

A REVIEW OF THE APPLICATIONS OF NANOCARBON POLYMER COMPOSITES

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Nanotechnology offers fundamentally new capabilities to architect a broad array of novel materials, composites and structures on a molecular scale. It is potentially capable of redefining the methods used for developing lighter, stronger, high-performance structures and processes with unique and nontraditional properties. This review summarizes different classes of nanocarbon-based polymer composites and their applications. Also, it highlights different ways to create smaller, cheaper, lighter and faster devices using nanocarbon-based polymer composites. The potential applications of such materials are in the fields of membrane, aviation, electronics, polymer composites, as well as the marine and transport industries. A detailed description of nanocarbon-based composite materials manufactured from PE, PP, PS, PS, PVC, PPS, ABS, PMMA, nitrile rubber, etc. is also reviewed. Some of the major applications of carbon-based polymer nanocomposites are in the tyre industry, semiconductors, and many more, which has brought about the new, developing and exciting research field called nanoscience.

Keywords: Polymer composite; nanocarbon; carbon black; applications.

1. Introduction

Nanocomposites play a significant role in one of the most promising technologies, known as nanotechnology. Nanocarbon polymers provide enormous possibilities to human civilization. Activated carbons have been used since the prehistoric age and have been playing major roles in many applications.^{1–4} In the last decade, nanocomposite materials, consisting of polymeric matrix materials and nanofillers, have held scientific, industrial and academic significance due to their improved properties.

At low filler contents as compared with the conventional micro and macro or neat counterparts, they exhibit superior property enhancements. They will constitute 20% of demand in 2025. Thermoplastic composites are superior to conventional microscale composites and can be synthesized using simple and inexpensive techniques. Polymer nanocomposite markets have been slow in development to date, but seem ready to take off with increasing application in the automotive and packaging sectors, aviation and many more.⁴ As commercial interest

has moved beyond pilot programs and niche applications, it appears that nanocomposites are finally ready for a breakthrough in these markets. By 2011, nanocomposite demand will reach by 150,000 tpa in the USA. Growth will be fueled by declining prices of nanomaterials and nanocomposites, as production levels increase while the technical issues concerning the dispersion of nanoadditives in the compounds are resolved. By 2025, it is expected that nanocomposites will be a US\$9 billion market, with volumes nearing 5 million tons.⁵ Whereas thermoplastics currently constitute virtually all demands for nanocomposites, and the compounds based on thermoset resins will eventually become a substantial part of the market, in the coming decades the most rapid gains will be seen in higher-priced resins such as engineering plastics, for which the additional cost of nanomaterials is not a critical factor. In the future, however, nanocomposites based on commodity plastics, such as polypropylene, polyethylene and PVC, will dominate the market. Among thermosets, nanocomposites will make the strongest impact as enhancements for reinforced polyester and epoxy compounds. However, by 2025, electrical and electronic applications will gain in prominence, as nanotube-based composites will penetrate a sizable portion of the market as a substitute for other conductive materials. Construction will emerge as a significant market as nanocomposites begin to replace fiber-reinforced plastics in a number of applications. Nanocomposites are expected to penetrate a number of key packaging applications, including soft drinks, beer, food, pharmaceuticals and electronics, driven by the improved barrier, strength and conductive properties that they offer.⁶ The automotive segment is projected to generate the fastest demand for nanocomposites if the cost-performance ratio is acceptable. Some automotive production examples of nanocomposites are the following: first commercial application on the 2002 GMC Safari and Chevrolet Astro van; body side molding of the 2004 Chevrolet Impala (7% weight savings per vehicle and improved surface quality compared with TPO and improved mar/scuff resistance); cargo bed for GM's 2005 Hummer H2 (seven pounds of molded-in-color nanocomposites); fuel tanks (increased resistance to permeation); under-hood timing gage cover (Toyota) and engine cover (Mitsubishi). In 2006, nearly all nanomaterial demand consisted of carbon black in conductive composites. However, as material and production costs of clay-based nanocomposites fall,

clays will rise to account for over half of all nanomaterial demand by volume in 2025.⁶ Similarly, a decline in price will enable rapid commercialization of carbon nanotubes, which will eventually gain over 60% of the nanocomposite material market in value terms.

According to a report by Global Industry Analysts Inc., the global nanocomposite market will reach 989 million by 2010. Worldwide demand for nanocomposites is increasing rapidly in packaging, automotive, electrical and other applications due to their superior thermal, electrical, conductive and other properties.⁴ Development of industry-related nanocomposites with enhanced features and expanding research activities in development of new nanocomposites are among the factors that will drive the nanocomposite market in the coming years. The US and Europe dominate the global nanocomposite market, with a collective share of over 80% of the volume sales for 2008 (Table 1). Research institutions and companies are engaged in the exploration of efficient methods for developing nanocomposites in large volumes, and at low cost. Increased R&D activities and the advent of innovative materials are expected to widen the application areas for nanocomposites. The packaging segment represents the largest end-use market for nanocomposites in the world, with consumption estimated at 284 million pounds for 2008. The automotive segment has been projected to generate the fastest demand for nanocomposites during the period 2001–2010. Several global plastic suppliers have already commercialized products based on nanocomposite materials, with the majority of the efforts focused on either nylons or polyolefins.² Industries are also optimistic about the future role of these novel materials, owing to the growing number of research studies conducted across the world. The development of innovative nanocomposite polyolefins and an array of other resin matrices and nanofillers is expected to

Table 1. Representation of US nanocomposite demand (million pounds).⁴

| | 2005 | 2010 | 2020 | % annual growth 2005–2020 |
|----------------------|------|------|------|------------------------------|
| Nanocomposite demand | 154 | 344 | 7030 | 29 |
| Thermoplastics | 152 | 329 | 5600 | 27 |
| Thermosets | 2 | 15 | 1430 | 55 |

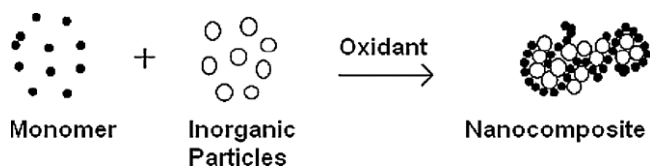


Fig. 1. Formation of nanocomposites.⁷

bolster the market scenario. Technological advancements will reduce manufacturing costs, and enable the development of low-cost nanocomposites. The major players profiled in the report include 3M ESPE, Arkema Group, BASF AG, Cabot Corporation, Cyclics Corporation, DSM Somos, Du Pont (E. I) De Nemours and Company, Technologies Inc., Evonik Degussa GmbH, Foster Corporation, Hybrid Plastics, Industrial Nanotech Inc., Inframat Corporation, In Mat Inc., Nanocor Incorporated and Nanodynamics Inc.⁴ Continuous demand from different end-use sectors and development of advanced and superior nanocomposites will stimulate their growth. The need of end-users for new and better nanocomposites is one of the major reasons expected to drive the development of a new array of nanocomposites. Identifying potential markets, intensifying research activities, and government funding for R&D operations constitute major factors in the commercialization of nanocomposites. A few nanocomposites have already reached the marketplace, while a few others are on the verge, and many remain in the laboratories of various research institutions and companies. Polymer nanocarbon composite materials have attracted the interest of a number of researchers, due to their synergistic and hybrid properties derived from several components.⁷ A simple representation for the formation of nanocomposites is presented in Fig. 1.

2. Future Perspectives on Nanocarbon Polymer Composites in Nanoscience

The science and technology of nanoscale materials has roots as old as chemistry itself, from the formulation of precious metal colloids for medieval stain glass to the Romans' use of cement.⁸ As a separate field, nanoscience and nanotechnology began to emerge some 20 years ago,⁹ and a database search yields more than 500 review articles in this area. The focus here will be on materials with domain dimensions below 100 nm (1 nm = 1 billionth of

a meter), e.g. length scales below those observable by simple optical or even confocal microscopy. For scale, nanosized objects are 100–10,000 times smaller than mammalian cells. The tiny, black and tubular-type nanomaterials will change the global scenario, the way we live, work and communicate. Nanotechnology could provide the ability to better understand and design complex solutions on an atomic and molecular scale. The most attractive nanotechnology-related nanomaterial is considered to be one-dimensional carbon nanotubes (CNTs). A large number of CNT-derived products are already in use and their viability strongly depends on the success of their commercialization. Although nanotube-filled polymers show obvious application for high-strength, lightweight and high-performance composites, there have not been many traditional carbon fibers.

