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A DETAILED REVIEW OF RECENT PROGRESS IN CARBON NANOTUBE/CHITOSAN NANOCOMPOSITES

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The interest manifested, in recent decades, in biocomposites, is explained by the wide range of their potential applications in many fields. Special attention has been paid to carbon nanotubes, which exhibit superior electrical and mechanical properties that can improve the properties of biopolymer composites. The current review focuses on the progress made in carbon nanotube/chitosan composites. The effect of the properties of carbon nanotubes used as fillers was evaluated in chitosan biocomposites. Several methods are in use for the carbon nanotubes/chitosan composites formed by films and microfibers. The advances registered in the creation of nanofibers of carbon nanotube/chitosan composites prepared by electrospinning will be presented.

Keywords: nanobiocomposites, biopolymer composites, chitosan, carbon nanotubes

INTRODUCTION

At present, terms like "nanobiocomposites" or "biopolymer nanocomposites" are most frequently observed in environmentally friendly research studies. The synthetic polymers have been widely used in various applications of nanocomposites. However, they become a major source of waste after use, because of their poor biodegradability. On the other hand, most of the synthetic polymers show no biocompatibility in *in vivo* and *in vitro* environments. Hence, scientists were interested in biopolymers as biodegradable materials,[1] so that several groups of natural biopolymers, such as polysaccharides, proteins, and nucleic acids, came to be used in various applications.[2] Nevertheless, the use of these materials has been limited, because of their relatively poor mechanical properties. Therefore, research efforts have been made to improve the properties of biopolymers as a matrix by means of reinforcement techniques.[3]

Chitosan (CHT) is a polysaccharide biopolymer widely used as a matrix in nanobiocomposites, due to its high biocompatibility and biodegradibility.[4]

Numerous studies have focused on improving the physical properties of biopolymer nanocomposites by using the fundamental behavior of carbon nanotubes.[5]

The present study summarizes the recent advances in the production of carbon nanotubes/chitosan nanocomposites by several methods, special stress being laid on the preparation of CNTs/CHT nanofiber composites by the electrospinning method.

1. Biopolymers

Biomaterials have been defined as materials biocompatible with the living systems. Biocompatibility implies a chemical, physical (surface morphology) and biological suitability of an implant surface to the host tissues. Over the last 30 years, S. Ramakrishna *et al.* reviewed various biomaterials and their applications, as well as the utilizations of biopolymers and of their biocomposites for medical purposes.[6] These materials can be classified into natural and synthetic biopolymers. Synthetic biopolymers are cheaper and possess high mechanical properties. However, their low biocompatibility, compared with that of natural biopolymers, such as polysa-ccharides, lipids, and proteins, oriented the attention towards the latter. On the other hand, natural biopolymers usually have weak mechanical properties. Therefore, many efforts have been done to improve them by blending with some filler.[7]

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Among natural biopolymers, polysaccharides seem to be the most promising materials for various biomedical fields. They come from various sources, of animal, plant, algal and microbial origin. Among polysaccharides, chitosan is the most often applied, due to its chemical structure.[8]

1.1 Chitosan

Chitin (Fig. 1), the second most abundant natural polymer in the world, is extracted from various plants and animals.[9] Also, derivatives of chitin have been noticed, because of its insolubility in aqueous media. Chitosan (Fig. 2) is deacetylated by the derivation of chitin with free amine. Unlike chitin, chitosan is soluble in diluted and organic acids. The polysaccharides contain 2-acetamido-2-deoxy-β-D-glucose and 2-amino-2-deoxy-β-D-glucose. Deacetylation of chitin converts the acetamide groups into amino groups.[10] The deacetylation degree (DD), an important parameter defining chitosan properties, has been defined as “the mole fraction of deacetylated units in the polymer chain”.[11]

A wide variety of chitosan applications have been reported in recent decades due to the fact that they possess suitably modified specifications to impart the desired properties. Chitosan has the highest sorption capacity for several metal ions[12] and anionic dyes[13] by chemical or physical adsorption due to the existence of different functional groups. Also, chitosan has chromatographic properties according to the presence of hydroxyls and amino groups.[14] The high biocompatibility[15] and biodegradability[16] of chitosan recommend it for potential applications in biomedical,[17-22] cosmetic,[23] food preservative,[24] agriculture[25] and paper finishing[26] industries. Some other properties of chitosan, such as optical properties and ionic conductivity, have been utilized for numerous engineering applications.[27-29] Table 1 shows chitosan applications in various fields and their main characteristics.

1.2 Nanobiocomposites with chitosan matrix

Chitosan biopolymers have a great potential in biomedical applications, due to their biocompatibility and biodegradability. However, the low physical properties of chitosan limited their applications. The development of high performance chitosan biopolymers involves the incorporation of fillers that display significant mechanical reinforcement.[30]

Polymer nanocomposites have been reinforced by nano-sized particles with a high surface area to volume ratio, including nanoparticles, nanoplatelets, nanofibers and carbon nanotubes. Nowadays, carbon nanotubes are considered as potential fillers, as they improve the properties of biopolymers.[31] Based on such reports, the researchers assessed the effect of CNT fillers in the chitosan matrix, and evidenced the appropriate properties of CNT/chitosan nanobiocomposites with a high potential for biomedical applications.

2. Carbon nanotubes

Carbon nanotubes, which are tubulars of Buckminster fullerene, were discovered[32] by Iijima in 1991. They are straight segments of tube with arrangements of carbon hexagonal units.[33-34] In recent years, scientists have paid great attention to CNTs, as due to their superior electrical, mechanical and thermal properties.[35] Carbon nanotubes are classified as single-walled carbon nanotubes (SWNTs) formed by a single graphene sheet, and multi-walled carbon nanotubes (MWNTs) formed by several graphene sheets wrapped around the tube core.[36] The typical range of diameters of the carbon nanotubes are of a few nanometers (~0.8-2 nm at SWNTs[37-38] and ~10-400 nm at MWNTs,[39] respectively), and their lengths are up to several micrometers.[40] There are three significant methods for synthesizing CNTs, including arc-discharge,[41] laser ablation,[42] chemical vapor deposition (CVD).[43] The production of CNTs can be also realized by other synthesis techniques, such as the substrate,[44] the sol-gel[45] and the gas phase metal catalyst.[46]

The C−C covalent bonding between the carbon atoms is similar to that of the graphite sheets formed by sp^2 hybridization. The C−C covalent bonding between the carbon atoms is similar to that of the graphite sheets formed by sp^2 hybridization. As a result of this structure, CNTs exhibit a high specific surface area (about 10^3)[47] and, consequently, high tensile strength (more than 200 GPa) and elastic modulus (typically, 1-5 TPa).[48] The carbon nanotubes also show very high thermal and electrical conductivity. However, these properties differ as to the synthesis methods employed, defects, chirality, degree of graphitization and diameter.[49] For instance, depending on chirality,[50] the CNT can be metallic or semiconducting. The preparation of CNT solutions is impossible, because of their poor solubility.

