors. A project funded by the EU Erasmus Mundus programme which started in 2010, seeks to develop ceramic nano-particle/polymer nano-composites for use in embedded passive components with high dielectric constants. Other research at Georgia Tech involves the development of new silicon and carbon nano-composites for use as electrode materials in Li-ion batteries. Silicon nano-spheres with diameters of 30 nm were created within the carbon structures using a chemical vapour deposition process. Electrical measurements of the nano-composite anodes in small coin cells showed they had a capacity of more than five times greater than the theoretical capacity of graphite. Figure (6) shows a schematic of a silicon-carbon nano-composite granule and an SEM of the carbon coated silicon nano-particles is shown in Figure (7). There has been some commercial activity. For example, Inframet is developing families of unique magnetic nano-composites for use as alternatives to ceramic ferrites in inductive components. With support from various US Government and military agencies, the company has succeeded in producing a range of magnetic nano-composite materials which include Ni-Fe/SiO2, Co/SiO2, Fe-Co/SiO2, Fe-Ni-ferrite, Ni-Zn-ferrite/SiO2, Fe-Ni/polymer and Co/polymer. These are converted from powder form into bulk components by tape casting and hot pressing processes as in Figure (8). Most importantly for high frequency applications, the complex permeability of the Co/SiO2 material is flat across a wide range of frequencies whereas it falls off with increasing frequency for most ferrites (Simonsen and Palaniyandi, 2004).
Fig. 6. JDEC trays can benefit from polymer nano-composites due to their enhanced electrical conductivity

Fig. 7. SEM showing carbon-coated silicon nano-particles on the surface of the composite granules

Fig. 8. Fabrication of magnetic nano-composites for electronic applications
3.5 Biomedical Application

From a biological viewpoint, almost all of the human tissues and organs are deposited in nano-fibrous forms or structures. Examples include: bone, dentin, collagen, cartilage, and skin. All of them are characterized by well-organized hierarchical fibrous structures realigning in nanometer scale. As such, current research in electrospun polymer nano-fibers has focused one of their major applications on bioengineering. We can easily find their promising potential in various biomedical areas. Some examples are listed:

1- Medical prostheses
2- Tissue template
3- Wound dressing
4- Cosmetics
5- Drug delivery and pharmaceutical composition

Bio-nano-composites form a fascinating interdisciplinary area that brings together biology, materials science, and nanotechnology. New bio-nano-composites are impacting diverse areas, in particular, biomedical science. Generally, polymer nano-composites are the result of the combination of polymers and inorganic/organic fillers at the nanometer scale. The extraordinary versatility of these new materials springs from the large selection of biopolymers and fillers available to researchers. Existing biopolymers include, but are not limited to, polysaccharides, aliphatic polyesters, polypeptides and proteins, and polynucleic acids, whereas fillers include clays, hydroxyapatite, and metal nano-particles. The interaction between filler components of nano-composites at the nanometer scale enables them to act as molecular bridges in the polymer matrix. This is the basis for enhanced mechanical properties of the nano-composite as compared to conventional micro-composites. Bio-nano-composites add a new dimension to these enhanced properties in that they are biocompatible and/or biodegradable materials. Hydrogel nano-composites are a new class of bio-nano-composites that have recently attracted a lot of attention for applications in medical and pharmaceutical areas. The nano-composites may consist of various types of nano-particles, such as clay, ceramic, metallic, or metal oxides dispersed in a hydrogel matrix. The hydrogel nano-composites have been investigated for various biological applications including drug delivery, tissue engineering, antimicrobial materials, and thermal therapy (Nitin et al., 2009).

