National Composites Network

Technology Review

Nanocomposites

National Composites Network

FARADAY ADVANCE

Materials

Knowledge Transfer Network

dti

Technology review – Nanocomposites

Amir Bahrami- TWI Ltd[1]

[1] http://www.twi.co.uk

Contents

1 Introduction

What is needed for 21st century competitiveness, is accelerated, high-technology innovation, to design new technologies into new products with higher performance and cost effectiveness. This has created a drive in the plastics industry among others to move towards improved technology and higher added value products. For the plastic industry, a particularly fruitful and promising area is nanocomposites (NCs).

NCs are materials produced by dispersing nanometre size particles in a matrix. The matrix can be single or multi-component, containing additional materials that add other attributes to the system (eg conductivity, toughness, reinforcement, barrier properties, etc.).

The technology for the first generation NCs was developed by Toyota between 1975 and 1985 in order to produce engine parts that were lighter and better performing than steel. The technology has progressed since, with most development efforts being directed towards the automotive and packaging industries.

In contrast to conventional composites, where the reinforcing component is in the order of a few micrometers in dimensions, NCs are exemplified by discrete constituents in the order of a few nanometers (at least in one dimension). The value of NC technology is not solely based on the mechanical enhancement of the matrix (unlike majority of the conventional composites) or the direct replacement of current filler or blend technology. Rather, its importance comes from providing value added properties, which are not present in the neat matrix of conventional composites. Additionally, in most cases, the mechanical enhancement resulting from incorporation of nanomaterials to plastics comes without sacrificing the matrix's inherent processability and toughness. Since high degrees of enhancement in many properties are seen at very low filler contents. Weight savings compared with conventional composites are immense and the demand for the row materials is reduced.

2 Nanomaterials

As a broad definition, nanomaterials are those that have structured components with at least one dimension less than a 100nm. Two principal factors cause the properties of nanomaterials to differ significantly from materials with larger dimensions; increased relative surface area and quantum effects. These factors can enhance properties such as reactivity, strength as well as optical, electrical and thermal characteristics.

The term "material" refers to an almost infinite number of constituents, (eg atoms, molecules, defects etc.) collectively displaying an averaged statistical behaviour. Therefore the behaviour of nanomaterials is dominated by particular interface effects and exhibit characteristics affected by size and the limited number of constituents.

As particles decrease in size, their surface area per unit mass increases. For example, a particle of size 30nm has 5% of its atoms on its surface, which increases to 20% at 10nm and 50% for a 3nm particle (The Royal Society report 2004). Thus nanoparticles have a much greater surface area per unit mass compared with larger particles. As growth and catalytic chemical reactions occur at surfaces, this means that a given mass of material in nanoparticulate form will be much more reactive than the same mass of material made up of larger particles (Global Watch 2005). In a multi component material the uniform dispersion of any isotropic or anisotropic nanostructure can lead to ultra-large interfacial area between the constituents. In addition the distance between the nano elements will approach molecular dimensions at low loadings. For example, for a system made up of 1nm thick plates the distance between plates assuming disc diameter of 1 m m approaches 10nm at only 7 vol. % of plates. These factors clearly differentiate NCs from conventional composites.

In tandem with surface area effects, quantum effects can begin to dominate the properties of matter as size is reduced to the nanoscale. These can affect the optical, electrical and magnetic behaviour of materials, particularly as the structure or particle size approaches the smaller end of the nanoscale. Such properties can impart unique attributes to a composite material.

It is convenient to classify nanomaterials in terms of the dimensionality of the nanostructures involved (The Royal Society Report 2004) and according to this definition nanomaterials can be classified as follows (Figure 1):

- 1-D: (confined in 1-D, extended in 2-D) e.g. surface coatings, thin films, device junctions (eg diodes), interfaces etc. 1-D nanosystems are generally well understood and technologically advanced. Atom scale control is already possible for devices and coatings by various deposition techniques.
- 2-D: (confined in 2-D, extended in 1-D) e.g. nanotubes, fibres, interconnects/wires, fibrils, etc. 2-D systems are moderately understood in terms of properties, but manufacture is much less advanced.
- 3-D: (confined in three dimensions) e.g. quantum dots, particles, precipitates, colloids, catalysts, etc. 3-D nanosystems provide the greatest challenges in terms of both properties and controlled manufacture.

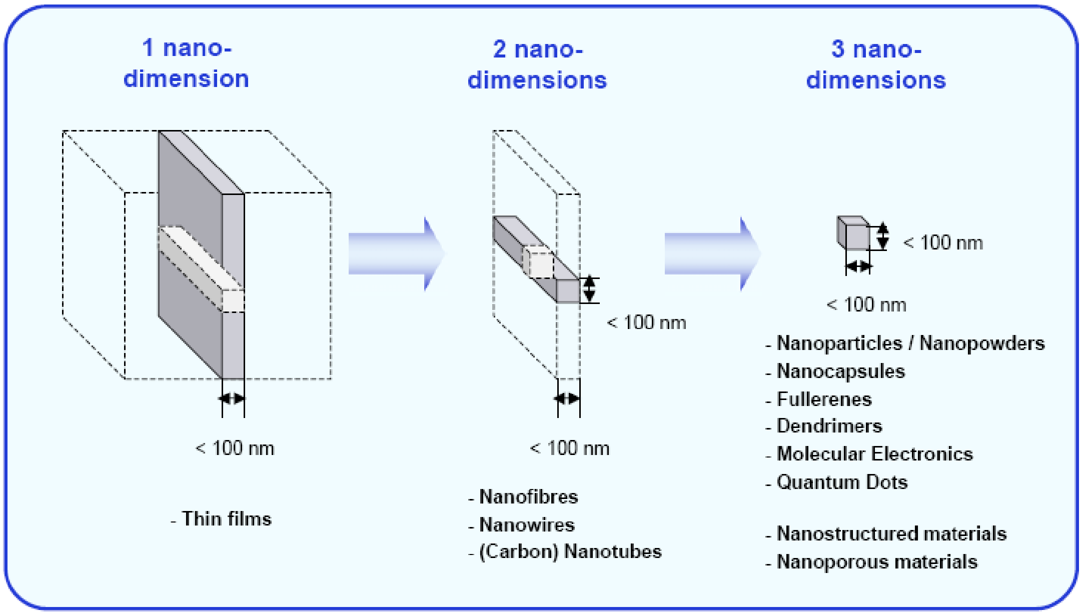


Figure 1 The classification of nanomaterials according to their dimensionality (NRM Report).