3. Processing and Tailoring

Because of their nanometer scale and high aspect ratio, fabrication and investigation of nanotube/polymer composites present considerable challenges. The main problem is in creating a good interface between nanotubes and the polymer matrix to achieve the load transfer necessary for enhanced mechanical response in high-performance polymers.⁸ CNTs are usually supplied in highly entangled bundles, making handling and dispersion during composite processing a formidable hurdle. To optimize CNT composites, one must maintain high CNT aspect ratios, orient the CNTs, enhance interfacial interactions and eliminate slippage between the CNTs in ropes or between the layers in MWNTs. Regarding nanotube availability, since very little SWNT material is available, most investigators have been limited to working with milligram quantities.¹⁰ This may be problematic, since benchtop processing may not always be representative of larger-scale processing. This problem has been partially solved by working with vapor-grown carbon fibers (VGCFs), a cheaper and more readily available material similar to CNTs, to build a knowledge base that can be applied to SWNT composites. Rapid upscaling of CNT manufacturing on one hand, and development of new and efficient small-scale mixers on the other, will resolve this issue. To date, several companies have been working on commercially viable processes for mass production of CNTs, striving to lower costs. For example, Carbon Nanotechnologies Inc. (CNI)

aspires to produce 1000 kg of nanotubes weekly by 2014. The goal is to achieve low-cost, high-yield and large-scale production resulting in high-purity material with controllable length, diameter and chirality. Several new methods have recently been suggested for reaching this goal. The most critical factor is production cost. Until cost is reduced to a competitive level with existing fibers, large-scale use of nanotubes is unlikely. Additional issues are quality (which requires reliable characterization methods still under development), how to handle CNTs, and health risks associated with CNT exposure. Before considering the use of CNTs in commercial products as a success, at least four obstacles have to be overcome: (1) how to obtain high-purity CNTs, as metallic impurities often remain after the fabrication process, which can give rise to toxic properties; (2) how to manipulate these tiny materials; (3) the most important “safety” issue has to be clarified based on long-term and systematic biological studies; (4) how to control the chirality of CNT.^{9,10} Extensive and intensive efforts in both academy and industry are looking for a solution to these obstacles, and once a solution has been found, CNTs will play a key role as an innovative material of the 21st century in a number of industrial processes.

We have gone beyond the first mountain of science, the second mountain of technology and the third mountain of economy by producing CNTs successfully on a large scale and at reasonable cost (Fig. 2). Now we are striving to climb the mountain of society. By sharing information on risks

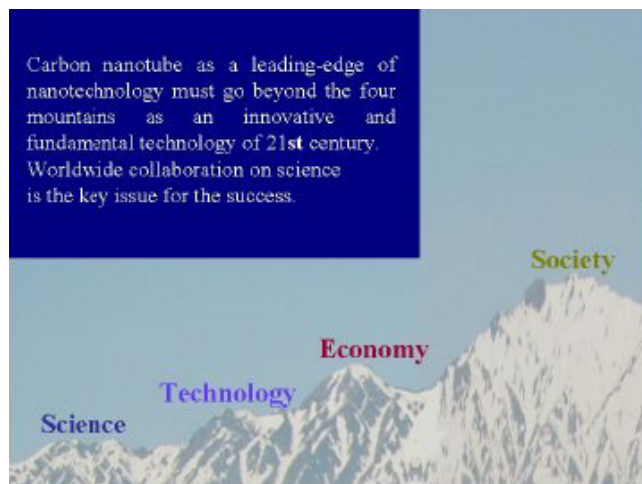


Fig. 2. The carbon nanotube as a leading edge of nanotechnology must go beyond the four mountains as an innovative and fundamental technology of the 21st century.¹⁰

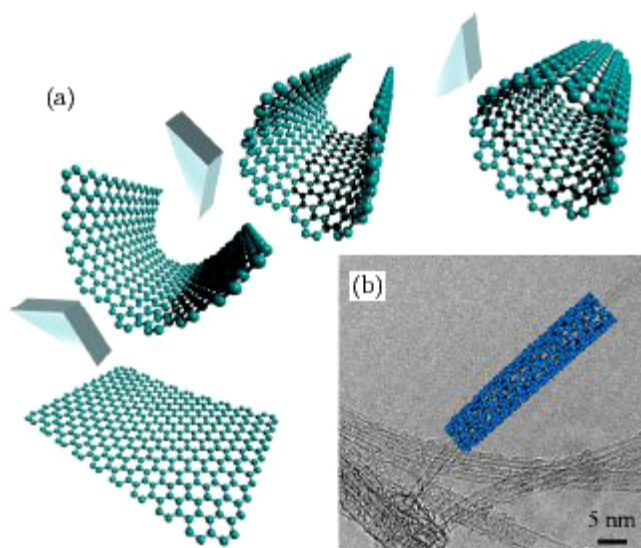


Fig. 3. (a) CNTs could be visualized by rolling sheets of graphene (sp^2 carbon honeycomb lattice) into a cylinder of nanometer size diameter. (b) The structure of CNTs has been explored early on by high-resolution transmission electron microscopy.¹¹

and benefits of CNTs with all stakeholders, we will finally reach the top of a nanotube mountain and prove that the CNT is an e-material for the 21st century.

Worldwide collaboration on science is the key issue for the success. Over the last decade, nanotechnology has received lots of attention from within society as a potential source of novel solutions to many of the world’s existing and emerging problems. Geometrically, CNTs can be visualized by rolling sheets of graphene into a long hollow tubule (Fig. 3). The unique configuration of this material imparts excellent physicochemical properties.¹¹ For instance, Young’s modulus of CNTs is stiffer than any other material, while their tensile strength is 100 times that of steel. Maximal electrical current density is 100 times greater than for copper wire, and carrier mobility is *ca.* $105 \text{ cm}^2/\text{Vs}$. CNTs show great promise for numerous applications in the near future and their excellent properties have already resulted in their use in commercially available products.

The field of materials science is currently undergoing a shift from developing traditional materials such as metals, ceramics, polymers and composites to a more revolutionary trend of developing nanostructures, which are functionalized, self-assisting and occasionally even self-healing materials. The question is whether CNT polymer composites can meet these requirements: they

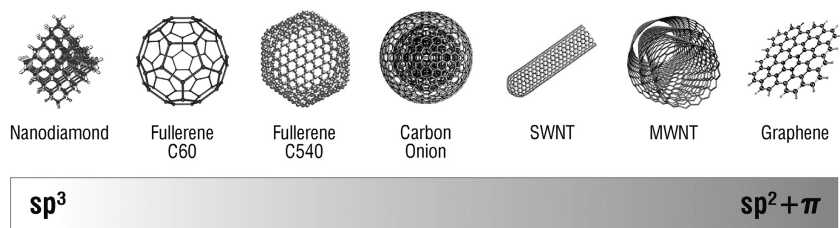


Fig. 4. Hybridization states of carbon-based nanomaterials. Many chemical and electronic properties of carbonaceous nanomaterials are determined by the dominant hybridization state of the carbon-carbon bonds.¹⁴

appear attractive for many applications; however, significant breakthroughs still need to be realized.