Also, a strong van der Waals interaction of CNTs among several nanotubes leads to aggregation into bundles and ropes.[51] Therefore, various chemical and physical modification strategies will be necessary for improving their chemical affinity.[52] There are two approaches to the surface modification of CNTs, including covalent (grafting) and non-covalent bonding (wrapping) of the polymer molecule onto the surface of CNTs.[53] In addition, the reported cytotoxic effects of CNTs *in vitro* may be mitigated by chemical surface modification.[54] On the other hand, other studies show that the end-caps on nanotubes are more reactive than the sidewalls. Hence, the adsorption of polymers onto the CNT surface can be utilized, together with the functionalization of defects and associated carbons.[55]

Chemical modification of CNTs by covalent bonding is one of the important methods for improving their surface characteristics. Because of the extended π-network of the sp^2-hybridized nanotubes, CNTs have a tendency for covalent attachment, which introduces the sp^3-hibrydized C atoms.[56] These functional groups can be attached to the termini of tubes by surface-bound carboxylic acids (grafting), or by direct side-wall modifications of CNTs based on "*in situ* polymerization processing" (grafting form).[57] Chemical functionalization of CNTs creates various activated groups (such as carboxyl,[58] amine,[59] fluorine,[60] etc.) onto the CNT surface by covalent bonds. However, there are two disadvantages for these methods. First, the CNT structure may be decomposed, due to the functionalization reaction[61] and to a long ultrasonication process.[62]

Disruption of the π electron system is reduced as the result of these damages, leading to a decrease of the electrical and mechanical properties of CNTs. Secondly, the acidic and oxidation treatments often used for the functionalization of CNTs are environmentally unfriendly.[63] Thus, non-covalent functionalization of CNTs is largely recommended, as it preserves their intrinsic properties, while improving solubility and processability. According to this method, the non-covalent interaction between the π electrons of the sp^2 hybridized structure at the side-walls of CNTs and other π electrons is formed by π-π stacking.[64] These non-covalent interactions can appear between CNTs and the amphiphilic molecules (surfactants) (Fig. 3a),[65] polymers,[66] and biopolymers, such as DNA,[67] polysaccharides,[68] etc. In the first method, surfactants – including non-ionic surfactants, anionic surfactants and cationic surfactants – are applied for CNT functionalization. The hydrophobic parts of the surfactants are adsorbed onto the nanotube surface and the hydrophilic parts interact with water.[69] Polymers and biopolymers can functionalize CNTs by two methods, including the endohedral one (Fig. 3b) and wrapping (Fig. 3c). The endohedral method is a strategy for CNT functionalization. According to this method, nanoparticles – such as proteins and DNA – are entrapped in the inner hollow cylinders of CNTs.[70] In another technique, the van der Waals interactions and π-π stacking between CNTs and polymer lead to wrapping of the polymer around the CNTs.[71]

Various polymers and biopolymers, such as polyaniline,[72] DNA[73] and chitosan,[74] interact physically through wrapping of the nanotube surface and π-π stacking by the solubilized polymeric chain.

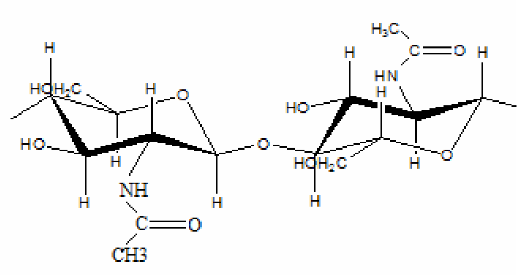

Figure 1: Structure of chitin

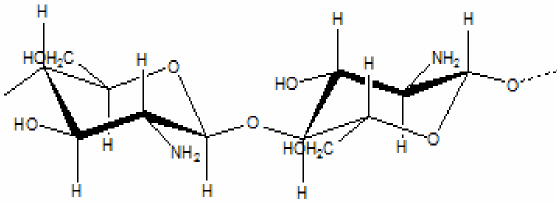

Figure 2: Structure of chitosan

Table 1

Chitosan applications in various fields and its main characteristics

Chitosan application		Main characteristics	Ref.
Water engineering		metal ionic adsorption	[12]
Textile industry		microorganism resistance, absorption of anionic dyes	[13]
Chromatographic separations		presence of free -NH2, primary -OH, secondary -OH	[14]
Biomedical application	biosensors and immobilization of enzymes and cells	biocompatibility, biodegradability to harmless products, non-toxicity, antibacterial properties, gel-forming properties and hydrophilicity, remarkable affinity to proteins	[18]
	antimicrobial and wound dressing	wound-healing properties	[19]
	tissue engineering	biocompatibility, biodegradable, and antimicrobial properties	[20]
	drug and gene delivery	biodegradable, non-toxicity, biocompatibility, high charge density, mucoadhesion	[21]
	orthopedic/periodontal application	antibacterial properties	[22]
Cosmetic application		fungicidal and fungi static properties	[23]
Food preservative		biodegradability, biocompatibility, antimicrobial activity, non-toxicity	[24]
Agriculture		biodegradability, non-toxicity, antibacterial properties, cell activator, disease and insect resistant ability	[25]
Paper finishing		high density of positive charge, non-toxicity, biodegradability, biocompatibility, antimicrobial and antifungal properties	[26]
Photography		resistance to abrasion, optical characteristics, film-forming ability	[27]
Solid-state batteries		ionic conductivity	[28]
Chitosan gel for LED and NLO applications		dye-containing chitosan gels	[29]

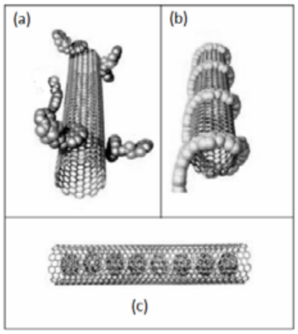

Figure 3: Non-covalent functionalization of CNTs by (a) surfactants, (b) wrapping, (c) the endohedral method

However, Jian *et al.*[75] created a technique for the non-covalent functionalization of SWNTs most similar to π-π stacking by PPE, without polymer wrapping.

Such functionalization methods can provide many applications of CNTs, the most important one being in biomedical science, as biosensors,[76] for drug delivery[77] and tissue engineering.[78]

2.1 Nanotube composites

Considering the low physical characteristics of biopolymers, fillers are recommended for the reinforcement of their electrical, mechanical and thermal properties. Following the discovery of CNTs, many efforts have been made for their application as fillers in other polymers, for improving the properties of the matrix polymer.[79] Ajayan was the first one to apply, in 1994, CNTs as a filler in epoxy resin, by the alignment method.[80] Later on, numerous studies have focused on CNTs as excellent substitutes for conventional nanofillers in nanocomposites. Recently, numerous polymers and biopolymers have been reinforced by CNTs. As already mentioned, these nanocomposites have remarkable characteristics, compared to the bulk materials, due to their unique properties.[81]

Several parameters affect the mechanical properties of the composites, including a proper dispersion, a large aspect ratio of the filler, interfacial stress transfer, a good alignment of reinforcement, and solvent selection.[82]

The uniformity and stability of nanotube dispersion in polymer matrices are most important parameters for the performance of composites. A good dispersion leads to efficient load transfer concentration centers in composites and to uniform stress distribution.[83] Pemg-Cheng Ma *et al*. reviewed the dispersion and functionalization techniques of carbon nanotubes for polymer-based nanocomposites, as well as their effects on the properties of CNT/polymer nanocomposites. They demonstrated that the control of these two factors led to uniform dispersion. Overall, the results showed that a proper dispersion enhanced a variety of mechanical properties of nanocomposites.[71]

The fiber aspect ratio, defined as "the ratio of average fiber length to fiber diameter", is one of the main effective parameters on the longitudinal elastic modulus.[84] Generally, the carbon nanotubes have a high aspect ratio, but their ultimate performance in a polymer composite is different. The high aspect ratio of the dispersed CNTs could lead to a significant load transfer.[85] However, the aggregation of nanotubes could lead to a decrease in the effective aspect ratio of the CNTs. Hence, the properties of nanotube composites are more enhanced than predicted, which is one of the processing challenges raised by poor CNT dispersion.[86]

The interfacial stress transfer has been performed by applying external stresses to the composites. The assessments showed that fillers take a significantly larger share of the load, due to the CNTs-polymer matrix interaction. Also, the literature on the mechanical properties of polymer nanotube composites explains the enhancement of Young's modulus by CNT addition.[87] Wagner *et al*. investigated the effect of stress-induced fragmentation of multi-walled carbon nanotubes in a polymer matrix. The results showed that polymer deformation generates tensile stress, which is transmitted to CNTs.[88]

A homogeneous CNT/polymer matrix alignment in the composite is another effective parameter of carbon nanotube composites. Some researchers[89] assessed the effects of CNT alignment on electrical conductivity and mechanical properties of SWNT/epoxy nanocomposites. The electrical conductivity, Young's modulus and tensile strength of the SWNT/epoxy composites increase with increasing SWNT alignment, due to an increased interface bonding of CNTs in the polymer matrix.