2.1 Nanoscale in one dimension

One-dimensional nanomaterials, such as thin films and engineered surfaces, have been developed and used for decades in fields such as electronic device manufacture, chemistry and engineering. In the silicon integrated-circuit industry, many devices rely on thin films for their operation, and control of film thickness approaching the atomic level is routine. Monolayers (layers that are one atom or molecule deep) are also routinely made and used in chemistry. Advances are being made in the control of the composition and smoothness of surfaces, and the growth of films.

Engineered surfaces with tailored properties, such as large surface area or specific, reactivity are used in a range of applications such as in fuel cells and catalysts. The large surface area provided by nanoparticles, together with their ability to self assemble on a support surface, could be of use in all of these applications.

2.2 Nanoscale in two dimensions

Two-dimensional nanomaterials, such as tubes and wires, have generated considerable interest among the scientific community in recent years. In particular, their novel thermal, electrical and mechanical properties are the subject of intense research.

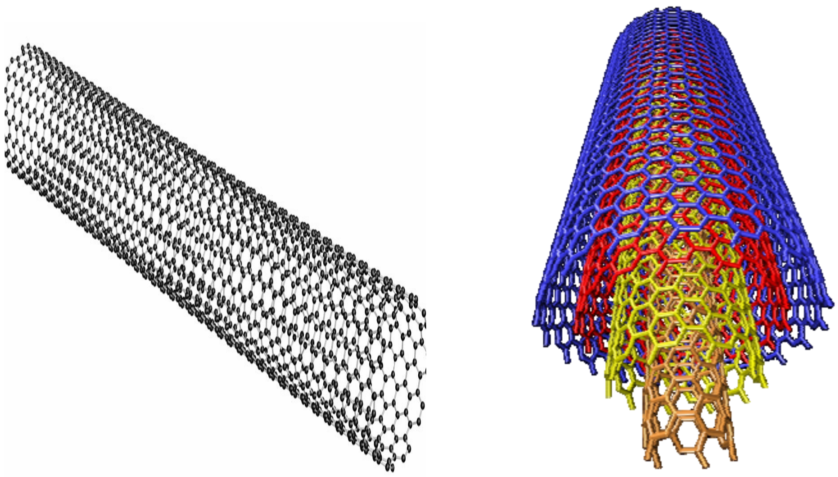
Carbon nanotubes

Carbon nanotubes (CNTs) are an example of two dimensional nano materials. They are molecular scale carbon fibres made up of honeycomb lattices rolled into a cylinder. They can be thought of as a layer of a graphite sheet (graphene) rolled up into a cylindrical shape with diameters of 1 to 100nm depending on the structure, and length of up to several microns. Such structures can consist of, a single wall tube, two concentric double wall tubes or many concentric multiwall tubes.

CNTs have physical and mechanical properties which opens the door to a whole new generation of devices. For example their sp^2 bonding structure is much stronger than the sp^3 bonds found in diamond, providing molecules with unique strength. Their stiffness is in the order of 1TPa, with tensile strength of 200GPa and specific strength 500 times greater than that of aluminium. However, like any other structure and material, they can have defects such as vacancies or non-hexagonal lattices which can subsequently compromise their properties.

Another important property of CNTs is their transport behaviour; they are superb conductors of electricity and heat. In terms of electrical conductivity, they can be metallic or semiconducting depending on the twist in the tube along the tube axis. The conductivity in perfect metallic tubes is of ballistic nature where the transport of electrons along the length of the tube is not disturbed by lattice vibrations or defects. They also have a very high thermal conductivity in the orders of 3000 W/mK, which is three times higher than that of diamond. This is thought to be due to the large mean free path for the lattice vibration quantum, where the conduction of heat by phonons is not disturbed over short distances.

All of these remarkable properties give CNTs a range of potential application: for example, in reinforced composites, sensors, and electronics and display devices.



(a) (b)

Figure 2 Schematic of carbon nanotubes (The Royal Society Report):
a) Schematic of a single-walled carbon nanotube (SWNT);
b) Schematic of a multi-walled carbon nanotube (MWNT).

2.3 Nanoscale in three dimensions (nanoparticle)

In line with the definition of nanomaterials, nanoparticles are classified as being particles with diameters less than 100nm. Nanoparticles are of interest because as size decreases surface properties such as chemical, electrical, optical, magnetic and mechanical begin to dominate over the bulk material properties.

Manufactured nanoparticles are typically not products in their own right, but generally serve as raw materials, ingredients or additives in existing products. Their production is currently low compared with other nanomaterials. However, they are already in a small number of commercial products such as sports equipments and cosmetics.

Fullerenes (carbon 60)

In the mid-1980s a new class of carbon material was discovered called carbon 60 or C60. These are spherical molecules about 1nm in diameter, comprising 60 carbon atoms arranged as 20 hexagons and 12 pentagons; the configuration of a football. In 1990, a technique to produce larger quantities of C60 was developed by resistively heating graphite rods in a helium atmosphere (Krätschmer et al. 1990). Several applications are investigated for fullerenes, such as miniature ‘ball bearings’ to lubricate surfaces and in electronic circuits.

Dendrimers

Dendrimers are spherical polymeric molecules, formed through a nanoscale hierarchical self-assembly process. There are many types of dendrimers; the smallest is several nanometres in size. Dendrimers are used in conventional applications such as coatings and inks, but they also have a range of interesting properties, which could lead to useful applications. For example, dendrimers can act as nanoscale carrier molecules. Environmental clean up could be assisted by dendrimers as they can trap metal ions, which could then be filtered out of water with ultra-filtration techniques.

3 Polymer Nanocomposites

Nanostructure modification of polymers has opened up new perspectives for multi-functional materials. This multi-functionality applies not only to mechanical properties, but extends to optical, thermal, electrical and magnetic ones. Currently, carbon fibres and bundles of multi-wall CNTs are used in polymers to control or enhance conductivity, for anti-static applications. Nanoparticles are used as reinforcements in matrices; an example is the routine use of carbon black used to reinforce car tyres.

There are three main material constituents in any composite: the matrix, the reinforcement (fiber), and the so-called interfacial region. The interfacial region is responsible for communication between the matrix and filler, and its conventionally ascribed properties differ from the bulk matrix because of its proximity to the surface of the filler (Siochi et al. 2004). Considering the constituents, the development of NCs, as with any multi-component material must simultaneously balance four interdependent areas: constituent selection, cost-effective processing, fabrication, and performance.

Polymer/layered NCs in general, can be classified into three different types, namely (i) intercalated NCs, (ii) flocculated NCs, and (iii) exfoliated NCs (Siochi et al. 2004).