4. Carbonaceous Nanomaterials

Arguably the oldest, and easiest nanoparticles to make, are of those of carbon: the use of carbon black from fuel-rich partial combustion for ink, pigment and tattoos dates back more than 3000 years, but remains a topic of current research interest.^{11,12} The largest modern use of nanophase carbon, by far, is filler in rubber tyres, for which more than 8 million metric tons are produced each year; roughly another million tons are used as pigments. Various synthetic carbon materials exist that have nanometer scale features. Macroporous carbon materials can be created via inverted opal synthesis (colloidal template method) but they are usually amorphous.¹¹ Crystalline carbon nanomaterials can be created via high-voltage arc electricity, laser ablation, or growth under high temperatures with metal-based precursors or nanoparticles as catalysts.¹³ In addition, fullerenes (e.g. C₆₀, C₇₂) and CNTs, either single-walled or multiwalled, can be synthesized in this way (Fig. 4).^{11,14}

5. Porous Nanomaterials

Long before the recent interest in nanoscience, the IUPAC divided porous materials and pore size into three categories: microporous (<2 nm), mesoporous (2–50 nm) and macroporous (>50 nm).¹⁵ There are increasingly popular use of “nanoporous” to describe all three of these categories. Synthetic methods for such materials range from crystal engineering to cooperatively assembled template methods and sol-gel chemistry.^{16,17} One of the biggest challenges in porous material synthesis is the precise control of the pore size while maintaining overall structural integrity as well as overall size.¹⁸ Mesoporous materials such as MCM-41¹⁹ and SBA-15^{20–22} have been the most successful porous materials to date and their application in catalysis,

photonics and tissue engineering, depending upon the pore size and type of material,^{16,23} has been particularly interesting. Synthesis of mesoporous materials involves the use of surfactant or block copolymer and a polymerizing inorganic precursor, preferably carried out at a pH near the isoelectric point (IEP) of the inorganic species.²⁴ It is a cooperative molecular assembly process²⁴ that makes use of all components of the synthesis solution. Functionalization of SWNTs takes place with polymers, zeolites, clay track-etched polycarbonate, anodized alumina, nanoporous membranes²⁵ or the self-assembly of functional molecules such as surfactants,²⁶ polyelectrolytes²⁷ or complex, etc. are used as hard templates, whereas surfactants like micelles, liquid crystals, etc. are used as soft templates, represented in Figs. 4 and 5.

6. Nanocarbon Polymer Composites

Nanocarbon polymer composites are materials that incorporate nanosized particles into a matrix of standard materials such as polymers. Adding nanoparticles can generate a drastic improvement in properties that include mechanical strength, toughness and electrical or thermal conductivity. The effectiveness of the nanoparticles is such that the amount of material added is normally only 0.5–5.0% by weight. They have properties that are superior to those of conventional microscale composites and can be synthesized using simple and inexpensive techniques.²⁸ A few nanocomposites have already reached the marketplace, while a few others are on the verge, and many remain in the laboratories of various research institutions and industries globally. The global nanocomposite market is projected to reach 989 million pounds by the end of the 2010, as stated in a report published by Global Industry Analysts, Inc. Nanocomposites comprising nanoparticles such as nanoclays (70% of volume) or nanocarbon fillers, carbon nanotubes, carbon nanofibers and graphite platelets are expected

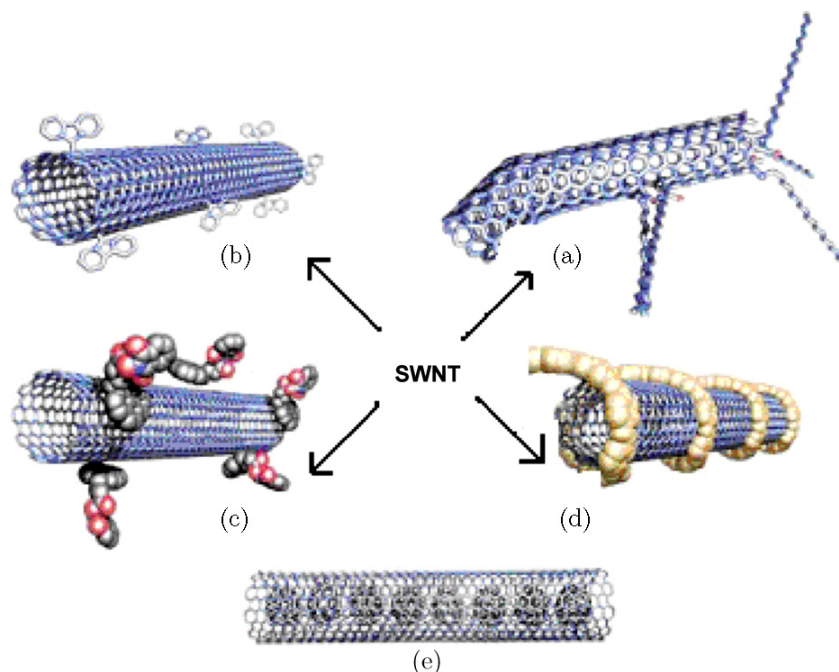


Fig. 5. Several functionalization mechanisms for SWNTs: (a) Defect-group functionalization; (b) covalent side wall functionalization; (c) noncovalent exohedral functionalization with surfactants; (d) noncovalent exohedral functionalization with polymers; and (e) endohedral functionalization with C_{60} .²⁴

Table 2. List of the main applications of nanocomposite polymers.²⁸

| Reference market | Nanofiller | Polymer matrix |
|---|---------------|------------------------|
| Barrier films | Organic clays | Nylon 6 |
| Packaging | Organic clays | PP |
| Electroconductive materials | Nanotubes | Nylon 12 |
| Colored parts in the automotive sector | Nanotubes | PPO/nylon |
| Bottles and films | Organic clays | Nylon 6 |
| Electroconductive materials | Nanotubes | PETG, PBT, PPS, PC, PP |
| Cables and wires | Organic clays | EVA |
| Various uses | Organic clays | Nylon 6 |
| Injection | Organic clays | PP |
| Beer bottles | Organic clays | Nylon MDX6 |
| Transport, the sea sector | Organic clays | Unsaturated polyester |
| Various uses, electroconductive materials | Organic clays | Nylon 6, PP |
| Flame-retardant materials | Clay, mica | Nylon 6 |
| Various uses | Clay, mica | POM |
| Various uses | Organic clays | Nylon 6, 12 |
| Fuel systems for cars | Organic clays | Nylon 6, 66 |
| Various uses | Organic clays | Nylon 6 |

to be a major growth segment for the plastics industry.

7. Different Types of Nanocarbon

The different types of nanocarbon include:

- (1) Carbon nanotubes
- (2) Carbon fullerenes
 - Carbon beads
 - Carbon cactus
- (3) Carbon honeycomb
 - Carbon fibers
 - Carbon diamond
 - Carbon graphite
 - Carbon black
 - Fishbone carbon nanofibers

The impact of nanocarbon on industry is expected to be quite disruptive, since performance improvements may be 100–1000 times greater than previous technological solutions. A conceptual scheme for the synthetic method is presented in Fig. 6. Further work demonstrated that intercalative polymerization of 1-caprolactam could be realized without needing to render the MMT surface organophilic.²⁸

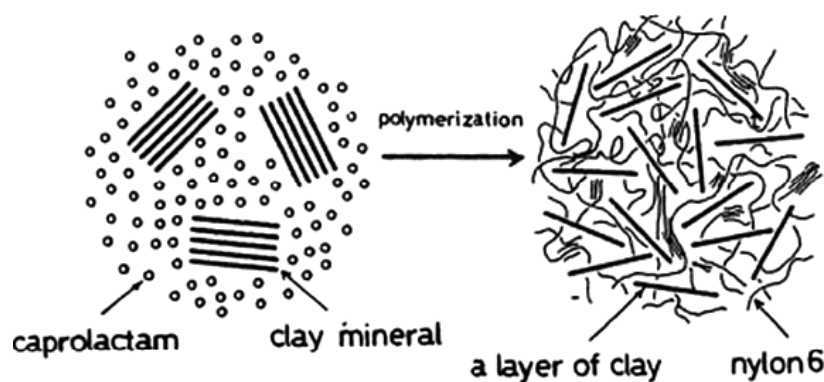


Fig. 6. Schematic illustration for synthesis of nylon 6/clay nanocomposite. (Reproduced from Usuki, Kojima, Kawasumi, Okada, Fukushima, Kurauchi and Kamigaito by permission of Materials Research Society, USA.²⁸)