In 2007, Umar Khan *et al.* examined the effect of solvent selection on the mechanical properties of CNT-polymer composites fabricated from double-walled nanotubes and polyvinyl alcohol composites in different solvents, including water, DMSO and NMP. This work shows that solvent selection can have a dramatic effect on the mechanical properties of CNT-polymer composites.[90] Also, a critical CNT concentration was viewed as an optimum improvement in the mechanical properties of nanotube composites.[91]

Other parameters influencing the mechanical properties of nanotube composites are the size, crystallinity, crystalline orientation, purity, entanglement, and straightness. Generally, the ideal CNT properties depend on both matrix and type of application.[92]

The various functional groups on the CNT surface permit coupling with the polymer matrix. A strong interface between the coupled CNT/polymer creates an efficient stress transfer. As a previous point, stress transfer is a critical parameter for controlling the mechanical properties of a composite. However, the covalent treatment of CNT reduces the electrical[93] and thermal[94-95] properties of CNTs. Finally, these reductions affect the properties of nanotubes.

The matrix polymer can be wrapped around the CNT surface by non-covalent functionalization, which improves the composite properties through various specific interactions. In their turn, these interactions can improve the properties of nanotube composites.[96] In this context, researchers[97] evaluated the electrical and thermal conductivity in CNT/epoxy composites. Figures 4 and 5 show the electrical and, respectively, thermal conductivity in various filler contents, including carbon black (CB), double-walled carbon nanotube (DWNT) and multi-functionalization. The experimental results showed that electrical and thermal conductivity in nanocomposites is improved by the non-covalent functionalization of CNTs.

2.2 Mechanical and electrical properties of carbon nanotube/natural biopolymer composites

Table 2 provides mechanical and electrical information on a CNT/natural biopolymer composites compared to a neat natural biopolymer such as collagen,[98] chitosan,[99,100] silk[101] and cellulose,[102-105] using various preparing methods. The investigations show the higher mechanical and electrical properties of CNT/natural biopolymers, compared to those of natural biopolymer counterparts.

2.3 Carbon nanotube composite application

In recent years, special attention has been paid to applying nanotube composites in various fields. Researchers[106] reviewed nanotube composites based on gas sensors, known as playing an important role in industry, environmental monitoring, biomedicine, and so forth. The unique geometry, morphology and material properties of CNTs permitted their application in gas sensors.

There are many topical studies for biological and biomedical applications of carbon nanotube composites, based on their biocompatibility,[107] such as biosensors,[108] tissue engineering[95] and drug delivery[109] in biomedical technology.

On the other hand, the light weight, mechanical strength, electrical conductivity and flexibility are significant properties of carbon nanotubes for aerospace applications.[110]

Researchers[111] overviewed carbon nanotube composite applications, including electrochemical actuation, strain sensors, power harvesting and bioelectronic sensors, discussing the appropriate elastic and electrical properties for using smart nanoscale materials in the synthesis of intelligent electronic structures. In this context, a polyaniline/SWNT composite fiber was previously developed,[112] for evidencing its high strength, robustness, good conductivity and pronounced electroactivity. New battery materials[113] were presented, mention being made of the enhanced performance of artificial muscles[114] by using these carbon nanotube composites.

Researchers[115] addressed a sustainable environment and green technologies perspective for carbon nanotube applications. These contexts include many engineering fields, such as waste water treatment, air pollution monitoring, biotechnologies, renewable energy technologies and green nanocomposites.

Researchers[116] first discovered the photo-induced electron transfer from CNTs, after which the optical and photo-voltaic properties of carbon nanotube composites have been studied. The results obtained suggested a possible creation of photo-voltaic devices, due to the hole-collecting electrode of CNTs.[117]

Food packaging is another remarkable application of carbon nanotube composites. Usually, poor mechanical and barrier properties limit the application of biopolymers. Hence, an appropriate filler is necessary for promoting matrix properties. The unique properties of CNTs have improved thermal stability, strength and modulus, as well as the water vapor transmission rate of the industrially applied composites.[118]

3. Chitosan/carbon nanotube composites

The scientists' interest of recent decades in the creation of chitosan/CNT composites is explained by the unique properties of such composites. They attempted to create new properties by adding CNTs to chitosan biopolymers. For example, several articles were published, devoted to their various applications, summarized in the graph plotted in Figure 6.

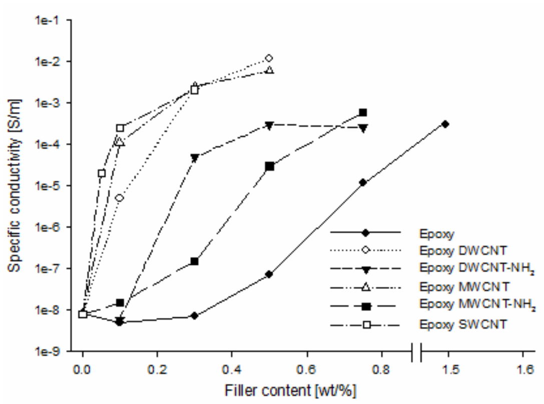

Figure 4: Electrical conductivity of nanocomposites as a function of filler content in weight percent[97]

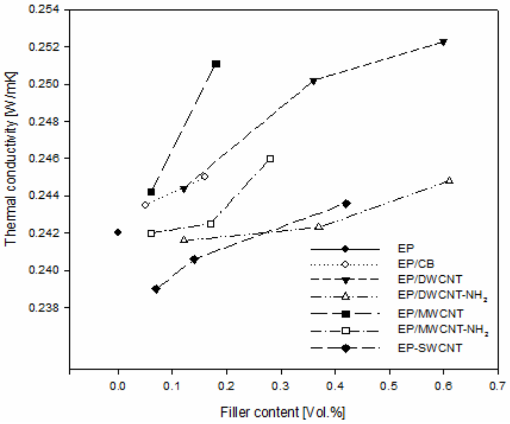

Figure 5: Thermal conductivity as a function of the provided relative interfacial area per gram composite (m^2/g)[97]

3.1 Chitosan/carbon nanotube nanofluids

The viscosity and thermal conductivity of nanofluids containing MWNTs stabilized by chitosan were investigated.[119] The MWNT fluid was stabilized with a chitosan solution. The investigations showed that the thermal conductivity enhancements obtained were significantly higher than those predicted by Maxwell's theory. It was also observed that dispersing chitosan into deionized water significantly increased the viscosity of the nanofluid, which explains its non-Newtonian behavior.

3.2 Preparation methods of chitosan/CNTs nanocomposites

There are several methods for the creation of nanobiocomposites, some of them considered for the preparation of chitosan/CNT nanocomposites. These methods are discussed in the following.

3.2.1 Solution-casting-evaporation

The electrochemical sensing of a carbon nanotube/chitosan system on dehydrogenase enzymes for preparing glucose biosensors was first assessed[120] in 2004. The nanotube composite was prepared by a solution-casting-evaporation method, according to which the CNT/CHT films were prepared by casting the CNT/CHT solution on the surface of a glassy carbon electrode, and then dried. Such a CNT/CHT system showed a new biocomposite platform for the development of dehydrogenase-based electrochemical biosensors, due to the provided signal transduction of CNT. The highly encouraging results of this composite's utilization in biomedical applications challenged numerous other investigations.