- In phase separated composites, polymer chains are inserted into layered structures such as clays, which occur in a crytallographically regular fashion, with a few nanometers repeat distances and irrespective of the ratio of polymer to layered structure.
- In intercalated composites, flocculation of intercalated and stacked layers to some extent takes place due to the hydroxylated edge–edge interactions of the clay layers.
- Finally separation of the individual layers in the polymer matrix occurs in the exfoliated type by average distances that depend only on the loading of layered material such as

clay. In this new family of composite materials, high storage modulus, increased tensile and flexural properties, heat distortion temperature, decrease in gas permeability, and unique properties such as self extinguishing behaviour and tunable biodegradability are observed, compared to matrix material or conventional micro and macro-composite materials.

Other types of structures could exist depending on the type of reinforcement used. For example, CNTs form a connected network of many tubes that meet end to end due to their high aspect ratio when embedded in a polymer matrix. Such networks are usually formed at very low loadings (percolation threshold) and composites of these materials even at loadings as low as 5wt% are electrically conductive.

3.1 Properties of NCs

In addition to mechanical enhancement nano-reinforcements impart other functionalities in to the composite system due to their size effects. Some of such properties are listed below:

Magnetic properties
The decrease of the particle size to the nanometers, often results in improved magnetic behaviour (as compared to their bulk counterparts) (NRM report). Two major applications benefiting from the above are medical imaging applications and high density media storage particularly if the nanoparticles are uniformly dispersed in a matrix or substrate.

Optical properties (eg transparency)
The absorption or emission wavelength can be controlled through size selection. For example, transparency can be achieved if the nanoparticle size is below the critical wavelength of light. This makes nanoparticles (e.g. metals, silicates or metal oxide ceramics) suitable for barrier films and coating applications, combining transparency with other properties (UV, IR-absorption, conductivity, mechanical strength, etc).

Electrical properties
Transport can be controlled via the individual properties of the nanoparticles. For example, the use of CNTs which are thought of as ballistic conductors in their perfect form, can create a conductive NC from an insulating polymer matrix. This is usually achieved at very small loadings due to the high aspect ratio of these tubes and low percolation threshold.

Thermal properties
If homogeneously disseminated, certain nanoadditives such as metal nanoparticles or CNTs can achieve significant improvement in thermal properties for polymer systems, leading to faster processing time or higher temperature performance.

It is widely known that layered silicates generally improve the heat deformation temperature of a thermoplastic compound, i.e. the temperature where an object of certain dimensions begins to deform under a specified load. This can widen the use of low cost thermoplastics to environments where only far higher-cost polymers have been used. For example, cheap polypropylene compounds could replace more expensive polyamides in applications under the bonnet in a car. Silicates can influence the flammability of polymers, increasing the glass transition temperature (Tg) and the heat deflection temperature. Such properties can be useful for the building and the mining industries.

Chemical properties (e.g. reactivity)
Reactivity can be considered the most relevant aspect for catalysis and related applications (sensors, etc.). Combining reactivity and catalytic activity promises some important application fields, such as fuels (and fuel additives), fuel cells etc. Catalysis is enhanced by high surface area to volume ratio, and potential homogenous distribution of nanoparticles.

Doping polymer composites with complex oxide nanoparticles dramatically increases their environmental properties during exposure to strong, aggressive media. With metals it is the chemical, especially catalytic, properties of metal oxides that are showing the most interesting potential. Transparency is often an essential co-ingredient, as in photocatalytic self-cleaning windows (and can even be a key property on its own, as in the well-known sunscreen applications). Rare earth oxides are sensitive to air moisture and other contaminants, therefore the chemical reactivity can strongly influence the surface properties, in particular the light emission from dopants present on the surface.

Mechanical properties
With composites, it is possible to obtain different reinforcing levels on mechanical properties of the final composites. This depends on the chemistry of the reinforcing nanoparticles, its aspect ratio, dissemination and interfacial interactions with the polymer matrix (regulated through surface coating and compatibilising agents into the polymer formulation.). Metal oxide ceramic nanoparticles can be used to increase the mechanical strength in special alloys, resulting also in lower weight materials (NRM report). Depending on the chemistry of the metal oxide, its morphology and interfacial interactions with the matrix material, different effects on mechanical properties of the final composite can be obtained (e.g. high or low stiffness, strength, toughness, etc). This can be achieved at relatively low particle volume fractions.

3.2 Processing

The incorporation of nanoparticles into NCs has five main steps, which are illustrated in Figure 3:

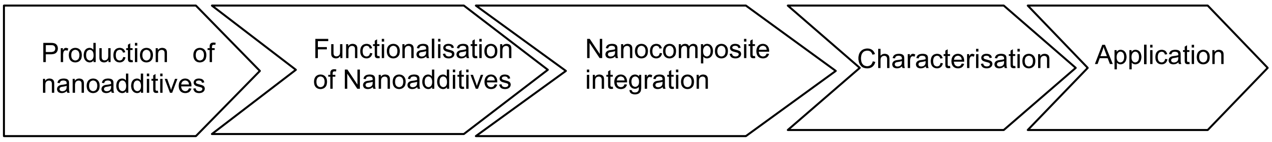


Figure 3 Steps involved in taking advantage of NCs.

It should be noted that this is not always a linear approach with sequential independent steps (NRM report). In many cases each application has specific production, purification and functionalisation processes to obtain the desired properties for the lowest amount of time and cost. Also, some processes combine steps; for example, sol gel processes can combine the creation of particles with their dispersion and integration into a matrix material.

In many instances the NCs have proven to be easily extruded and processed to near final shape simplifying their manufacturing. However, one of the challenges which impede the bulk production of NCs is essentially the general understanding and even a simple structure property model. In the absence of such models and the role of processing in engineering NCs, the progress in this field has remained largely empirical.

The properties of NCs are dependent on the dispersion of nano-fillers in the polymer matrix. For example, polymer-clay NCs show significant property improvement when exfoliated microstructures are formed as opposed to phase separated or even intercalated (Lee, 2005). Under processing conditions of high shear, nanoparticles tend to aggregate rather than exfoliate, losing many of their potential benefits. Also, the temperatures used for many polymer processing methods, will cause degradation to some nano-additives such as organo-clays. However, for viable manufacture of NCs, they must be capable of being processed using traditional machinery that is only subject to (at most) relatively minor modifications. The areas of importance in NC processing are:

- Achieving uniform dispersion and exfoliation at the nanoscale
- Methods and chemical modifiers to effectively bond nanomaterials to the polymer matrix
- The development of NC plastic compounds that would offer new and unmatched sets of properties and cost for specific applications
- Development of technologies that give reproducible results

- Understanding process-induced structuring of nanomaterials
- Cost-effective processing methods.