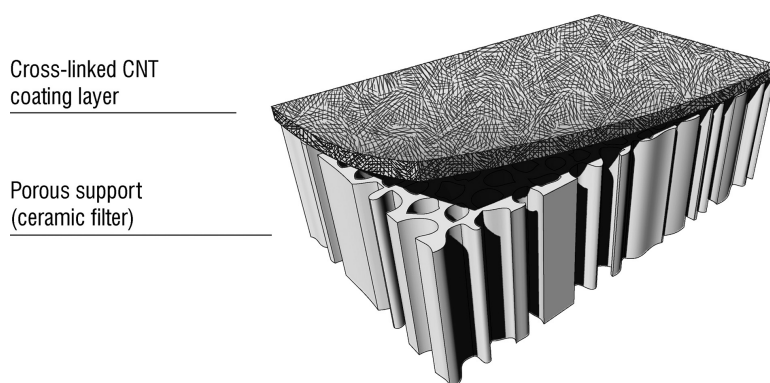


Fig. 7. Schematic of a CNT hybrid filter. A cross-linked CNT filtration layer atop a porous ceramic support provides the basis for a robust, regenerative water purification device.²⁸

8. Why We Need CB Nanocomposites

CB-filled polymers are widely used in industrial applications due to their cost advantage over other fillers. Typically, polymer matrices require large concentrations of CB to achieve sufficient electrical conductivity for various applications. One way to accomplish this is to increase the electrical conductivity of carbon nanofillers; for example, carbon nanotubes, nanofibers and CB²⁹ are electrically conductive and useful for improving polymer properties.²³ However, at the same time, the requirements with regard to activated carbons have become rigorous, thereby necessitating not only a high surface area but also a sharp pore size distribution, with pores of appropriate sizes. To meet these requirements and also from the viewpoints of energy and the environment, various precursors and their activation processes have been proposed. Carbon materials play an indispensable role in almost all electrochemical devices — to name a

few, batteries, supercapacitors and fuel cells.³⁰ The choice of carbon as the material is due to its unique properties of electrical conductivity and structural diversity. The polymers, strengthened with very low percentages of nanometric particles (about 2–5%), offer (when compared to the base resin) enormous improvements in terms of thermomechanical properties, barrier properties and fire resistance. Moreover, they can outperform traditional fillers and fibers (e.g. CB, glass, mineral fillers, calcium carbonate, graphite, metal oxides) in terms of heat resistance, dimensional stability and electrical conductivity. High CB concentrations can produce high viscosity during processing and impair mechanical performance.³¹ It is precisely this ease of processing and durability of the final object that makes CPC an attractive alternative for applications traditionally reserved for metals. Therefore, it is important to increase the electrical conductivity of CB-filled polymer composites, while preserving beneficial mechanical properties. Typically, polymer matrices require large concentrations of

CB to achieve sufficient electrical conductivity for various applications. These high CB concentrations can produce high viscosity during processing and impair mechanical performance.³²

9. Different Types of Polymers Used to Prepare CB Composites

Different types of polymers and fillers have been used so far to prepare nanocomposites. The polymers represented below show various applications incorporated with CB. PE, PP, PS, PVC, PPS, ABS, PMMA and poly(ethylene-coethyl acrylate)-carbon black (EEA-CB) were investigated.⁶

9.1. Types of polymers

- (i) *PVC*. Poly(vinyl chloride) is a well known plastic at the hardware store as PVC. The plumbing in houses is commonly a PVC pipe, unless it is an older house. PVC pipes in rural high schools with small budgets are used to make goalposts for their football fields. But there is more to PVC than just pipes. The “vinyl” siding used on houses is made of PVC. Inside the house, PVC is used to make linoleum for the floor. PVC is useful because it resists two things that hate each other: fire and water. Because of its water resistance it is used to make raincoats, shower curtains and water pipes. It has flame resistance, since it contains chlorine.
- (ii) *PMMA*. Poly(methyl methacrylate) is a plastic, used as a shatterproof replacement for glass. The clear barrier at an ice rink which keeps pucks from flying into the faces of hockey fans is made of PMMA. The chemical company Rohm and Haas makes windows out of it and calls it Plexiglas. PMMA has another advantage over glass. It is more transparent than glass. When glass windows are made too thick, they become difficult to see through. PMMA windows can be made as much as 13 inches (33 cm) thick and are still faultlessly transparent. This makes PMMA a wonderful material for building large aquariums, with windows which must be thick in order to contain the high pressure of millions of gallons of water. But PMMA is more than just plastic and paint. The painting *Acrylic Elf* (Fig. 8) was done by Pete Halverson with acrylic paints. Acrylic “latex” paints often contain



Fig. 8. PMMA used in paints.⁶

PMMA suspended in water. Lubricating oils and hydraulic fluids tend to get really thick and even gummy when they get really cold.

- (iii) *PE*. Polyethylene is probably the commonest polymer seen in daily life and the most popular plastic in the world. PE is employed to make grocery bags, and all types of bags used for packaging purposes, as well as shampoo bottles, children’s toys, and even bulletproof vests. At times some of the carbons, instead of having hydrogens attached to them, will have long chains of PE attached to them; this is also known as low-density polyethylene (LDPE). When there is no branching, it is called linear polyethylene, or high-density polyethylene (HDPE). Linear polyethylene is much stronger than branched polyethylene, but branched polyethylene is cheaper and easier to make. Inexpensive food containers are made from HDPE.
- (iv) *PS*. *Polystyrene is one of those popular polymers that are available globally.* It is an inexpensive hard plastic, and is probably the commonest polyethylene in everyday life. The outside housing of the computer is probably made of PS, as well as housings like those of hairdryers, TVs, CD and DVD players, and kitchen appliances. Model cars, airplanes and toys are made from PS. There are also foam packaging and insulation, and a lot of the molded parts on the inside of the car, like the radio knobs. In addition, PS is used to make drinking cups — hard plastic ones and also soft foamy ones (Fig. 9). A popular brand of PS foam is Styrofoam.
- (v) *PP*. Polypropene is a thermoplastic polymer, made by the chemical industry and used in a wide variety of applications, including packaging, textiles (e.g. ropes, thermal underwear



Fig. 9. Three containers made from PS.⁶

and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, automotive components and polymer banknotes. An additional polymer made from the monomer propylene, it is rugged and unusually resistant to many chemical solvents, bases and acids.

- (vi) *PPS*. Polyphenylene sulfide is an organic polymer consisting of aromatic rings linked with sulfides. Synthetic fiber and textiles derived from this polymer are known to resist chemical and thermal attacks. PPS is used to make filter fabric for coal boilers, paper-making felts, electrical insulation, specialty membranes, gaskets and packings. It is the precursor to a conducting polymer of the semiflexible rod polymer family. PPS, which is otherwise insulating, can be converted to the semiconducting form by oxidation or use of dopants.
- (vii) *ABS*. Poly(acrylonitrile butadiene styrene) is a very strong and lightweight polymer. It is strong enough to be used to make automobile body parts, but so light that Wasana can lift this front bumper fascia over her head with only one hand. Using plastics like ABS makes automobiles lighter, so they use less fuel, and therefore pollute less. ABS is a stronger plastic than polystyrene because of the nitrile groups of its acrylonitrile units. The nitrile groups are very polar, so they are attracted to each other. This allows opposite charges on the nitrile groups to stabilize each other. This strong attraction holds ABS chains together tightly, making the material stronger. Also, the rubbery polybutadiene makes ABS tougher than polystyrene.
- (viii) *Nitrile rubber*, well known as Buna-N, Perbunan, or NBR, is a synthetic rubber copolymer of acrylonitrile (ACN) and butadiene.

Tradenames include Nipol, Krynac and Europrene. Nitrile butadiene rubber (NBR) is a family of unsaturated copolymers of 2-propenenitrile and various butadiene monomers (1,2-butadiene and 1,3-butadiene). While its physical and chemical properties vary depending on the polymer's composition of nitrile, this form of synthetic rubber is generally resistant to oil, fuel and other chemicals (the more nitrile within the polymer, the higher the resistance to oils but the lower the flexibility of the material). Its resilience makes NBR a useful material for disposable labs, cleaning of lab equipment, sophisticated instruments and examination gloves. Nitrile rubber is more resistant than natural rubber to oils and acids, but has inferior strength and flexibility. Nitrile gloves are nonetheless three times more puncture-resistant than natural rubber gloves.