The effect of the CNT/CS matrix on the direct electron transfer of glucose oxidase and glucose biosensor was examined by some researchers.[121]

They exhibited high sensitivity and better stability, compared with pure chitosan films. Other investigators[122] used SWNT/CS films for preparing a new galactose biosensor with highly reliable detection of galactose. Some researchers[123] immobilized lactate dehydrogenase within MWNT/CS nanocomposite for producing lactate biosensors, as they provided fast response time and high sensitivity. Also, other investigators[124] demonstrated that immobilization of GOD molecules into a chitosan-wrapped SWNT film is an efficient method for the development of a new class of very sensitive, stable and reproducible electrochemical biosensors.

Several experiments were performed on a DNA biosensor based on chitosan film doped with carbon nanotubes.[125] The observation made was that a CNT/CHT film can be used as a stable and sensitive platform for DNA detection. The results demonstrated improved sensor performance by adding CNT to a chitosan film. Moreover, the analytical performance of glassy carbon electrodes modified with a dispersion of MWNT/CS for DNA quantification was reported.[126] This new platform immobilized the DNA and opened the doors to new strategies for the development of biosensors.

Other experiments[127] reported the high sensitivity of glassy carbon electrodes modified by MWNT-CHT for cathodic stripping voltametric measurements of bromide (Br-).

Qian *et al.*[128] prepared an amperometric hydrogen peroxide biosensor based on composite films of MWNT/CS. The results showed the excellent electrocatalytical activity of the biosensor for H_2O_2, with good repeatability and stability.

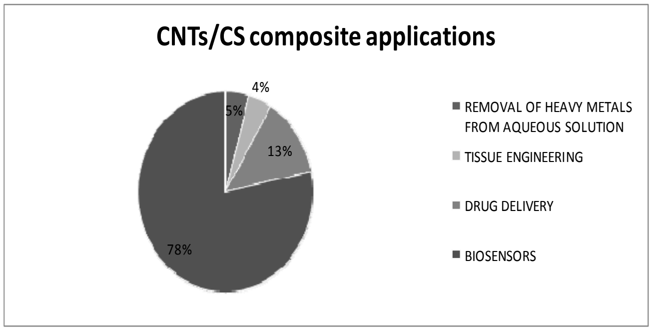

Figure 6: Chitosan/CNT nanocomposite applications

Some researchers[129] reported the effect of the CNT/CHT matrix on an amperometric laccase biosensor, evidencing some of its major advantages, involving detection of different substrates, high affinity and sensitivity, durable long-term stability, and facile preparation procedures.

Others[130] paid particular attention to the preparation of a SWNT/CHT film by the solution-cast method, then characterized their drug delivery properties. They found out that the SWNT/CS film enhanced the slowing down release of dexamethasone.

The growth of apatite on chitosan-multi-walled carbon nanotube composite membranes at low MWNT concentrations was also reported.[131] Apatite was formed on composites with low concentrations. CS-DA-MWNTs, and improved detection sensitivity. According to this new method, glutaraldehyde crosslinked CHT-DA, with covalent attachment of DA molecules to the CHT chains formed by Schiff bases. Further on, the solution of MWNT dispersed in the CHT-DA solution was dropped on an Au electrode for preparing a CHT-DA-MWNT film, and finally dried.

CNT/CHT nanobiocomposites for immunosensors were produced by some researchers.[132] In such nanobiocomposites, the electron transport enhanced and improved the detection of ochratoxin-A, due to the high electrochemical properties of SWNT. Also, the CNT/CHT nanocomposite used for the detection of human chorionic gonadotrophin antibody was prepared,[133] displaying high sensitivity and good reproducibility.

Table 2
Mechanical and electrical information of neat biopolymers compared to their carbon nanotube nanocomposites

Method	Biopolymer	Mechanical properties					Conductivity	Ref.
		Tensile modulus (Mpa)	Tensile strength (Mpa)	Strain to failure (%)	Comparison modulus (Pa)	Stage modulus (Gpa)		
Polymerized hydrogel	neat collagen				1284±94		11.37 ms±0.16	[98]
	collagen/CNTs				1127±73		11.85 ms±0.67	
Solution-evaporation	neat chitosan	1.08±0.04	37.7±4.5				0.021 nS/cm	[99-100]
	chitosan/CNTs	2.15±0.09	74.3±4.6				120 nS/cm	
Wet spinning	neat chitosan	4250						[101]
	chitosan/CNTs	1025 0						
Electrospinning	neat silk	140±2.21	6.18±0.3	5.78±0.65			0.028 S/cm	[102]
	silk/CNTs	4817.24±69.23	44.46±2.1	1.22±0.14			0.144 S/cm	
Dry-jet wet spinning	neat cellulose	13100±1100	198±25	2.8±0.7		5.1	negligible	[103-104]
	cellulose/CNTs	14900±13 00	257±9	5.8±1.0		7.4	3000 S/cm	
Electrospinning	neat cellulose	553±39	21.9±1.8	8.04±0.27				[105]
	cellulose/CNT	1144±37	40.7±2.7	10.46±0.33				

3.2.1.1 Properties and characterization

The morphology and mechanical properties of chitosan were promoted[134] by adding CNTs. Besides, it was demonstrated[135] that conducting direct electron is very useful for the adsorption of hemoglobin in a CNT/CHT composite film. Studies have demonstrated that this nanobiocomposite can be used in many fields, such as biosensing and biofuel cell applications.

Some researchers[136] evaluated the water transport behavior of chitosan porous membranes containing MWNTs. They characterized two nanotube composites with low molecular weight CSP6K and high molecular weight CSP10K. Because of the hollow nanochannel of MWNTs, located in the pore network of the chitosan membrane, the water transport results for CSP6K enhanced, when the MWNTs content exceeded a critical content. However, for CSP10K series membranes, the water transport rate decreased with increasing the MWNTs content, due to the strong compatibilizing effect of MWNTs.

Other researchers[137] used CNT/CHT nanocomposites with poly(styrene sulfonic acid)-modified CNTs. The thermal, mechanical, and electrical properties of CNT/CHT composite films prepared by solution-casting have potential applications as separation membranes and sensor electrodes.

3.2.2 Crosslinking-casting-evaporation

Researchers discovered that MWNTs can be functionalized with –COOH groups at the sidewall defects of nanotubes by carbon nanotubes.[138]

According to a novel method,[139] chitosan was cross-linked with free –CHO groups by glutaraldehyde and then MWNTs were added to the mixture. The cross-linked MWNT-CHT composite was immobilized with acetylcholinesterase (AChE), for detecting both acetylthiocholine and organophosphorous insecticides. On the other hand, resarchers[140] created a new method for cross-linking CHT with carboxylated CNT, involving the addition of glutaraldehyde to the MWNT/CHT solution. They immobilized AChE on the composite for preparing an amperometric acetylthiocholine sensor. The suitable fabrication reproducibility, rapid response, high sensitivity and stability obtained could provide amperometric detection of carbaryl and treazophos[141] pesticide. The results[142] showed the removal of heavy metals, including copper, zinc, cadmium and nickel ions from an aqueous solution in MWNT/CHT nanocomposite films.

3.2.3 Surface deposition crosslinking

Researchers[143] decorated carbon nanotubes with chitosan by surface deposition and crosslinking processes. In this way, the chitosan macromolecules as polymer cationic surfactants were adsorbed on the CNT surface. In this step, CHT assures a stable dispersion of CNT in an acidic aqueous solution. The pH value of the system was increased by the ammonia solution, to become non-dissolvable of chitosan in aqueous media. Consequently, the soluble chitosan was deposited on the surface of carbon nanotubes similarly to chitosan coating. Finally, the surface-deposited chitosan was crosslinked to CNTs by glutaraldehyde, for potential applications in biosensing, gene and drug delivery of this composite.

3.2.4 The electro-deposition method

Researchers[144] used the nanocomposite film of CNT/CHT as a glucose biosensor by a simple and controllable method. In this one-step electro-deposition method, a pair of gold electrodes was connected to a direct current power supply, and then dipped into the CNT/CHT solution. Herein, the pH near the cathode surface increased, thereby the solubility of chitosan decreased. At a pH of about 6.3, chitosan becomes insoluble and the chitosan-entrapped CNT will be deposited on the cathode surface.