In genera,l out of many nanoparticles produced and explored in polymer NC production three have been receiving the most attention and have already found applications in many areas and industry sectors. These are: metal and metal oxide nanoparticles, clay nanoparticles and CNTs.

3.2.1 Metal, and metal oxide, NC polymers

Several methods have been used to make these NCs. For example laser vaporisation of metals in the presence of a small concentration of butadiene vapour leads to the polymerisation of butadiene and incorporation of the metal nanoparticles within the polymer matrix (Abdelsayed et al, 2006). The laser vaporisation-polymerisation method provides the ability to encapsulate several different metals or metal oxides which undoubtedly will play a significant role in tuning various properties of the polymer composites.

Another possibility is saturating polymer matrices with metal salts and using chemical reduction to form metallic nanoparticles within the polymeric matrix (Figure 4).

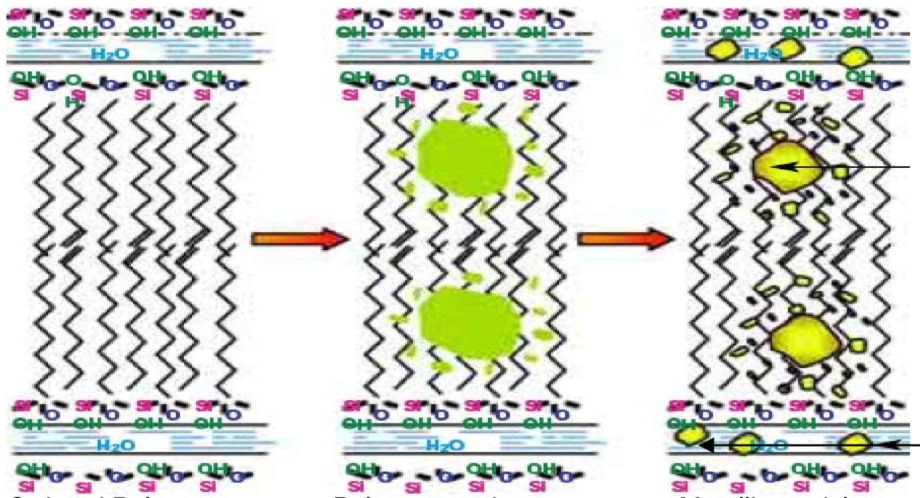


Figure 4 Formation of nanoparticles in polymer matrices (Global Watch 2005).

3.2.2 Clay NC polymers

Nanoclays are the true start of polymer NCs history when in the 1990's Toyota first used clay-nylon-6 NCs to produce timing belt covers. After that, other automotive applications were implemented including Mitsubishi's GDI clay-nylon-6 NC engine covers and General Motors' clay-polyolefin NCs step assistant GMC Safari and Chevrolet Astro vans (nanocompositetech). The potential applications go beyond automotive industry, with one of the most promising being drink packaging applications, considering increased barrier properties of polymer clay NCs.

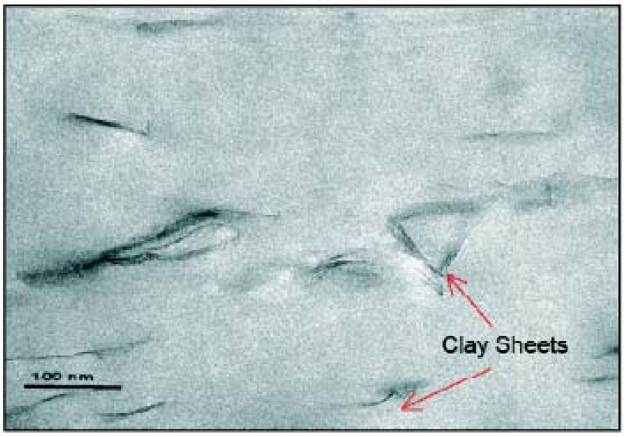


Figure 5 Transmission electron microscopy (TEM) of a polymer-layered silicate NC prepared in a twin screw extruder (Gacitua et al, 2005).

Most polymers are hydrophobic and are not compatible with hydrophilic clays so in order to disperse clay layers into a polymer matrix, it is very important to consider polymer-clay compatibility. This provides organo-philic characteristics to the clay by pretreatment (however in the case of hydrophilic polymers and silicate layers pre-treatment is not necessary). Such pretreatments involve only clays in order to obtain organic compatibility. Organophilic clay can be formed from normally hydrophilic clays by means of amino acids, organic ammonium salts, or tetra organic phosphonium solution. Some of the well established methods of producing clay nanocomposites are:

- Solution induced intercalation
- In situ polymerisation
- Melt processing.

Solution induced intercalation method starts with a polymer in an organic solvent, then the clay is dispersed in the obtained solution and subsequently either the solvent is evaporated or the polymer precipitated. This approach leads to poor clay dispersion, besides other problem such as the need for large amounts of solvent to achieve appreciable filler dispersion, phase separation problems and health and safety issues.

In situ polymerization consists of dispersing clay layers into matrix through polymerisation, by mixing the silicate layers with the monomer, initiator and/or the catalyst.

In melt processing, the silicate layers are directly dispersed into the polymer during the melt. In order to use this method, the silicates need to be previously surface treated through the organo-modification previously mentioned. Direct melt compounding has also been used for production of other polymer-clay NCs including nylon 6–organoclay NC using a conventional twin screw extruder. The mechanical properties of the organo-clay NCs can be significantly improved and show even greater values than glass fibre composite (Cho et al 2001).

Rubber–clay NCs, such as styrene butadiene rubber (SBR)–clay, can also be prepared by direct co-coagulation of rubber and clay aqueous suspension (Wo et al. 2005). These NCs possess a unique structure; the rubber molecules separate the clay particles into either individual layers or just silicate layer aggregates of nanometre thickness without the intercalation of rubber molecules into clay galleries. Such a structure is the result of competition between separation of rubber particles and re-aggregation of single silicate layers during the co-coagulating process. The glass transition temperature of SBR–clay NCs increases compared with that of the pure SBR. The tensile strength of SBR–clay NC is 6 times higher than conventional SBR.

Rubber-clay composites have improved permeation properties, for example the gas permeability of separated rubber–clay NCs is 50% less than the corresponding rubber. The relative permeability of polymer-clay NCs is reduced due to the presence of impermeable and oriented clay layers. Furthermore, the chain-segment immobility enhances the barrier properties of NCs. Therefore it is possible to tailor clay layer length, volume fraction and dispersion for fabricating polymer–clay NC with unique barrier properties. For example, nylon6-clay NC shows resistance to solvent permeation superior to that of pure nylon6. In addition, the clay content significantly influences the solvent permeation resistance of nylon6, and the maximum improvement in barrier properties is found when the clay content reaches an “optimum” value. By using optimised composites and processing conditions, the permeation rate of toluene and ethanol in nylon6/clay NC is about three and four times slower than pure nylon 6 (Jiang et al. 2005).