10. Tire Industry

Pneumatic tires are manufactured according to relatively standardized processes and machinery, in around 450 tire factories in the world. Over 1 billion tires are manufactured annually, making the tire industry the major consumer of natural rubber. Tire factories start with bulk raw materials such as rubber, carbon black, and chemicals producing numerous specialized components that are assembled and cured. The first radial tire designs were patented in 1915 by Arthur W. Savage, a successful tire manufacturer and inventor in San Diego, California. Savages patents expired in 1949. The design was further developed and widely commercialized by Michelin in 1946.³³ Due to its advantages, it has the standard design for essentially all automotive tires. Tires are not just fabricated from rubber. They would be far too flexible and weak. Within the rubber is a series of plies of cord that act as reinforcement. All common tires (since 1960s) are made of layers of rubber and cords of polyester, steel and other textile materials. This network of cords that gives the tire strength and shape is known as Carcass. In the past, the fabric was built up on a flat steel drum, with the cords at an angle of about $+60^\circ$ and -60° from the direction of travel, so they crisscrossed each other. They were called cross-ply or bias ply tires. The plies were turned up around the steel wire beads and the combined tread-sidewall applied.

11. Uses of Nanocarbon Composites as Membrane

CNTs have been identified as fundamentally new nanoporous materials that show great potential for sensors,³⁴ composites³⁵ and catalytic supports,³⁶ and as membrane materials.^{37,38} In particular, CNTs, whose inner core diameter can be as low as 4 Å³⁹ have been earmarked as possible selective nanopores in membrane materials.^{40,41} Atomistic simulations have predicted that if used as membranes, CNTs should have unprecedented flux and selectivity properties compared to other branded inorganic materials. The transport of gases in CNTs with a diameter of ~ 1 nm was predicted in the orders of magnitude faster than zeolites.^{17–21} These exceptionally high transport rates have been attributed to the inherent molecular smoothness of the nanotubes. Some of these theoretical predictions have been verified experimentally with larger CNTs. Holt *et al.*³⁵ have constructed nanotube–Si₃N₄ composite membranes using chemical vapor deposition. They used aligned double-walled carbon nanotubes (DWNTs) having a diameter of about 1.6 nm and showed that gas flow through the CNTs is 1–2 orders of magnitude faster than would be expected for flow through a commercial polycarbonate nanoporous membrane with a 15 nm pore size. Holt *et al.*³⁵ also found that the liquid water flow through their nanotube membranes was more than three orders of magnitude faster than expected from hydrodynamic flow calculations. Moreover, these nanotube membranes exhibited extraordinarily high size exclusion selectivity. In related work, Hinds *et al.*³⁴ constructed polymer–nanotube composite membranes using multiwalled carbon nanotubes (MWNTs) having large 3 diameters (6–7 nm). They have verified that transport of liquids (higher alkanes, water) is orders of magnitude faster than can be accounted for by conventional hydrodynamic flow.³⁵ The use of single-walled (SWNT), smaller-diameter CNTs as membranes is particularly intriguing, because, in addition to fast transport rates, the 4–12 Å pore openings are in the range that might be size-selective for gas mixtures. In order for SWNTs to effectively act as channels in a membrane, however, they have to be aligned vertically relative to penetrate the stream. This is perhaps the single most important challenge facing the fabrication of SWNT membranes (Figs. 10 and 11).³⁷ In their studies, Hinds *et al.*³⁴ and Holt

*et al.*³⁵ used chemical vapor deposition to grow oriented CNTs. While producing well-aligned CNTs, this process is expensive and tedious, and is limited to fabricating samples with small areas (e.g. sub-cm²). Alternatively, CNTs have been aligned by employing filtration methods,^{36,37} although to date this approach has been successful only with MWNTs. CNTs have been identified as fundamentally new nanoporous materials that show great potential for sensors, composites and catalytic supports,³³ and as membrane materials.^{34,35} In particular, CNTs, whose inner core diameter can be as low as 4 Å,^{7,8} have been earmarked as possible selective nanopores in membrane materials.^{31,32} In order for SWNTs to effectively act as channels in a membrane, however, they have to be aligned vertically relative to the penetrant stream. This is perhaps the single most important challenge facing

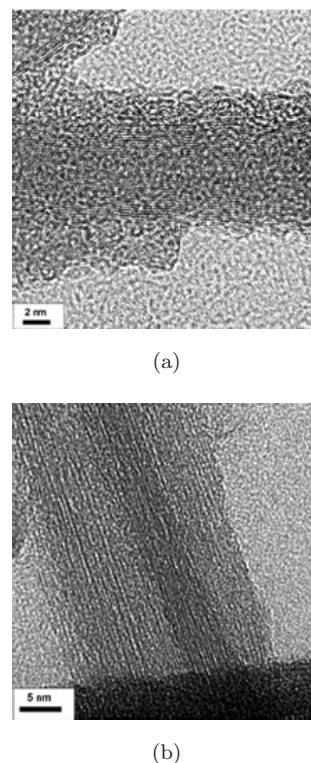
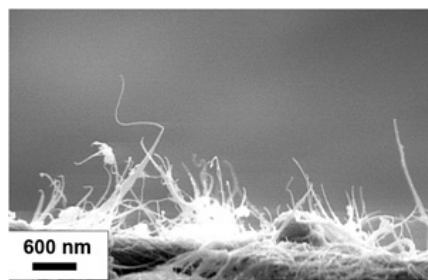
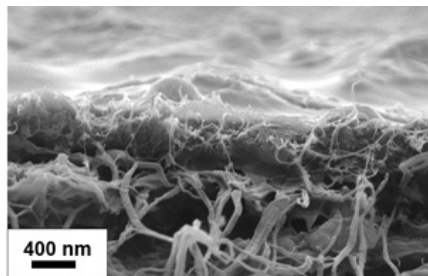


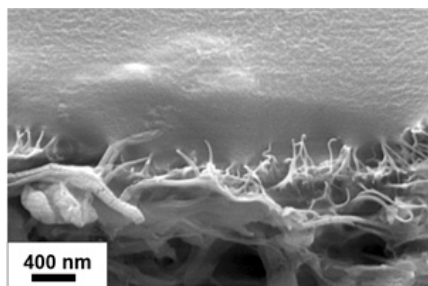
Fig. 10. SWNT pore structure. (a) Differential pore volume plot of the SWNT at 77 K using N₂. The pore diameter of the SWNT sample was calculated by the Horvath–Kawazoe (H–K) method. The H–K method used here was derived for cylindrical pores. The distribution in micropore diameter of the SWNT ranges from 0.95 to 1.8 nm, showing strong peak intensity at 1.2 nm. Therefore, the average pore diameter of the SWNT in this study is estimated to be 1.2 nm. (b) Zero-loss filtered (energy slit width of the 10 eV) high-resolution TEM (HRTEM) image of the multiwalled CNT that is transformed from SWNTs after acid treatment.³⁷



(a)



(b)



(c)

Fig. 11. SWNT pore structure. (a) Differential pore volume plot of SWNT ranges from 0.95 to 1.8 nm, showing strong peak intensity at 1.2 nm. (b) Zero-loss filtered (energy slit width of 10 eV) high-resolution TEM (HRTEM) image of the multiwalled CNT that is transformed from SWNTs after acid treatment. (c) Zero-loss HRTEM image of several SWNT bundles. CNT samples for high-resolution TEM experiments were prepared by utilizing dimethylformamide (DMF) as solvent to disperse them on an ultrathin amorphous carbon support film.³⁷

the fabrication of SWNT membranes. In their studies, Hinds *et al.*³⁴ and Holt *et al.*³⁵ used chemical vapor deposition to grow oriented CNTs. Alternatively, CNTs have been aligned by employing filtration methods,³⁷ although to date this approach has been successful only with MWNTs.