Other investigators[145] characterized electrocatalytic oxidation and sensitive electroanalysis of NADH on a novel film of

3.2.5 Covalent grafting

Carboxylic acid (-COOH) groups were formed on the walls of CNTs by their refluxing in an acidic solution. Carboxylated CNTs were added to the aqueous solution of chitosan. Grafting reactions were accomplished by purging the CNT/CS solution with N_2 and heating to 98 °C. Researchers[146] compared the mechanical properties and water stability of CNTs-grafted-CS with the ungrafted CNTs. A significantly improved dispersion in the chitosan matrix resulted, as well as an important improvement storage modulus and water stability of the chitosan nanocomposites.

Researchers[147] created another process for obtaining a CHT-grafted MWNT composite. By this method, after preparing oxidized MWNT

(MWNT-COOH), they generated the acyl chloride functionalized MWNT (MWNT-COCl) in a solution of thionyl chloride. In the end, the MWNT-grafted-CS was synthesized by adding CHT to the MWNT-COCl suspension in anhydrous dimethyl formamide. Covalent modification has improved interfacial bonding, resulting in a high stability of the CNT dispersion. Biosensors and other biological applications are evaluated as potential uses of this component. Others[148] prepared a similar composite by reacting CNT-COCl and chitosan with potassium persulfate, lactic acid and acetic acid solution at 75 °C. They estimated that the CNT-grafted-CHT composite can be used in bone tissue engineering, as it may improve the thermal properties.

3.2.5.1 Nucleophilic substitution reaction

Covalent modification of MWNT was accomplished with low molecular weight chitosan (LMCS).[149] This novel derivation of MWNTs can be solved in DMF, DMAc and DMSO, but also in aqueous acetic acid solutions.

3.2.6 Electrostatic interaction

Some authors[150] synthesized CHT nanoparticles-coated fMWNT composites by electrostatic interactions between the CHT particles and the functionalized CNT. They prepared CHT nanoparticles and CHT microspheres by the precipitation and, respectively, crosslinking method. The electrostatic interactions between CHT particles solved in distilled deionized water and the carboxylated CNTs were confirmed by changing the pH solution. The results obtained showed the same surface charges at pH 2 (both were positively charged) and pH 8 (both were negatively charged). Electrostatic interactions may occur at pH 5.5, due to the different charges between the CHT particles and fCNT, with positive and negative surface charges, respectively. The CHT particles/CNT composite materials could be utilized for potential biomedical applications.

Researchers[151] prepared SWNTs/phosphotungstic acid modified SWNT/CS composites using the phosphotungstic acid as an anchor reagent, to modify SWNTs. They succeeded in using PW_{12}-modified SWNT with a negative surface charge, and also positively-charged chitosan, by electrostatic interactions. These strong interfacial interactions between SWNTs and the chitosan matrix showed favorable cyto-compatibility for their potential use as scaffolds for bone tissue engineering.

3.2.7 Microwave irradiation

Researchers[152] created a new technique for the synthesis of chitosan-modified carbon nanotubes by microwave irradiation. According to this technique, solutions of MWNTs in nitric acid were placed under microwave irradiation and dried for purification of MWNTs. A mixture of purified MWNTs and chitosan solution was reacted in the microwave oven and then centrifuged. The yield black-colored solution was adjusted to pH 8 and centrifuged for precipitation of the CNT/CHT composite. This technique is much more efficient than the conventional methods.

3.2.8 Layer-by-layer

Researchers[153] characterized MWNT/ CHT composite rods with layer-by-layer structure prepared by the *in situ* precipitation method. The samples were prepared by coating the CHT solution on the internal surface of a cylindrical tube and then filling with a MWNT/CHT solution in acetic acid. The morphological, mechanical and thermal properties of this composite rod were also examined.

3.2.8.1 Layer-by-layer self-assembly

Researchers[154] produced a homogeneous multilayer film of MWNT/CHT by the layer-by-layer self-assembly method. According to this method, the negatively charged substrates were dipped into a poly(ethyleneimine) aqueous solution, a MWNT suspension, and a CHT solution, respectively, and finally dried. In this process, both the CHT and PEI solutions contained NaCl for the LBL assembly. The films showed stable optical properties and were appropriate for biosensor applications.

3.2.9 Freeze-drying

Researchers[155] synthesized and characterized a highly conductive, porous and biocompatible MWNT/CHT biocomposite film by the freeze-drying technique. The process was preformed by freezing a MWNT/CHT dispersion into an aluminum mold, followed by drying.[156]

3.2.10 Wet-spinning

A recent report[157] showed that chitosan is a good dispersing agent for SWNT. The authors also proposed several methods for preparing a

SWNT/CHT macroscopic structure in the form of films, hydrogels and fibers.[158] The CNT/CHT dispersed in acetic acid was spun into an ethanol:NaOH coagulation solution bath. Better mechanical properties of wet spun fibers resulted from improved dispersion.[159]

3.2.11 Electrospinning

Chitosan (CHT)/multi-walled carbon nanotube (MWNT) composite nanofibers can be fabricated by electrospinning.[157] In our experiments, different solvents, including acetic acid 1-90%, formic acid and Tri-Fluoroacetic Acid TFA/DCM, were tested for electrospinning of chitosan/carbon nanotube. No jet was seen when applying a high voltage (even above 25 kV), with 1-30% acetic acid and formic acid as solvent for the chitosan/carbon nanotube.

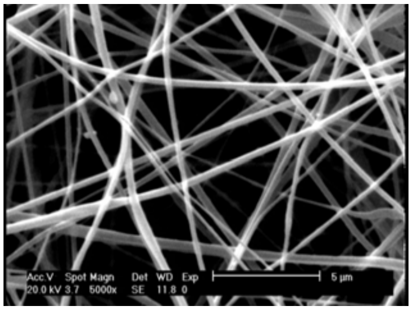

Figure 7: Electron micrograph of electrospun fibers at chitosan concentration of 10 wt%; 24 kV, 5 cm, TFA/DCM: 70/30

FA/DCM (70:30) was the only solvent obtained during electrospinning of chitosan/carbon nanotubes. The scanning electron microscopic images showed homogenous fibers with an average diameter of 455 nm (306-672), prepared by dispersing the chitosan/carbon nanotubes in TFA/DCM 70:30. These nanofibers have potential biomedical applications.

CONCLUSIONS

In less than ten years, dozens of research studies have been devoted to chitosan biocomposite reinforcements using carbon nanotubes. As a conclusion, much progress has been made in the preparation and characterization of CNT/CHT nano-composites. Several methods for preparing these nanobiocomposites are reported. In addition, the CNT/CHT applications have been classified, including biomedicine (tissue engineering, biosensors, and drug delivery) and wastewater domains. Numerous potential applications of these nanobiocomposites in tissue engineering and drug delivery are expected. It is believed that an improvement of the preparation methods of CNT/CHT nanocomposites and their characterization will bring a promising future to biomedicine.

REFERENCES

[1] W. Praznik and C. V. Stevens, in “Renewable Bioresources: Scope and Modification for Non-food Applications”, John Wiley & Sons, Ltd, Hoboken, 2004, p. 49.

[2] D. A. D. Parry and E. N. Baker, *Rep. Prog. Phys.*, **47**, 1133 (1984).

[3] S. Bhattacharyya, S. Guillot, H. Dabboue, J.-F. Tranchant and J.-P. Salvetat, *Biomacromolecules*, **9**, 505 (2008).

[4] M. Lavorgna, F. Piscitelli, P. Mangiacapra and G. G. Buonocore, *Carbohydr. Polym.*, **82**, 291 (2010).

[5] X. Cao, Y. Chen, P. R. Chang and M. A. Huneault, *J. Appl. Polym. Sci.*, **106**, 1431 (2007).