In reality, mechanical properties in the best clay/polymer NCs are much lower than conventional fibre reinforced composites. Only in the low filler range 4% NCs show better mechanical performance. To obtain higher performance the filler content should be increased, however significant physical-technological problem occurs as increasing reinforcing load increases the surface area to volume ratio of the filler, leading to insufficient polymer molecules to wet enormous clay surface and the main advantage of nano-size filler becomes a difficult hurdle to overcome.

Despite all of the work done on clay nanoparticles, certain nanoparticle based composites will have a brief heyday and then be overtaken by nanotube composites (NRM report). There is no doubt that in terms of mechanical properties, nanotubes are poised to make a very important contribution to this field, as has been already shown by a number of research groups. In addition the other physical characteristics of these tubes will give them an edge as they are more likely to impart other functionalities than just mechanical enhancement into a matrix and are a viable option in production of multifunctional materials.

3.2.3 Carbon nanotube nanocomposite polymers

Due to the combination of their remarkable electrical, thermal and mechanical properties, CNTs are expected to enable a paradigm shift in composite design concepts. However, significant challenges still exist in translating these CNT properties into the macrostructures required for future generations of composites. Significant improvements in mechanical and electrical properties of CNT nanocomposites with very low loadings of CNTs lend credence to the potential for using these tubes in achieving technological leaps in composite development.

From the materials perspective, efficient vehicles with reduced life cycle costs can be enabled by the incorporation of multifunctional structures. State-of-the-art structures use graphite fibre composites to achieve weight reduction without sacrificing mechanical properties. However, while graphite fibre composites satisfy the weight reduction requirements, they do not depart from their primary utility as load bearing structures (Siochi et al, 2004). In contrast to graphite fibres, CNTs possess the mechanical properties to enable the necessary weight reduction, as well as superior electrical and thermal properties (Biercuk et al, 2002). This suggests that they can be used to replace graphite fibre in load bearing structures and impart sensing and thermal management capabilities as well, thus producing a multifunctional structure.

Although there is a great potential for the development of the next generation of polymer matrix composites, which take advantage of the impressive properties possessed by CNTs, there are still significant challenges to overcome.

Taking advantage of the combination of electrical and mechanical properties of CNTs for the development of multifunctional structures is possible when the fundamental problems of chemical interactions and characterization method development are approached with the aid of computation and analytical modeling. Improved electrical and mechanical properties obtained for NCs containing very low concentrations of CNTs demonstrate that there is a promise in the translation of excellent properties at the nanoscale to useful bulk structures with improved properties compared to state-of the- art materials (Siochi et al 2004).

An example of carbon nanotube polymer NC is a high performance ultrahigh molecular weight polyethylene (UHMWPE) films witch contain 1wt% multiwall CNTs (MWCNTs) (see Figure 6). Polyethylene/MWNTs can be prepared by melt blending using twin screw extruders. Investigating the morphology and degree of dispersion of the MWNTs in the PE matrix at different length scales reveals compressive forces exerted on the MWNTs by PE chains indicating intercalation of PE into the MWNT bundles (McNally et al, 2005).

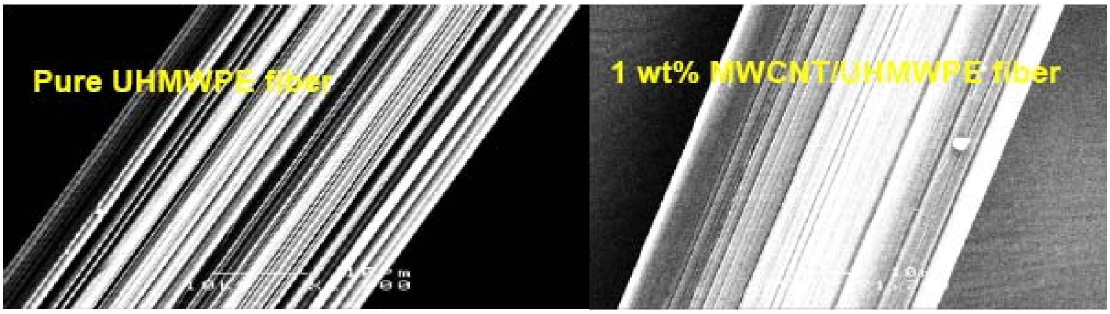


Figure 6 UHMWPE and MWCNT/UHMWPE composite (Lee 2005).

Single wall CNTs have been used to augment the thermal transport properties of industrial epoxies. Samples loaded with 1 wt % un-purified single wall CNTs material show a 70% increase in thermal conductivity at 40K, rising to 125% at room temperature; the enhancement due to 1wt % loading of vapour grown carbon fibres is three times smaller (Biercuk et al 2002). The Vickers hardness rises monotonically with loading, up to a factor of 3.5 at 2 wt %. These results suggest that the thermal and mechanical properties of epoxy can be immensely improved by addition of CNTs.

Electrical conductivity data show a percolation threshold between 0.1 and 0.2 wt% loading. Chemical vapours deposition, grown CNTs have been used as conductive fillers in an epoxy system (Windle et al 2005). The application of both AC and DC electric fields during NC curing induced the formation of aligned conductive nanotube networks between the electrodes. The approach offers the possibility of achieving bulk conductive nanotube–polymer composites with anisotropic electrical properties and a degree of optical transparency.

Good adhesion between the CNTs and the polymeric matrix is a key issue and to increase this, co-spraying method of binary mixture and SWNT nanotubes in plasma stream has been carried out to produce NCs. The electrical characterisations, Fourier transform-infrared spectroscopy (FTIR) and Raman spectra showed a chemical bonding of the polymeric matrix to the nanotube surface (Nastase et al 2006).

Another issue is the dispersion of CNTs within the matrix with minimum coagulation. Haggenmueller et al studied the interfacial polymerisation of nylon with single wall via in situ polymerisation. Single wall NCTs were incorporated in purified, functionalised or surfactant stabilised forms. It was seen that functionalisation and surfactant stabilisation improves the nanotube dispersion in solvents but only functionalised tubes show a good dispersion in composites, whereas purified and surfactant stabilised tubes result in poor dispersion and nanotube agglomeration. CNT reinforced polyimide NCs are also synthesised by in situ polymerisation of monomers in the presence of sonication. This process enabled uniform dispersion of nanotube bundles in the polymer matrix. The resultant NC films are electrically conductive (anti-static) and optically transparent with significant conductivity enhancement (Ten orders of magnitude) at a very low loading (0.1 vol%). Mechanical properties and thermal stability were also improved (Park et al 2002).