12. Advantages of Nanocarbon Composites

The advantage of nanocarbon was meant large industries in tires, cars, printing, pencils, laptops,

computers, printers, photocopiers, laboratory tables, and nanocarbon composites have huge hydrogen as energy source with combustion product is water (Figs. 12–19). Hydrogen is one of the important elements in chemical sciences and is easily regenerated.⁴¹ It is highly important and with the development of nanotechnology a suitable hydrogen storage system is necessary, satisfying a combination of volume and weight limitations.

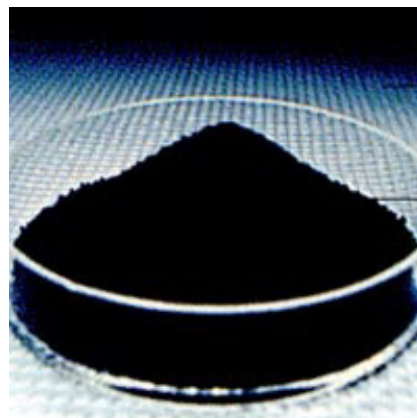
Fig. 12. Carbon black.⁴¹

Fig. 13. Tires.



Fig. 14. Train.



Fig. 15. Carbon graphite.

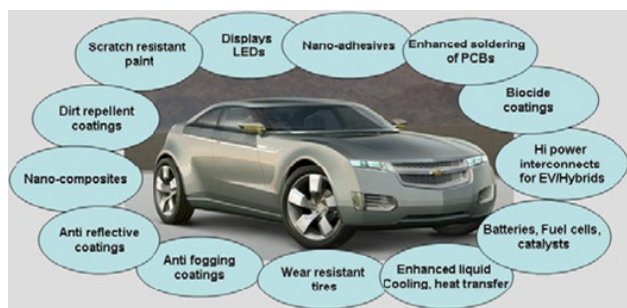
Fig. 16. C₆₀: 1000× better resolution than ink.

Fig. 17. Car.

The two commonly used means of storing hydrogen are gas phase and electrochemical adsorption. Because of their cylindrical and hollow geometry, and nanometer-scale diameters, it has been predicted that CNTs can store a liquid or a gas in the inner cores through a capillary effect. As a threshold for economical storage, the Department of Energy has set storage requirements of 6.5% by weight as the minimum level for hydrogen fuel cells. It has been reported that SWNTs were able to meet and sometimes exceed this level by using gas phase adsorption (physisorption). Yet, most experimental reports of high storage capacities are rather controversial, so that it is difficult to assess the



Fig. 18. Laptop.



Fig. 19. Madshus nanocarbon HP Skate Ski Package 2010/2011.

application potential. Another possibility for hydrogen storage is electrochemical storage. In this case, not a hydrogen molecule but a hydrogen atom is adsorbed, which is known as chemisorption. The main limitation is that a detailed understanding of the hydrogen storage mechanism and the effect of materials processing and its mechanism, which has been a major issue for decades and the nanocarbon process, can bring new technology/challenges for hydrogen storage.

13. The Most Promising Automotive Applications of Nanotechnology

These include:

- Improved materials with CNTs, graphene and other nanoparticles/structures

- Improved mechanical, thermal and appearance properties for plastics
- Coatings and encapsulants for wear and corrosion resistance, permeation barriers, and appearance
- Cooling fluids with improved thermal performance and joining interfaces for improved thermal cycle and crack resistance
- Metal alloys with greater mechanical strength
- Metal matrix and ceramics with improved mechanical properties
- Solder materials with crack resistance or lower processing temperature
- Displays with lower cost and higher performance
- Batteries for electric vehicles and fuel cells with improved energy capacity
- Automotive sensors with nanosensing elements, nanostructures and nanomachines
- Hybrid electric vehicles using electrical interconnects for high-frequency and high-power applications
- Electrical switching including CNT transistors, quantum transistors, nanoelectromechanical switches, electron emission amplification, and more efficient solar cells and self-assembly using fluid carriers.

14. Composite Materials

Composite materials have been in demand for decades, owing to their potential applications. Because of the stiffness of CNTs, they should be ideal candidates for structural applications. For example, they may be used as reinforcements in high-strength, low-weight and high-performance composites. Theoretically, SWNTs could have a Young's modulus of 1 TPa. MWNTs are less strong. Because the individual cylinders slide with respect to each other. Ropes of SWNTs are also less strong. The individual tubes can pull out by shearing and finally the whole rope will break. This happens at stresses far below the tensile strength of individual nanotubes. Nanotubes also sustain large strains in tension without showing signs of fracture. In other directions, nanotubes are highly flexible.^{39–44} One of the most important applications of nanotubes based on their properties will be as reinforcements in composite materials. However, there have not been many successful experiments showing that nanotubes are better fillers than the traditionally used carbon fibers. The main problem is to create a

good interface between the nanotubes and the polymer matrix, as nanotubes are very smooth and have a small diameter, which is nearly the same as that of a polymer chain. Secondly, nanotube aggregates, which are very common, behave differently toward loads than individual nanotubes. Limiting factors for good load transfer could be sliding of cylinders in MWNTs and shearing of tubes in SWNT ropes. To solve this problem, the aggregates need to be broken up and dispersed or cross-linked to prevent slippage. A main advantage of using nanotubes for structural polymer composites is that the nanotube reinforcements will increase the toughness of the composites by absorbing energy during their highly flexible elastic behavior. Another possibility, which is an example of a nonstructural application, is filling of photoactive polymers with nanotubes. PPV (poly-p-phenylenevinylene) filled with MWNTs and SWNTs is a composite which has been used in several experiments.^{45,46} These composites show a large increase in conductivity, with only a little loss in photoluminescence and electroluminescence yields. Another benefit of composites is that they are more robust than the pure polymer. Nanotube–polymer composites could also be used in other areas. One of the fastest-developing areas is in the biochemical field, as membranes for molecular separations for osteointegration (growth of bone cells). However, these areas are less well explored. The most important thing about nanotubes for efficient use of them as reinforcing fibers is how to maneuver the surfaces chemically to enhance interfacial behavior between the individual nanotubes and the matrix material. This plays an intriguing part in the development of CNTs.

15. Electrical Properties of Nanocarbon Composites

The electrical properties of nanocarbon composites are affected in different ways by several parameters.^{46–49} The dielectric properties of these materials depend on the frequency and the nature, concentration and size parameters of the conducting particles and the permittivity of the compounds.^{50–53} Achour *et al.*⁶³ reported that the electrical properties were investigated by impedance spectroscopy in the frequency range of 100 Hz to 0.2 MHz and in the temperature range of -120°C to 80°C . They showed that the dielectric response, for the carbon black volume concentrations near and above the conductivity threshold ϕC , can be fairly

well described by the anomalous low-frequency dispersion identified by Jonscher.⁵⁴ Achour *et al.*⁶³ reported on differential scanning calorimetry (DSC) measurements. DSC measurements were performed on a Shimadzu DSC-50 system.

16. Electrical Properties

Low frequencies (domain 1). As shown in Figs. 20(a) and 20(b), the terms ε' and ε'' , respectively, decrease with increasing frequency. This phenomenon is the anomalous low-frequency dispersion, characterized by a linear regime at these frequencies. This behavior is modeled by the fractional power laws given by Eq. (1). The fractional exponent p is obtained by the slope of the best lines fitting of the loss spectrum below the crossover frequency FC1. The AC conductivity is almost independent of the frequency [(Fig. 20(c))] and is dominated by a percolative behavior^{55–57}: $\sigma \bar{\omega} \rightarrow 0 \mathbb{P} \propto \bar{\delta} \phi - \phi C \mathbb{P}$, where t is the percolation exponent related to the dimensionality of the system. The lines represent the Jonscher empirical terms: Eq. (1) (domain 1) and Eq. (2) (domain 2), with $p = 0.99$ and $n = 0.21$.