[6] S. Ramakrishna, J. Mayer, E. Wintermantel and K. W. Leong, *Compos. Sci. Technol.*, **61**, 1189 (2001).

[7] D. Liang, B. S. Hsiao and B. Chu, *Adv. Drug Deliver. Rev.*, **59**, 1392 (2007).

[8] Z. Liu, Y. Jiao, Y. Wang, C. Zhou and Z. Zhang, *Adv. Drug Deliver. Rev.*, **60**, 1650 (2008).

[9] O. C. Agboh and Y. Qin, *Polym. Adv. Technol.*, **8**, 355 (1997).

[10] I. Aranaz, M. Mengíbar, R. Harris, I. Paños, B. Miralles, N. Acosta, G. Galed and Á. Heras, *Current Chemical Biology*, **3**, 203 (2009).

[11] Y. Zhang, C. Xue, Y. Xue, R. Gao and X. Zhang, *Carbohydr. Res.*, **340**, 1914 (2005).

[12] J. T. Bamgbose, S. Adewuyi, O. Bamgbose and A. A. Adetoye, *Afr. J. Biotechnol.*, **9**, 2560 (2010).

[13] K.-S. Huang, W.-J. Wu, J.-B. Chen and H.-S. Lian, *Carbohydr. Polym.*, **73**, 254 (2008).

[14] M. H. Ottøy, K. M. Vårum, B. E. Christensen, M. W. Anthonsen and O. Smidsrød, *Carbohydr. Polym.*, **31**, 253 (1996).

[15] P. J. VandeVord, H. W. T. Matthew, S. P. DeSilva, L. Mayton, B. Wu and P. H. Wooley, *J. Biomed. Mater. Res.*, **59**, 585 (2002).

[16] M. Ratajska, G. Strobin, M. Wiśniewska-Wrona, D. Ciechańska, H. Struszczyk, S. Boryniec, D. Biniaś and W. Biniaś, *Fibers Text. East Eur.*, **11**, 75 (2003).

[17] R. Jayakumar, M. Prabaharan, S. V. Nair and H. Tamura, *Biotechnol. Adv.*, **28**, 142 (2010).

[18] B. Krajewska, *Enzyme Microb. Technol.*, **35**, 126 (2004).

[19] H. Ueno, T. Mori and T. Fujinaga, *Adv. Drug Deliver. Rev.*, **52**, 105 (2001).

[20] I.-Y. Kim, S.-J. Seo, H.-S. Moon, M.-K. Yoo, I.-Y. Park, B.-C. Kim and C.-S. Cho, *Biotechnol. Adv.*, **26**, 1 (2008).

[21] V. R. Sinha, A. K. Singla, S. Wadhawan, R. Kaushik, R. Kumria, K. Bansal and S. Dhawan, *Int. J. Pharm.*, **274**, 1 (2004).

[22] A. D. Martino, M. Sittinger and M. V. Risbud, *Biomaterials*, **26**, 5983 (2005).

[23] R. A. A. Muzzarelli, C. Muzzarelli, R. Tarsi, M. Miliani, F. Gabbanelli and M. Cartolari, *Biomacromolecules*, **2**, 165 (2001).

[24] P. K. Dutta, S. Tripathi, G. K. Mehrotra and J. Dutta, *Food Chem.*, **114**, 1173 (2009).

[25] S. Boonlertnirun, C. Boonraung and R. Suvanasara, *J. Metals Materials Minerals,* **18**, 47 (2008).

[26] P. Lertsutthiwong, S. Chandrkrachang and W. F. Stevens, *J. Metals Materials Minerals*, **10**, 43 (2000).

[27] M. N. V. Ravi Kumar, *React. Funct. Polym.*, **46**, 1 (2000).

[28] R. H. Y. Subban and A. K. Arof, *Phys. Scripta*, **53**, 382 (1996).

[29] P. K. Dutta, J. Dutta and V. S. Tripathi, *J. Sci. Ind. Res.*, **63**, 20 (2004).

[30] Q. Li, J. Zhou and L. Zhang, *J. Polym. Sci., Pol. Phys.*, **47**, 1069 (2009).

[31] E. T. Thostenson, C. Li and T.-W. Chou, *Compos. Sci. Technol.*, **65**, 491 (2005).

[32] S. Iijima, *Nature*, **354**, 56 (1991).

[33] D. S. Benthune, C. H. Kiang, M. S. D. Vries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers, *Nature*, **363**, 605 (1993).

[34] S. Iijima and T. Ichihashi, *Nature*, **363**, 603 (1993).

[35] M. Trojanowicz, *TrAC Trends Anal. Chem.*, **25**, 480 (2006).

[36] L. Duclaux, *Carbon*, **40**, 1751 (2002).

[37] Y. Y. Wang, S. Gupta, J. M. Garguilo, Z. J. Liu, L. C. Qin and R. J. Nemanich, *Diam. Relat. Mater.*, **14**, 714 (2005).

[38] J. Guo, S. Datta and M. Lundstrom, *IEEE Transaction on Electron Devices*, **51**, 172 (2004).

[39] C.-S. Kuo, A. Bai, C.-M. Huang, Y.-Y. Li, C.-C. Hu and C.-C. Chen, *Carbon*, **43**, 2760 (2005).

[40] R. L. Jacobsen, T. M. Tritt, J. R. Guth, A. C. Ehrlich and D. J. Gillespie, *Carbon*, **33**, 1217 (1995).

[41] C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. L. l. Chapelle, S. Lefrant, P. Deniard, R. Leek and J. E. Fischer, *Nature*, **388**, 756 (1997).

[42] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer and R. E. Smalley, S*cience*, **273**, 483 (1996).

[43] A. M. Cassell, J. A. Raymakers, J. Kong and H. Dai, *J. Phys. Chem., B*, **103**, 6482 (1999).

[44] S. Fan, W. Liang, H. Dang, N. Franklin, T. Tombler, M. Chapline and H. Dai, *Physica E.*, **8**, 179 (2000).

[45] S. Xie, W. Li, Z. Pan, B. Chang and L. Sun, *Mater. Sci. Eng., A*, **286**, 11 (2000).

[46] Z. K. Tang, L. Zhang, N. Wang, X. X. Zhang, G. H. Wen, G. D. Li, J. N. Wang, C. T. Chan and P. Sheng, *Science*, **292**, 2462 (2001).

[47] A. Peigney, C. Laurent, E. Flahaut, R. R. Bacsa and A. Rousset, *Carbon*, **39**, 507 (2001).

[48] Z. W. Pan, S. S. Xie, L. Lu, B. H. Chang, L. F. Sun, W. Y. Zhou, G. Wang and D. L. Zhang, *Appl. Phys. Lett.*, **74**, 3152 (1999).

[49] L. Forro, J. P. Salvetat, J. M. Bonard, R. Basca, N. H. Thomson, S. Garaj, L. Thien-Nga, R. Gaal, A. Kulik, B. Ruzicka, L. Degiorgi, A. Bachtold, C. Schonenberger, S. Pekker and K. Hernadi, *Science Application Nanotubes*, 297 (2000).

[50] S. Frank, P. Poncharal, Z. L. Wang and W. A. d. Heer, *Science*, **280**, 1744 (1998).

[51] D. A. Britzab and A. N. Khlobystov, *Chem. Soc. Rev.*, **35**, 637 (2006).

[52] R. Andrews and M. C. Weisenberger, *Curr. Opin. Solid St. Mater. Sci.*, **8**, 31 (2004).

[53] A. Hirsch, *Angew. Chem. Int. Ed.*, **41**, 1853 (2002).

[54] C. P. Firme and R. B. Prabhakar, *Nanomed. Nanotechnol. Biol. Med.*, **6**, 245 (2010).

[55] S. Niyogi, M. A. Hamon, H. Hu, B. Zhao, P. Bhowmik, R. Sen, M. E. Itkis and R. C. Haddon, *Acc. Chem. Res.*, **35**, 1105 (2002).