4 Market

4.1 Nanocomposites current applications

As a consequence of the advantages discussed, NCs are targeted at applications in automotive, packaging, aerospace, electronics, civil engineering, industries. Table 1 shows some of the current applications of NCs specific to automotive and packaging industries, which are the main two sectors in the field.

Table 1 Some of the current commercial polymer NCs (NC)

Product	Properties	Applications	Manufacturer
Nylon NCs	improved modulus, strength, heat distort temperature, barrier properties	automotive parts (eg timing belt cover, engine cover, barrier, fuel line), packaging , barrier film	Bayer Honeywell Polymer RTP Company Toyota Motors Ube Unitika
Polyolefin NCs	stiffer, stronger, less brittle, lighter, more easily recycled, improved flame retardancy	step-assist for GMC Safari and chevrolet Astro vans, heavy-duty electrical enclosure	Basell, Blackhawk Automotive, Plastics Inc, General Motors, Gitto Global Corporation, Southern Clay Products
M9	High barrier properties	Juice or beer bottles, multi-layer films, containers	Mitsubishi Gas Chemical Company
Durethan KU2-2601 (nylon 6)	Doubling of stiffness, high gloss and clarity, reduced oxygen transmission rate, improved barrier properties	Barrier films, paper coating	Bayer
Aegis NC (nylon 6/barrier nylon)	doubling of stiffness, higher heat distort temperature, improved clarity	medium barrier bottles and films	Honeywell Polymer
Aegis TM OX	Highly reduced oxygen transmission rate, improved clarity	High barrier beer bottles	Honeywell Polymer
Forte NC	improved temperature resistance and stiffness, very good impact properties	automotive furniture appliance	Noble Polymer

Some of the other industrial applications include:

Medical Plastics
Some of the medical applications include tubing and thin films, as well as specialty tubing and stent-delivery balloons with very small diameters (< 200μm) and ultra-thin walls. Also diameters of < 2.5μm is used in the catheters inserted into the cardiovascular system

Advantages include: high bending stiffness, pull/push strength, kinking and buckling resistance and good toughness, as well as smooth surface finishing, good scratch resistance and excellent processability.

Surface Coating
Tough and transparent NCs are used as scratchproof coating. Such NCs provide high abrasion and chemical resistant which result in polymers that do not craze, crack or shatter upon impact or aggressive environment in commercial applications such as protective eyewear.

Flame retardant materials
Addition of nano-fillers improves flame retardancy of polymer resins. The nanofillers delay ignition, reduce smoke emissions and eliminate slumping and dripping of the molten polymer by formation of a strong, stable char. Some applications of the flame retardant NCs are: wire and cable covers, battery jars and electrical enclosures and home interior decoration materials.

Electrically conductive composites
CNT polymer composites provide improved conductivity for applications such as signal wire shielding, where reduced thickness and increased conductivity are imperative for use in aerospace, electronics and chemical markets. Some of the specific technology areas that will benefit from conductive NC materials are electromagnetic interference shielding and pulse hardening; electrical signal transfer; electrostatic painting; electrostatic discharge; and various electro-optical devices, such as photovoltaic cells.

Sports Equipment
One of the first products to contain semi-finished CNT products is the Volkl DNX tennis racket, in which CNTs are used to reinforce the frame at stress points and improve its ability to absorb shocks. The Fraunhofer CNT applications laboratory are currently producing their semi-finished CNT products in paper form which can be mixed with many different materials and combines as easily with plastics as with textiles. Also, carbon nanotube hockey sticks resist impact 60 to 70% better. Montreal Sports of Finland produce hockey sticks made of CNTs embedded in a polyurethane matrix, which are more durable, light and accurate. Called Nanohybtonite technology the material produces a more flexible shaft which helps the handling of the puck. The blade is made of a polyurethane core reinforced with carbon composite laminate. The Montreal approach is based on CNTs that are combined with a polymer on the molecular level. Other sports applications include Wilson tennis rackets and golf clubs, fishing rods made by Redington, base ball bats made by Easton and high performance bicycles.

4.2 NCs opportunities and potential applications

The industry for manufactured NC plastic products appears to be economically strong with very good prospects for growth. The plastic industry should focus on serving the provincial market primarily with some forays into more distant markets. The most important reason for this situation is that manufactured plastic products are difficult and costly to trade over long distances. Manufactured plastics products tend to be light and bulky, and, therefore more expensive to ship. They also are not commodities that can easily be interchanged regardless of vendor or region of origin. Proximity to customers enables a greater understanding of needs and requirements and results in more successful product design and marketing. One element however appears to be able to trump basic industry dynamics: technological advantage. The plastic manufacturers that succeed in export markets tend to be those with a technology advantage imbedded in their products or their manufacturing process. In effect, these manufacturers produce superior products in markets that value technical and quality superiority. These products command high prices and margins and shipping costs become a small percentage of overall costs.

If companies, whose business model is based on technological advantage and innovation imbedded in high value products, are started, they are likely to remain and grow. The key, therefore, is to find ways to encourage such start-up companies. Programs to promote innovation and entrepreneurship are proven to be effective in this respect (Lublick et al 2002). A preliminary list of potential applications and market includes the following:

4.2.1 Oil and gas

The oil sands mining industry has consistently made progress in improving and reducing costs using new technologies. Plastic materials are already making inroads, the scale of future oil sands projects is likely to create a large market for advanced plastics materials. Some of the opportunities are:

- Polyolefin pipe for steam assisted gravity drainage (SAGD) horizontal wells, allowing a sharper bending radius and more effective oil recovery. SAGD is the current leading technology for oil sands extraction and is critical to the future of oil sands development
- Polyethylene pipe with lower permeability to natural gas in order to reduce fugitive losses during gathering and delivery operations in natural gas wells to improve performance
- Current plastic tubes suffer limitations in terms of strengths, and tubes made with higher performance polyethylene would improve well performance further
- Plastic vessels with improved strength and temperature resistance properties that would replace steel in corrosive environments (Lublick et al 2002).

In terms of CO2 - enhanced oil recovery, there are also expectations that more projects will occur in the future, based on the convergence of two strong drivers: the need to produce more oil and the need to sequester CO2. These projects involve corrosion challenges and opportunities for advanced plastics materials to offer performance characteristics that are superior to steel.