Figure 20 shows the log–log plot of σ , obtained by extrapolation to zero frequency at 40°C as a function of $\phi - \phi C$ for concentration above the percolation threshold. By fitting Eq. (7) to $\sigma(\omega \rightarrow 0)$,

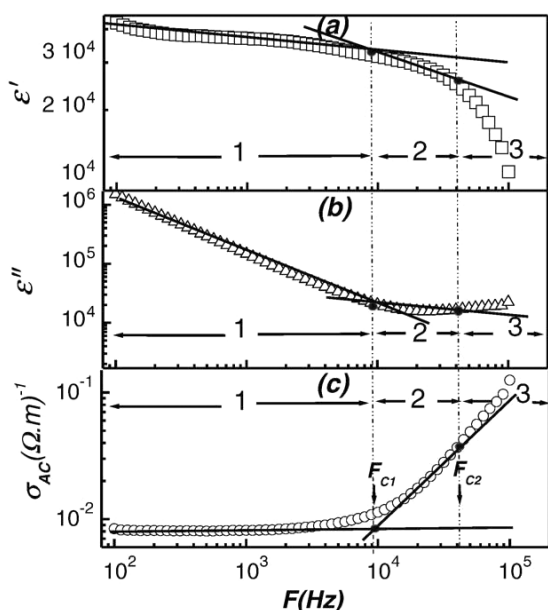


Fig. 20. (a) ε' , (b) ε'' and (c) σ_{AC} , as a function of frequency (logarithmic scales), for the EBA polymer/carbon composites at the volume concentration $\phi = 20\%$ and $T = 40^\circ\text{C}$.

one can obtain $\phi C = 11\%$ and $t = 2.24$.

$$\sigma \bar{\omega} \rightarrow 0 \mathbb{P} \propto \bar{\delta} \phi - \phi C \mathbb{P}. \quad (7)$$

The value of t is slightly greater than the universal value for three-dimensional percolating systems, which is equal to 2.^{58,59} The value of the percolation threshold obtained by fitting is lower than the theoretical value, which is equal to 17%.^{60,61} It is well known that the ϕC value depends strongly on the shape of the conducting inclusions,⁶² on the conductor particle structure and its morphology,⁴⁸ as well as on the materials processing.

Intermediate frequencies (domain 2). The terms ε' and ε'' decrease with increasing frequency. This phenomenon is the anomalous frequency dispersion, characterized by linear regimes [Eq. (2)] at the intermediate frequencies. The fractional exponents p and n are also obtained by the slope of the best lines fit of the loss spectrum below and above the crossover frequency $FC1 \approx 9\text{ kHz}$. These exponents p and n of the composite samples are for the concentrations above ϕC , at temperature 40°C.⁴³

High frequencies (domain 3). A third domain emerged near the second crossover frequency, $FC2 \approx 42\text{ kHz}$, which is probably the beginning of the transition to another electrical behavior which will appear at very high frequencies.

Mohamed *et al.*⁶⁴ have studied the dielectric response of PPy samples and PPy–PMMA composites in the radiofrequency and microwave ranges, with PPy concentrations varying from 6 to 12% by weight. This study has enabled one to identify the three domains: at low frequencies the conductivity is independent of frequency; at intermediate frequencies a relaxation phenomenon occurs; at microwave frequencies (FN1 GHz) a frequency-dependent conductivity appears, which is characteristic of the intrinsic hopping conductivity⁶⁴ and following a power law Fx , with the exponent x independent of the concentration of PPy. This last behavior can be explained by the hopping model of conductivity.

17. Electrical Conductivity of a Carbon Black-Styrene-Based Polymer

A new system of a thermoset styrene-based SMP filled with carbon black is presented. In order to realize the electroactive stimuli of the SMP, a

styrene-based SMP filled with carbon black (CB) is fabricated, and then its electrical conductivity is characterized.⁶⁵ Finally, the shape recovery demonstration of the SMP/CB (10%) composite is performed by passing an electric current.

18. Demonstration of Shape Recovery by Passing an Electric Current

Lan *et al.*⁶⁵ reported on a novel system of a thermoset styrene-based shape memory polymer incorporated with different amounts of nanocarbon powders. The SMP composite was cut into an “*n*” shape for demonstrating the shape memory effect. Upon heating by passing an electric current through it, the sample was cut into the “*n*” shape. The sample can be easily bent at 70°C (above T_g). After switching off the electric power and cooling back to the room temperature of 22°C, the temporary predeformed shape was formed. The sample was applied a voltage of 30 V through two conductive clampers [Figs. 21(a) and 21(b)]. The sample began to deploy about 5 s right after heating by the electric current. The whole deployment process lasted about 100 s. It is obvious that the deployment velocity of the sample in the range of 40–60 s is higher than those in other time ranges. Due to the high structures and homogeneous distribution of nanocarbon powders in the SMP matrix, the SMP composite shows excellent electrical conductivity, with a percolation threshold of 3.8%.

19. Mechanical Properties

The use of nanocarbon materials has been proposed to provide mechanical reinforcement to a polymeric

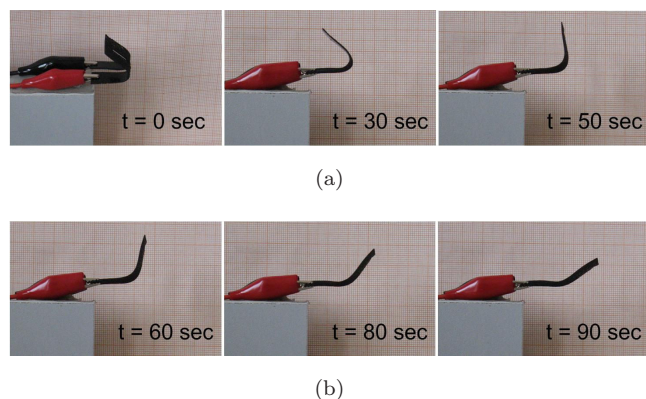


Fig. 21. (a) Sequences of shape recovery of CB by passing an electric current (30 V).⁶⁵ Sample dimensions of Fig. 21(b).⁶⁵

matrix. For example, polymer composites containing carbon nanofibers dispersed in a polymeric matrix have been known to exhibit mechanical properties such as stiffness, strength and toughness, and physical properties such as coefficient of thermal expansion, electrical and thermal conductivities which are superior to those of the polymeric matrix alone. Moreover, they do so at much lower loading levels than are required to reach comparable physical property thresholds using milled carbon fibers or carbon black. As a result, the processing characteristics of the polymer compound are modified to a much lower degree than polymer compounds synthesized by incorporation of milled carbon fiber or carbon black. For example, the one-dimensional structure of CNTs, their low density, their high aspect ratio, and extraordinary mechanical properties make them particularly attractive as reinforcements in composite materials. By now, hundreds of publications have reported on certain aspects of the mechanical enhancement of different polymer systems by CNTs.

20. Thermal Properties

Thermal properties of nanocarbon-containing polymer composites have been reported on in the literature. It has been found that these nanocarbon materials, such as CNTs and graphene, are very effective in improving the thermal stability of these composite materials. This may be due to the high thermal resistance of the nanocarbons, and another factor could be the contribution of nanocarbons to minimizing the permeation of the heat into the polymer matrix. Thermal degradation behavior of iPP/MWCNT nanocomposites

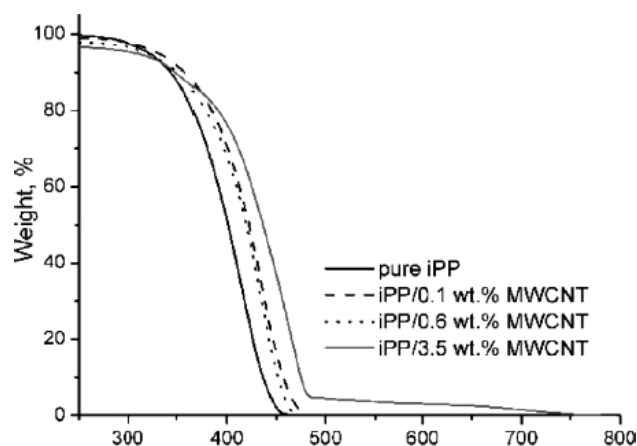


Fig. 22. TGA profile of the PP/CNT nanocomposite.