4. Processing Methods under Development

Composite materials consist of at least two different kinds of material phases, and therefore inherently contain the interfaces with which they both contact each other. In order to form a stable composite system, it is requisite to increase the compatibility between these phases, and decrease the interfacial tension between them to the utmost. Especially in the case of nano-composite materials which include nano-particles that are dispersed with nanometre scale separation even with their small amounts of addition and are consequently enormously large in terms of their total surface areas. Thus it is technically required to form such a material system stably without agglomeration and phase separation for production of nano-composites.
There are several methods available for nano-composites such as intercalation, sol-gel, molecular composite and direct dispersion, as shown in Table 5. Interfacial states between both of the two phases are modified in certain ways so as to form stable systems. In general, the interfacial tension is required to be below $10^{-4}$ N/m for polymer alloys of micrometre phase separation type, and below $5 \times 10^{-4}$ N/m for polymer composites with micrometre-sized fillers. In the case of nano-composites, these values should be far less than those given above. The layer exfoliation and intercalation method is one of the present major methods for polymer nano-composites. There are two processes available at present to conduct this method, i.e., the polymerization process, and the melt compound process. The former was first available to the public in 1987 and has been favoured since then. The latter, however, seems to have become a main stream for this type of nano-composites, since it costs less in terms of equipment and renders flexibility in application. The sol-gel method now attracts much more attention, because it might be comparatively easily modified to suit industrial manufacture (Mishra et al., 2005).

Table 5 preparative methods for polymer nano-composites

<table>
<thead>
<tr>
<th>(1) Intercalation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Polymer or pre-polymer intercalation from solution</td>
</tr>
<tr>
<td>(b) In-situ intercalation polymerization</td>
</tr>
<tr>
<td>(c) Melt intercalation</td>
</tr>
<tr>
<td>(2) Sol-gel method</td>
</tr>
<tr>
<td>(3) Molecular composite formation method</td>
</tr>
<tr>
<td>(a) Liquid crystal polymer alloy formation method</td>
</tr>
<tr>
<td>(4) Nano-filler direct dispersion method</td>
</tr>
<tr>
<td>(5) Other methods</td>
</tr>
</tbody>
</table>

Molecular composites can be manufactured by the solution re-precipitation method, and by the melt compound method. The latter is a new method in this manufacturing process that is expected to emerge. It is necessary to develop nanometric liquid crystal polyester (LCP) fibrils to realize an industrial manufacture line for the molecular composites (Tidjani, 2005).

4.1 Intercalation Method

The intercalation method is the most popular for polymer nano-composite formation. This is the method to intercalate monomers or polymers between layers of inorganic layered substances to cause to disperse them into polymers during a process of polymerization or melt compounding by exfoliating the layered substances by each layer. Layered silicates are often used in this method, as shown in Figure 9.
There are three methods in this category. The first method, i.e., intercalation of polymers or pre-polymers from a solution is based on a solvent system in which the polymer or pre-polymer is soluble and silicate layers are swellable.

The layered silicate is first swollen in a solvent, such as water, chloroform, or toluene. When the polymer and layered silicate solutions are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in a polymer-layered silicate nano-composite. In the second method, i.e., the in-situ intercalative polymerization method, the layered silicate is swollen within the liquid monomer or a monomer solution so that the polymer formation may occur between the intercalated sheets. Polymerization is initiated either by heat or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step. The last method, i.e., the melt intercalation method involves annealing, statically or under shear, a mixture of the polymer and an organically modified layered silicate above the softening point of the polymer. This method has great advantages over either in-situ intercalative polymerization or polymer solution intercalation. Firstly, it is environmentally benign due to the absence of organic solvents. Secondly, it is compatible with current industrial processes such as extrusion and injection moulding. The melt intercalation method allows the use of polymers that were previously not suitable for the other two methods (Greene et al., 2004).

Fig. 9. Intercalation and exfoliation process for polymer nano-composites (Greene et al., 2004).
4.2 Sol Gel Method

The sol gel method is characterized by the fact that inorganic or composite organic-inorganic materials are made at relatively low temperatures, and in principle, consist of the hydrolysis of the constituent molecular precursors and subsequent polycondensation to a glass-like form. It allows incorporation of organic and inorganic additives during the process of formation of the glassy network at room temperature. This method has been traditionally utilized to fabricate glasses and ceramics. Recently, at the same time, it has been used for polycrystals, porous composites, and organic-inorganic composites. The sol-gel reaction is started from a metal alkoxide, M (OR).n. It should be melted in water, or alcohol, acid, ammonia, and the like in order to be homogeneously dispersed. Metal alkoxide is hydrolyzed through reaction with water and turns out to be metal hydroxide and alcohol. There are many kinds of metals utilized such as Na, Ba, Cu, Al, Si, Ti, Zr, Ge, V, W and Y. Silicon alkoxides such as tetraethoxysilane (TEOS), and tetramethoxysilane (MTEOS) are often used. In the case of TEOS, for example, an amorphous polymer with three dimensional network structures of silica is formed by the polymerization reaction followed by hydrolysis (Ellis and D’Angelo, 2003).