4.2.2 Value-added agriculture through advanced packaging

Efficiency improvements in agriculture over the last 40 years have resulted in a substantial increase in agricultural production. As a consequence, world prices for agricultural commodities remain low by historical standards, with little prospects for improvements. In order to improve revenues, the agricultural sector has been diversifying crops and moving in the direction of value-added agriculture.

Value-added agriculture activities increase the revenue received for agricultural commodities. The idea is to increase revenues received for agricultural commodities, as opposed to increasing the amount produced. Activities proposed range from quality improvements and specialized crops, to additional transformation and the marketing of processed products.

A critical element in enabling value-added agricultural products, is packaging. Packaging serves multiple purposes: it, of course, protects the product during shipping and distribution in the same manner as the large containers used for transporting bulk commodities. However, packaging is necessary to reduce the unit of sale from large bulk quantities to the smaller quantities purchased by individual consumers. Finally, packaging is one of the media used to convey marketing messages to consumers, as well as operating, legal and safety instructions about the product. Where the real competitiveness arrives in the packaging sector is use of novel materials that not only preserve the agricultural products better, but add functionalities such as monitoring the conditions of the content, the thermal history etc. and such properties are only achieved through the use of novel nanomaterials.

4.2.3 Applications development for the energy industry

As discussed above, a large number of opportunities exist in the energy industry for advanced plastics materials, particularly in corrosive environments. Some of these involve marketing and promotion of existing products such as plastic pipes, while others require basic research and development as in the case for NCs. However, all of these opportunities are of a technological nature and proceed when technical personnel from the energy industry interact with their counterparts in the plastics industry. Value and opportunities would be created for both industries if the frequency and intensity of these interactions was increased in a systemic way. Applications such as ultra capacitors and highly efficient photovoltaic systems based on carbon nanotube composites are some of the potential applications where research and development is underway.

4.2.4 Electronics and optoelectronics

The drive for the electronic industry to produce smaller and higher performance products requires miniaturisation of the electronic devices and components. This in turn requires the use of material and components that are efficient and multifunctional. In addition the implementation of environmental legislation such as that concerning use of lead free processes has lead to the use of alternative materials, the majority of which require much higher processing temperatures.

It is important to note that the advances and opportunities in the electronic industry is one which will have an effect across most industries. As all sectors depend more and more on electronic equipment for better performance, higher efficiency, reduced waste and labour costs, the importance of NCs in the electronics sector is one which will have an impact across board.

4.2.5 Market size and value

There is a growing demand for NCs, the majority of which is from the packaging industry (see table 2). A variety of firms comprise the NC industry, including producers of resins and suppliers of nanoscale materials used as reinforcements and additives, as well as compounders and manufacturers of goods that include NCs. The NC industry is relatively new, especially when compared with the plastic, chemical and material industries. However, a large number of companies have become active in NC development. Enthusiasm about the prospects for NCs and nanotechnology as a whole have contributed to the speed with which so many makers of plastic and plastic additives, compounders and end users have gravitated to the industry.

The NC industry is fragmented. There are no companies that both produce resins and nanomaterials and use them to create finished products. Rather, the industry is an amalgamation of firms that perform one or two of these functions. Among the prominent companies are resin producers, including some that are also integrated producers of compounds; suppliers of nanoscale materials, including some that produce master batches or concentrates used in NC production; plastic compounders, including end users that do their own compounding; and users of the finished NC products, such as motor vehicle manufacturers or consumer goods producers. In addition to product manufacturers, governmental agencies and academic institutions also play a key role in the research and development of NC materials. Many of the companies involved in the development of NC products participate in cooperative agreements (Lublick et al 2002), often spanning several levels of the supply chain, including nanomaterials production, compounding and product manufacturing. For example, nanoscale clay producer Nanocor (a subsidiary of AMCOL International) has agreements in place with numerous companies including Mitsubishi Gas Chemical (Japan), PolyOne, Color Matrix and Toyota Central Research and Development Labs (Japan) (Freedonia group market report 2006).

Table 2 NC Demand by Market (million £) Source: The Freedonia Group, Inc

Sector	2000	2005	2010	2015
Packaging	42	58	100	290
Construction	18	25	55	235
Electrical and electronics	12	19	40	225
Motor vehicles	3	9	60	370
Other	34	43	90	305
Total	**109**	**154**	**345**	**1425**

Table 3 Global NCs market, to 2011 ($ Millions)

Commercialization Stage	2005	2006	2011	AAGR% 2006-2011
Established	241.2	286.4	1011.6	28.7
Developmental	0	0	124.5	--
Total	241.2	286.4	1136.1	31.7

Table 4 Global market forecast for commercial NC applications, through 2011 ($ Millions) (BCC Research 30-07-2006)

Application	2005	2006	2011	AAGR% 2006-2011
Automotive components	75.2	83.4	139.9	10.9
Food packaging	48.8	72.2	512.8	48
Wire and cable sheathing	4.2	4.6	31.0	46.5
Floor finishes	24.0	26.4	42.5	10
ESD applications	16.7	16.9	18.2	1.5
Electrical and electronic devices	68.0	76.4	137.1	12.4
Sporting goods	1.5	3.1	121.5	108.3
Thermal spray coatings	2.8	3.4	8.6	20.4
Total	**241.2**	**286.4**	**1011.6**	**28.7**

5 Conclusions

NC technology for plastics is at the commercial development stage, particularly in the automotive industry, where commercial products exist. The main opportunity is to develop expertise, products and applications with benefits for the energy and health industries.

Plastics and advanced materials are poised for continued growth, fueled by a constant steam of technological innovation and an increasing global demand for materials and manufactured products that enhance quality of life. NCs are in the forefront of this growth due to their potential and remarkable properties. However, there are certain technological hurdles which need to be overcome for this potential to be commercially realised.

As far as technical focus of basic research goes, the key capabilities that offer the most potential for improvement and resulting application are: fine control of nanoscale structure (ie size and morphology); appropriate functionalisation; and most importantly controlled dispersion methods in the polymer matrix. In the former, a key capability is the discipline of self-assembly, which will ultimately be the path to the most dramatic new materials. The other vital area to strongly support research is computer modelling and simulation. Predicting properties of complex materials through computer simulations is still in its infancy but will become an enormously powerful tool in future, allowing the bypassing of much laborious experimentation.

Most applications outside of bulk structural composites are relatively price insensitive. On the other hand, it is clear that the lack of industrialisation of processes not only results in variations in quality, but still also in excessive costs (e.g. polymeric NCs). Improving the production yield of nanoparticles would assist with barriers such as cost. Since size and size distribution is important for the activity of nanoparticles, understanding the optimum ranges of these characteristics is an essential first step. Production yield of specific active sizes and control of the size distribution would reduce waste and costs.