Table 3. Mechanical properties of CNT-based composite materials.^{66,67}

| Matrix | CNT type | CNT wt. fraction | Processing method | Composite tensile strength (% increase) | Composite modulus (% increase) |
|-------------|--------------------------------------|------------------|------------------------------------|---|--------------------------------|
| HDPE | Pristive MWCNTs | 5.00 | Melt missing | 12 | |
| HDPE | PEG-SiO ₂ modified MWCNTs | 1.00 | Melt extrusion | 20 | 50 |
| PP | Purified SWCNTs | 1.80 | Solution mixing | | |
| PP | Purified MWCNTs | 1.00 | Pan milling–melt mixing | 20 | 15 |
| Polystyrene | Purified MWCNTs | 1.00 | Solution casting | 25 | 42 |
| PVC | Grafted MWCNTs | 1.00 | Solution mixing | 280 | 200 |
| PMMA | Purified SWCNTs | 8.00 | <i>In situ</i> bulk polymerization | 50 | 100 |
| PC | Pristine MWCNTs | 1.00 | Solution mixing | 20 | 20 |
| PVA | Coated SWCNTs | 5.00 | Solution casting | 80 | 100 |

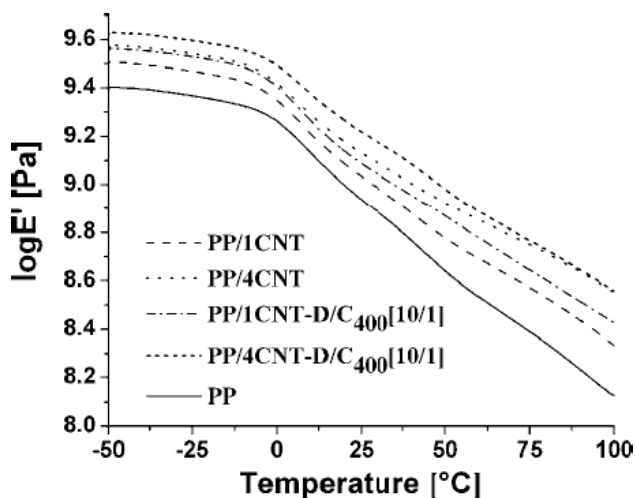


Fig. 23. Variation of the modulus of the PP/CNT nanocomposite with temperature.

has been investigated and found to improve by MWCNT at a very low level, as shown in Figs. 22 and 23 indicates the variation of the modulus of PP/CNT nanocomposite with temperature.^{68–70}

21. Uses of Nanocarbon Composites in the Aviation Industry

Nanocarbon composites have valuable applications in aviation/aerospace, cleantech and ballistic

protection. In the modern world, reducing soaring energy costs is critical to human survival. The aspiration of lightweight, fuel-saving technologies and the drive to go green have produced a tremendous upswing in demand for carbon-fiber-based composites, not only in aircraft but also in industrial and leisure applications. Cleantech applications for Fulcrum's technology include glass-coating of windows, doors and skylights with nanoparticles to reduce and regulate harmful UV, light, glare and heat. "Advanced composites" refers to materials in which a polymeric matrix (epoxy) serves as a type of glue that holds reinforcing material (carbon fiber, KevlarTM) in place.⁶³ Advanced composites are used in applications relating to all aspects of life. CNTs have extraordinary mechanical properties; 100 times stronger than stainless steel and 6 times lighter. They are the ultimate reinforcement material for advanced composites, owing to their very small diameters, high aspect ratios and exceptional strength.⁶⁴ CNT-reinforced composites are not produced at industrial levels of production, due to fundamental barriers: in dispersion studies, CNTs are uniformly dispersed in order to achieve efficient load transfer and uniform stress distribution. Interfacial stress transfer—external stress applied must be efficiently transferred to the CNTs.

22. Composite Materials' Market Potential

Aerospace market: in civil aviation, Boeing's new 787 Dreamliner and Airbus A-340 are made mostly from composites, and helicopters, a military aircraft and unmanned air vehicles (UAVs) are using composites at a greater rate. *Ballistics market:* composites are used in armor for military and civil vehicles.⁶⁴ *Sport equipment:* composites are widely used in equipment such as tennis rackets, golf clubs and skis. *Cleantech:* for example, propeller blades for wind generators constitute a fast-growing market of over US\$1 billion. The demands of aviation and sports for composites based on carbon fiber are estimated to be over 24,000 metric tons in 2010 and to double by 2015. The market value in 2010 is expected to be close to US\$23 billion.

23. Trends and Relevant Nanomaterials for Future Industrial Applications

In 2008, 3% of the total venture capital worldwide went into nanotechnology investment. Nanotechnology is expected to be incorporated into US\$2.6 trillion worth of goods by 2014, which represents 15% of the total global output. In recent years, the major emphasis in research activity regarding carbon-based nanomaterials has been on their production and characterization. Dresselhaus has commented that research has now achieved a good understanding of the structure and many basic properties of SWNTs, and their interrelation. Many of the properties of SWNTs are not observed in graphite. A basic understanding of the nanotube growth mechanism is still lacking, however. This information is important because of the close dependence of nanotube properties and their geometric structure. Major breakthroughs in the production of nanotubes are emerging. For example, Thomas Swann and Co. Ltd. has recently begun commercial production of high-purity single- and multiwalled nanotubes. The breakthrough was achieved as a result of ongoing collaboration with the University of Cambridge which resolved technical issues in scaling up laboratory procedures for the production of nanotubes. The produced nanotubes have an average diameter of 2 nm and a length of several microns, a purity of 70–90%, and cost 200 UK pounds/g. Field emission is seen as one of the most promising applications for carbon-based films. The

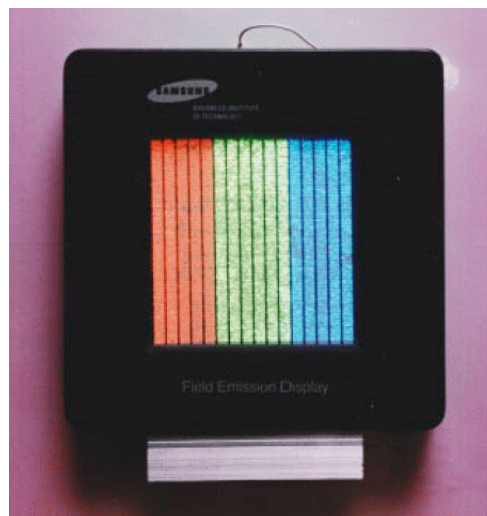


Fig. 24. The Samsung 4.5" full-color nanotube display. Emitting image of fully sealed SWNT-FED at color mode with red, green and blue phosphor columns.⁶⁶

most attractive forms of carbon for this application are CNTs which are capable of emitting high currents (Fig. 24). Controlled deposition of nanotubes on a substrate has recently become promising. There is concern, however, about the long-term stability of the films. Investigations have shown that the film can degrade due to resistive heating, and bombardment from gas molecules by the emitted electrons. Electrostatic deflection or mechanical stress can cause a change in the local shape of the emitter and a decrease in its effectiveness. Applications in nanotube flat panel displays have been anticipated and a demonstration model has been produced by Samsung. Field-emitting diode (FED) displays will counter the drawbacks of liquid crystal flat screens, such as low image quality and a restricted field of view. The viability of nanotubes for such applications is in question; problems in the correct deposition of the tubes, phosphor lifetime and charging of the spacers need to be overcome. There are further applications in lighting elements at the same time as in microwave amplification for commercial use.⁶⁶ A material for energy storage is a major area of research for carbon nanomaterials. Nanoporous carbon and CNTs are the important materials in this field.

24. Conclusions

Nanotechnology is expected to offer technological advantages in various important areas, such as production, processing, storage, transportation, safety and security. Products derived from

nanotechnology need to demonstrate their economic competitiveness prior to commercialization. Till now, information concerning the economic competitiveness of products derived from nanotechnology has been limited. This review has presented a wide spectrum of nanocarbon polymer composite materials and their applications in different important areas of science and technology. A wide range of properties and applications, especially in electronics, aerospace science, valuable household items, value-added products, polymers and the rubber industry, have been reviewed. Some of these applications are still at an early stage of research and development. It is expected that this review will help the scientific community to understand better this field of nanocarbon-based polymer composites and their applications.

Acknowledgments

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