[56] H. Kuzmany, A. Kukovecz, F. Simona, M. Holzweber, C. Kramberger and T. Pichler, *Synth. Met.*, **141**, 113 (2004).

[57] Z. Spitalsky, D. Tasis, K. Papagelis and C. Galiotis, *Prog. Polym. Sci.*, **35**, 357 (2010).

[58] R. Narain, A. Housni and L. Lane, *J. Polym. Sci., A, Polym. Chem.*, **44**, 6558 (2006).

[59] M. Wang, K. P. Pramoda and S. H. Goh, *Carbon*, **44**, 613 (2006).

[60] H. Touhara, A. Yonemoto, K. Yamamoto, S. Komiyama, S. Kawasaki, F. Okino, T. Yanagisawa and M. Endo, *Fluorine Chem.*, **114**, 181 (2002).

[61] W. Zhang, J. K. Sprafke, M. Ma, E. Y. Tsui, S. A. Sydlik, G. Rutledge and T. M. Swager, *J. Am. Chem. Soc.*, **131**, 8446 (2009).

[62] P. He, Y. Gao, J. Lian, L. Wang, D. Qian, J. Zhao, W. Wang, M. J. Schulz, X. P. Zhou and D. Shi, *Compos*., *A*, *Appl*. *S*., **37**, 1270 (2006).

[63] A. B. Sulong, C. H. Azhari, R. Zulkifli, M. R. Othman and J. Park, *Eur*. *J*. *Sci*. *Res*., **33**, 295 (2009).

[64] C. Wang, Z. X. Guo, S. Fu, W. Wu and D. Zhu, *Prog*. *Polym*. *Sci*., **29**, 1079 (2004).

[65] J. Rausch, R.-C. Zhuang and E. Mäder, *Compos*., *A*, *Appl*. *S*., **41**, 1038 (2010).

[66] N. G. Sahoo, S. Rana, J. W. Cho, L. Li and S. H. Chan, *Prog*. *Polym*. *Sci*., **35**, 837 (2010).

[67] D. Zheng, X. Li and J. Ye, *Bioelectrochemistry*, **74**, 240 (2009).

[68] X. Zhang, L. Meng and Q. Lu, *ACS Nano*., **10**, 3200 (2009).

[69] H. Wang, *Curr*. *Opin*. *Colloid Int*., **14**, 364 (2009).

[70] A. D. Schlüter, A. Hirsch and O. Vostrowsky, *Functional Molecular Nanostructures*, 245, 193 (2005).

[71] P.-C. Ma, N. A. Siddiqui, G. Marom and J.-K. Kim, *Compos*., *A*, **41**, 1345 (2010).

[72] V. Mottaghitalab, G. M. Spinks and G. G. Wallace, *Synth*. *Met*., **152**, 77 (2005).

[73] W. Cheung, F. Pontoriero, O. Taratula, A. M. Chen and H. He, *Adv*. *Drug Deliver*. *Rev*., **62**, 633 (2010).

[74] S. Piovesan, P. A. Cox, J. R. Smith, D. G. Fatouros and M. Roldo, *Phys*. *Chem*., *Chem*. *Phys*., **12**, 15636 (2010).

[75] J. Chen, H. Liu, W. A. Weimer, M. D. Halls, D. H. Waldeck and G. C. Walker, *J*. *Am*. *Chem*. *Soc*., **124**, 9034 (2002).

[76] V. Vamvakaki, M. Fouskaki and N. Chaniotakis, *Anal*. *Lett*., **40**, 2271 (2007).

[77] Y. Kang, Y.-C. Liu, Q. Wang, J.-W. Shen, T. Wu and W.-J. Guan, *Biomaterials*, **30**, 2807 (2009).

[78] B. S. Harrison and A. Atala, *Biomaterials*, **28**, 344 (2007).

[79] M. Moniruzzaman and K. I. Winey, *Macromolecules*, **39**, 5194 (2006).

[80] P. M. Ajayan, O. Stephan, C. Colliex and D. Trauth, *Science*, **265**, 1212 (1994).

[81] P. Liu, *Eur*. *Polym*. *J*., **41**, 2693 (2005).

[82] M. A. L. Manchado, L. Valentini, J. Biagiotti and J. M. Kenny, *Carbon*, **43**, 1499 (2005).

[83] Q. Wang and V. K. Varadan, *Smart Mater*. *Struct*., **14**, 281 (2005).

[84] P. K. Mallick, in “Fiber Reinforced Composites: Materials, Manufacturing, and Design”, Taylor & Francis Group, London, 2008, p. 43.

[85] M. S. P. Shaffer and J. K. W. Sandler, in “Processing and Properties of Nanocomposites”, World Scientific Publishing Co. Pte. Ltd., Singapore, 2006, p. 31.

[86] C. W. Nan, Z. Shi and Y. Lin, *Chem*. *Phys*. *Lett*., **375**, 666 (2003).

[87] J. N. Coleman, U. Khan, W. J. Blau and Y. K. Gun'ko, *Carbon*, **44**, 1624 (2006).

[88] H. D. Wagner, O. Lourie, Y. Feldman and R. Tenne, *Appl*. *Phys*. *Lett*., **72**, 188 (1998).

[89] Q. Wang, J. Dai, W. Li, Z. Wei and J. Jiang, *Compos*. *Sci*. *Technol*., **68**, 1644 (2008).

[90] U. Khan, K. Ryan, W. J. Blau and J. N. Coleman, *Compos*. *Sci*. *Technol*., **67**, 3158 (2007).

[91] A. Allaoui, S. Bai, H. M. Cheng and J. B. Bai, *Compos*. *Sci*. *Technol*., **62**, 1993 (2002).

[92] A. M. K. Esawi and M. M. Farag, *Mater*. *Design*, **28**, 2394 (2007).

[93] F. H. Gojny, M. H. G. Wichmann, B. Fiedler, I. A. Kinloch, W. Bauhofer, A. H. Windle and K. Schulte, *Polymer*, **47**, 2036 (2006).

[94] K. Kamaras, M. E. Itkis, H. Hu, B. Zhao and R. C. Haddon, *Science*, **301**, 1501 (2003).

[95] S. Shenogin, A. Bodapati, L. Xue, R. Ozisik and P. Keblinski, *Appl*. *Phys*. *Lett*., **85**, 2229 (2004).

[96] R. A. MacDonald, B. F. Laurenzi, G. Viswanathan, P. M. Ajayan and J. P. Stegemann, *J*. *Biomed*. *Mater*. *Res*., *A*, **74A**, 489 (2005).

[97] S. Bose, R. A. Khare and P. Moldenaers, *Polymer*, **51**, 975 (2010).

[98] Z. Tosun and P. S. McFetridge, *J*. *Neural Eng*., **7**, 1 (2010).

[99] S.-F. Wang, L. Shen, W.-D. Zhang and Y.-J. Tong, *Biomacromolecules*, **6**, 3067 (2005).

[100] G. M. Spinks, S. R. Shin, G. G. Wallace, P. G. Whitten, S. I. Kim and S. J. Kim, *Sensor*. *Actuat*. *B*, **115**, 678 (2006).

[101] M. Gandhi, H. Yang, L. Shor and F. Ko, *Polymer*, **50**, 1918 (2009).

[102] S. S. Rahatekar, A. Rasheed, R. Jain, M. Zammarano, K. K. Koziol, A. H. Windle, J. W. Gilman and S. Kumar, *Polymer*, **50**, 4577 (2009).

[103] H. Zhang, Z. Wang, Z. Zhang, J. Wu, J. Zhang and J. He, *Adv*. *Mater*., **19**, 698 (2007).

[104] P. Lu and Y.-L. Hsieh, *ACS Appl*. *Mater*. *Interfaces*, **2**, 2413 (2010).

[105] Y. Wang and J. T. W. Yeow, *J*. *Sensors*, **2009**, 1 (2009).