For nanomaterials integration in polymeric matrices, there are processing challenges and need for manufacturing methods that combine achieving uniform dispersion and exfoliation at the nanoscale and most importantly keeping the particles dispersed. Some of the key areas include:

- Methods and chemical modifiers to effectively bond nanomaterials to the polymer matrix.
- The development of NC plastic compounds that would offer new and unmatched sets of properties and cost for specific applications
- Development of technologies that give reproducible results
- Understanding process-induced structuring of nanomaterials
- Cost-effective processing methods
- Manufacture of NCs capable of being processed on traditional machinery that is only subject to (at most) relatively minor modifications.

In any case, the upscaling of different processes will need to be carried out taking into account the most demanding sustainability principles, in order to avoid potential dangers to life and the environment. Large quantities of contaminated solvents can be expected from industrialised processes, which could be difficult and uneconomical to recycle. The development of efficient solutions, such as closed-loop processes is needed.

Commercial focal point should be to increase the risk capital for production start-ups, which sell application oriented RTD on the side. The great majority of current applications are existing conventional applications of composites improved by the application of nanotechnology. The mass markets for these products are dominated by major multinationals such as oil companies, drug companies, consumer goods suppliers and others. The role for start-ups and SMEs in general will most likely be:

- As niche suppliers to end markets
- As technology providers to major corporations (intellectual property strategies are vital here)
- As intermediate suppliers for incorporation into the final product.

These types of companies typically do not have either the resources or the expertise to challenge major corporations in mass production or mass marketing. It is vital therefore to set up opportunities for exchange and dialogue between major corporations, SMEs, start-ups and R&D centres, something that networks such as the National Composites Network (NCN) are very well positioned to do.

6 Reference

The Royal Society report 2004.Nanoscience and nanotechnologies: opportunities and uncertainties. RS policy document 19/04. www.royalsoc.ac.uk

Global Watch. Nanoparticle technology: production and application development – a mission to Russia and Ukraine. http://www.globalwatchservice.com/Pages/ThreeColumns.aspx?PageID=102

NRM report. EU funded project of Road Maps for Nanomaterials, NRM, published by Willems&Van den wildenberg.

Krätschmer W, Lamb L D, Fostiropoulus K & Huffman D R. Solid C60: A new form of carbon. Nature, 1990 347, 354.

Emilie J. Siochi, Peter T. Lillehei, Kristopher E. Wise*, Cheol Park* and Jason H. Rouse* Design and characterization of carbon nanotube NCs NASA Langley Research Center http://techreports.larc.nasa.gov/ltrs/PDF/2003/mtg/NASA-2003-4ismn-ejs.pdf

Lee. R, HKSAR Innovation Expo'05 Hong Kong Convention and Exhibition Centre 2005.Emerging Trends of Advanced Materials and Their Potential Impacts http://www.itc.gov.hk/innotech/Ricky_Lee.pdf

V. Abdelsayed, Y. Ibrahim, M.S. El-Shall and S. Deevi. Polymerisation of butadiene on nanoparticles' surfaces and formation of metal / polymer NCs. Applied Surface Science, Volume 252, Issue 10, 15 March 2006, Pages 3774-3782. V.

www.nanocompositech.comreview-nanocomposite.htm

William Gacitua E. 1 – Aldo Ballerini A.2 – Jinwen Zhang.Polymer NCs: synthetic and natural fillers, a review Maderas. Ciencia y tecnología 7(3): 159-178, 2005

J. W. Cho and D. R. Paul Nylon 6 NCs by melt compounding. Polymer, Volume 42, Issue 3, February 2001, Pages 1083-1094.

You-Ping Wu, Yi-Qing Wang, Hui-Feng Zhang, Yi-Zhong Wang, Ding-Sheng Yu, Li-Qun Zhang and Jun Yang. Rubber–pristine clay NCs prepared by co-coagulating rubber latex and clay aqueous suspension. Composites Science and Technology, Volume 65, Issues 7-8, June 2005, Pages 1195-1202

Tao Jiang, Yu-hua Wang, Jen-taot Yeh and Zhi-qiang Fan. Study on solvent permeation resistance properties of nylon6/clay NC. European Polymer Journal, Volume 41, Issue 3, March 2005, Pages 459-466.

M. J. Biercuk, M. C. Llaguno, M. Radosavljevic, J. K. Hyun, and A. T. Johnson Applied Physics Letters -- April 15, 2002 -- Volume 80, Issue 15, pp. 2767-2769

Tony McNally, Petra Pötschke, Peter Halley, Michael Murphy, Darren Martin, Steven E.J. Bell, Gerard P. Brennan, Daniel Bein, Patrick Lemoine and John Paul Quinn. Polyethylene multi-walled carbon nanotube composites. Polymer, Volume 46, Issue 19, 8 September 2005, Pages 8222-8232.

C.A. Martin, J.K.W. Sandler, A.H. Windle, M. -K. Schwarz, W. Bauhofer, K. Schulte and M.S.P. Shaffer Electric field-induced aligned multi-wall carbon nanotube networks in epoxy composites. Polymer, Volume 46, Issue 3, 26 January 2005, Pages 877-886

Claudia Nastase, F. Nastase, A. Vaseashta and Ioan Stamatin NCs based on functionalised nanotubes in polyaniline matrix by plasma polymerisation. Progress in Solid State Chemistry, In Press, Corrected Proof, Available online 23 February 2006

Reto Haggenmueller, Fangming Du, John E. Fischer and Karen I. Winey. Interfacial in situ polymerisation of single wall carbon nanotube/nylon 6,6 NCs. Polymer, In Press, Corrected Proof, Available online 20 February 2006

Cheol Park, Zoubeida Ounaies, Kent A. Watson, Roy E. Crooks, Joseph Smith, Jr., Sharon E. Lowther, John W. Connell, Emilie J. Siochi, Joycelyn S. Harrison and Terry L. St. Clair. Dispersion of single wall CNTs by in situ polymerisation under sonication. Chemical Physics Letters, Volume 364, Issues 3-4, 4 October 2002, Pages 303-308

Gary Loblick Marc Godin. Plastics market opportunity study prepared for Alberta economic development March 2002 by: http://www.thecis.ca/working%20papers/Plastic%20Market%20Opportunity%20Study%20Final.pdf

Freedonia Group (03-01-2006), Market report on NCs to 2010

National Statistics Office http://www.statistics.gov.uk/abi/subsection_dh.asp.