\[
\text{Si (OC}_2\text{H}_5\text{)}_4 + \text{H}_2\text{O} \rightarrow (\text{OC}_2\text{H}_3)_3\text{Si-OH} + \text{C}_2\text{H}_5\text{OH}
\]

\[\equiv \text{Si-OH} + \text{HO-Si} \rightarrow \equiv \text{Si-O-Si} \equiv + \text{H}_2\text{O}\]

\[\equiv \text{Si-OH} + (\text{OC}_2\text{H}_3)_3\text{Si}^- \rightarrow \equiv \text{Si-O-Si} \equiv +\text{C}_2\text{H}_5\text{OH}\]

The sol gel method was not considered suitable for mass production, since it used water as a media in general. However, it is now expected to become a key technology in the near future, as new modified methods such as a continuous sol-gel have been developed recently. Various companies have introduced highly functional organosols of silic acid, produced either by solrgel condensation of tetraethoxsilane, or acidification of sodium silicates, followed by functionalization with various trisalkoxysilanes. Another very versatile solrgel route has led to the industrial preparation of dispersable boehmite nano-fillers. In the Sasol process aluminium or magnesium metal is activated by etching off the surface oxide layer. Reaction with alcohol produces alkoxides and hydrogen. Upon hydrolysis the aluminiumalkoxides form a boehmite mineral that is obtained as a nano-particle dispersion. The boehmite minerals can be rendered organophilic by reaction with carboxylic or benzenesulphonic acids. The by-product alcohol is recycled in this process. In contrast to natural organophilic boehmite, the solgel reaction product is much easier to redisperse and does not possess other metal ions as impurities (Ellis and D’Angelo, 2003).

4.3 Molecular Composite Formation Method: Possibility for Nano-composites

A molecular composite is a material system wherein discrete reinforcement is achieved with molecular rods. It was characterized originally by the fact that a rigid polymer such as liquid crystal polyester (LCP) was dispersed in a flexible polymer matrix in the molecular or microfibril dimension. This past method was conducted in such a way that two kinds of
materials were melted in a co-solvent to be precipitated afterwards. It was not built up to mass production. A new method was developed in the 1990’s that engineering plastics were melt-compounded with small amounts of liquid crystal polyester (LCP) (Winter, 2004). This was found to produce composites with excellent properties, and has attracted the attention of many people since then (Wypych and Satyanarayana, 2005). Typical examples of this type are polyamide, poly phenylene ether alloy, polyethyleneterephthalate, and polycarbonate all with aromatic polyester (LCP). It should be noted that a third substance is needed that functions as a compatibilizer. The third substance works to promote the formation of fibrils and to disperse it in the composites. It is recognized that the molecular composites have a greater advantage over pure materials in terms of mechanical properties. In this case the microfibrils to be used are 500 nm in size. In order to use nano-composites of this type in reality, it is necessary to be able to disperse the phase down to one order smaller than that we have now (Vaia and Wagner, 2004).

4.4 Nano-Particle Direct Dispersion Method

In this method, the surface of the nano-particles is chemically modified to increase compatibility with polymers, and are mixed with a polymer and dispersed homogeneously without agglomeration. There are several examples such as photo-hardening coating agents with modified Silica nano-particles, nano-particle paste of gold or silver protected by comb-shaped block copolymers and polyaamide 6 nano-composites with silica nano-particles surface-treated by amino butyric acid (Ray and Okamoto, 2003).

5. Conclusion

There have been many achievements in the field of polymer nano-composite technology. It is easy to see the potential for applications of polymer nano-composites in the civil and military fields. For example, polymer nano-composites have emerged as an attractive material in construction, aerospace, biomedical, marine, electronics, and recreation industries for their excellent properties. Great efforts have been undertaken to modify these materials at the nano-scale to optimize their performance. Carbon nanotube-reinforced nano-composites, multifunctional polymeric smart materials, and new functional polymer nano-composites are being explored for unusual behaviours in order to fulfil more than one task in the automotive, biological, aerospace, marine, manufacturing, and defence technologies. It is believed that multifunctional polymer nano-composites will dominate our lives in the future.

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