[106] W. Yang, P. Thordarson, J. J. Gooding, S. P. Ringer and F. Braet, *Nanotechnology*, **18**, 1 (2007).

[107] J. Wang, *Electroanal*., **17**, 7 (2005).

[108] M. Foldvari and M. Bagonluri, *Nanomed*. *Nanotechnol*. *Biol*. *Med*., **4**, 183 (2008).

[109] S. Belluccia, C. Balasubramanianab, F. Micciullaac and G. Rinaldid, *J*. *Exp*. *Nanosci*., **2**, 193 (2007).

[110] I. Kang, Y. Y. Heung, J. H. Kim, J. W. Lee, R. Gollapudi, S. Subramaniam, S. Narasimhadevara, D. Hurd, G. R. Kirikera, V. Shanov, M. J. Schulz, D. Shi, J. Boerio, S. Mall and M. Ruggles-Wren, *Compos*., *B*, **37**, 382 (2006).

[111] V. Mottaghitalab, G. M. Spinks and G. G. Wallace, *Polymer*, **47**, 4996 (2006).

[112] C. Y. Wang, V. Mottaghitalab, C. O. Too, G. M. Spinks and G. G. Wallace, *J*. *Power Sources*, **163**, 1105 (2007).

[113] V. Mottaghitalab, B. Xi, G. M. Spinks and G. G. Wallace, *Synth*. *Met*., **156**, 796 (2006).

[114] Y. T. Ong, A. L. Ahmad, S. H. S. Zein and S. H. Tan, *Braz*. *J*. *Chem*. *Eng*., **27**, 227 (2010).

[115] N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudi, *Science*, **258**, 1474 (1992).
[116] P. J. F. Harris, *Int. Mater. Rev.*, **49**, 31 (2004).
[117] H. M. C. D. Azeredo, *Food Res. Int.*, **42**, 1240 (2009).
[118] T. X. Phuoc, M. Massoudi and R.-H. Chen, *Int. J. Therm. Sci.*, **50**, 12 (2011).
[119] M. Zhang, A. Smith and W. Gorski, *Anal. Chem.*, **76**, 5045 (2004).
[120] Y. Liu, M. Wang, F. Zhao, Z. Xu and S. Dong, *Biosens. Bioelectron.*, **21**, 984 (2005).
[121] J. Tkac, J. W. Whittaker and T. Ruzgas, *Biosens. Bioelectron.*, **22**, 1820 (2007).
[122] Y.-C. Tsai, S.-Y. Chen and H.-W. Liaw, *Sensor. Actuat. B*, **125**, 474 (2007).
[123] Y. Zhou, H. Yang and H.-Y. Chen, *Talanta*, **76**, 419 (2008).
[124] J. Li, Q. Liu, Y. Liu, S. Liu and S. Yao, *Anal. Biochem.*, **346**, 107 (2005).
[125] S. Bollo, N. F. Ferreyr and G. A. Rivasb, *Electroanal.*, **19**, 833 (2007).
[126] Y. Zeng, Z.-H. Zhu, R.-X. Wang and G.-H. Lu, *Electrochim. Acta*, **51**, 649 (2005).
[127] L. Qian and X. Yang, *Talanta*, **68**, 721 (2006).
[128] Y. Liu, X. Qu, H. Guo, H. Chen, B. Liu and S. Dong, *Biosens. Bioelectron.*, **21**, 2195 (2006).
[129] S. Naficy, J. M. Razal, G. M. Spinks and G. G. Wallace, *Sensor. Actuat. A*, **155**, 120 (2009).
[130] J. Yang, Z. Yao, C. Tang, B. W. Darvell, H. Zhang, L. Pan, J. Liu and Z. Chen, *Appl. Surf. Sci.*, **255**, 8551 (2009).
[131] A. Kaushik, P. R. Solanki, M. K. Pandey, K. Kaneto, S. Ahmad and B. D. Malhotra, *Thin Solid Films*, **519**, 1160 (2010).
[132] H. Yang, R. Yuan, Y. Chai and Z. Ying, *Colloid. Surf., B*, **82**, 463 (2011).
[133] W. Zheng, Y. Q. Chen and Y. F. Zheng, *Appl. Surf. Sci.*, **255**, 571 (2008).
[134] C. Tang, Q. Zhang, K. Wang, Q. Fu and C. Zhang, *J. Membr. Sci.*, **337**, 240 (2009).
[135] Y.-L. Liu, W.-H. Chen and Y.-H. Chang, *Carbohydr. Polym.*, **76**, 232 (2009).
[136] M. E. Ghica, R. Pauliukaite, O. Fatibello-Filho and C. M. A. Brett, *Sensor. Actuat. B*, **142**, 308 (2009).
[137] V. B. Kandimalla and H. Ju, *Chem. Eur. J.*, **12**, 1074 (2006).
[138] D. Du, X. Huang, J. Cai, A. Zhang, J. Ding and S. Chen, *Anal. Bioanal. Chem.*, **387**, 1059 (2007).
[139] D. Du, X. Huang, J. Cai and A. Zhang, *Sensor. Actuat. B*, **127**, 531 (2007).
[140] M. A. Salam, M. S. I. Makki and M. Y. A. Abdelaal, *J. Alloys Compd.*, **509**, 2582 (2010).
[141] Y. Liu, J. Tang, X. Chen and J. H. Xin, *Carbon*, **43**, 3178 (2005).
[142] X.-L. Luo, J.-J. Xu, J.-L. Wang and H.-Y. Chen, *Chem. Commun.*, 16, 2169 (2005).
[143] B. Ge, Y. Tan, Q. Xie, M. Ma and S. Yao, *Sensor. Actuat. B*, **137**, 547 (2009).
[144] Y.-T. Shieh and Y.-F. Yang, *Eur. Polym. J.*, **42**, 3162 (2006).
[145] Z. Wu, W. Feng, Y. Feng, Q. Liu, X. Xu, T. Sekino, A. Fujii and M. Ozaki, *Carbon*, **45**, 1212 (2007).
[146] L. Carson, C. Kelly-Brown, M. Stewart, A. Oki, G. Regisford, Z. Luo and V. I. Bakhmutov, *Mater. Lett.*, **63**, 617 (2009).
[147] G. Ke, W. C. Guan, C. Y. Tang, Z. Hu, W. J. Guan, D. L. Zeng and F. Deng, *Chin. Chem. Lett.*, **18**, 361 (2007).
[148] S.-H. Baek, B. Kim and K.-D. Suh, *Colloid. Surf., A*, **316**, 292 (2008).
[149] Q. Zhao, J. Yin, X. Feng, Z. Shi, Z. Ge and Z. Jin, *J. Nanosci. Nanotechnol.*, **10**, 1 (2010).
[150] J.-G. Yu, K.-L. Huang, J.-C. Tang, Q. Yang and D.-S. Huang, *Int. J. Biol. Macromol.*, **44**, 316 (2009).
[151] Z.-K. Wang, Q.-L. Hu and L. Cai, *Chinese J. Polym. Sci.*, **28**, 801 (2010).
[152] X.-B. Li and X.-Y. Jiang, *New Carbon. Mater.*, **25**, 237 (2010).
[153] C. Lau and M. J. Cooney, *Langmuir*, **24**, 7004 (2008).
[154] J. A. Jennings, W. O. Haggard and J. D. Bumgardner, US Patent Application, 0266694.A1 (2010).
[155] J. M. Razal, K. J. Gilmore and G. G. Wallace, *Adv. Funct. Mater.*, **18**, 61 (2008).
[156] C. Lynam, S. E. Moulton and G. G. Wallace, *Adv. Mater.*, **19**, 1244 (2007).
[157] Z. Moridi Mahdieh, V. Mottaghitalab, N. Piri and A. K. Haghi, *Korean J. Chem. Eng.*, DOI: 10.1007/s11814-011-0129-y, in press.