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## Research Article

# POLYMER CONJUGATED CARBON NANO FIBER TO ENHANCE ITS APPLICATION: A REVIEW

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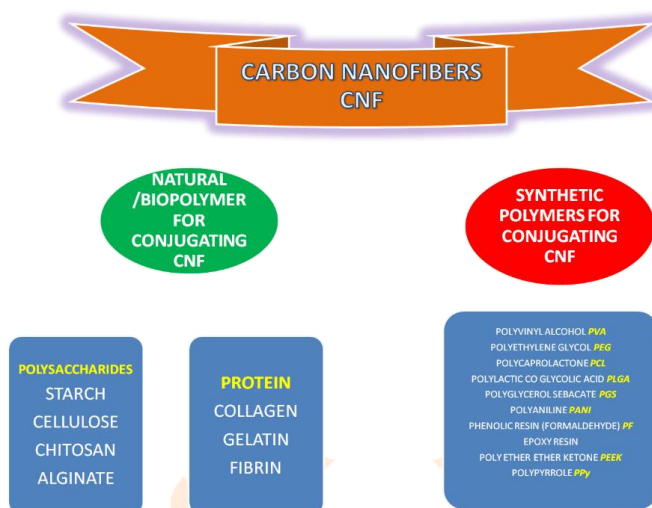
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## ABSTRACT

Carbon nanofiber (CNF) is an important nano form of graphitic carbon. It is competing with Carbon Nano Tubes (CNT) in many aspects, in both fundamental scientific research and practical applications. It is a promising material as an additive in polymers for its applications in many fields. The electrical property of CNF composites largely counts on the dispersion and percolation status of CNFs in matrix materials. In this review properties and applications of CNF nanocomposites are dealt with. Fabrication methods of CNF composites have also been discussed in brief. The suitable polymers that have been used for conjugating with CNF vary from natural biopolymers such as polysaccharides, fibrin, and proteins to various synthetic polymers. The review also encompasses various approaches involved in synthesizing polymer and CNF nanoconjugates as well as their application ranging from cosmetics to batteries and solar cells.

## KEYWORDS

Biopolymer. Carbon Nanofiber, Composites, Nanocomposites, Nanoconjugates, Polymer Nanoparticles.



## GRAPHICAL ABSTRACT

### INTRODUCTION

Nanotechnology is being recognized as one of the most advancing and promising fields in the recent scenario. The nano-sized inclusions, which range from 1 to 100nm including nanoparticles and quantum dots or Q particles are widely exploited for different applications and benefits. Several research studies reveal that the development of polymer nanocomposite is rapidly emerging as a multidisciplinary research activity whose could broaden the application of nanoparticle and polymer composite in various industries ranging from biomedical to aerospace.

Polymer nanocomposites are polymers that have been reinforced with small quantities mainly less than 5% weight of nanosized particles having a high aspect ratio. Polymer nanocomposite represents a radical alternative to conventional filled polymers or polymer blends. In contrast to conventional polymers where the re-enforcement is in the order of microns, polymer nanocomposites are exemplified by discrete

constituents in the order of a few nanometers. The research studies suggest that the development of polymer nanocomposites must simultaneously balance four different areas i.e. Constituent selection, Cost-effective processing, Fabrication, and Performance. A complete understanding of these areas and their interdependencies is still in its infancy but with progressive research, many perspectives will develop with its application in different fields.

This review article mainly focuses on the carbon nanofiber (CNF), both natural and synthetic polymers, and CNF-Polymer conjugated composites, various methods used in creating the CNF + polymer conjugate, and their futuristic application in different areas.

### COMPOSITES

A Composite is a material made from two or more components with varied physical and chemical properties, which when combined, result in the formation of new material with characteristics

different from the individual component. The individual components remain separate and distinct within the finished structure as compared to mixtures and solid solutions. These composites are mainly created to increase the efficacy of the product, its functionality, durability, sensitivity, longevity, cost-effectiveness, and many other parameters as compared to the traditional materials used for different purposes.

Composites may vary in their sizes; depending on their dimensions they may be named microcomposite measuring in micrometer or nanocomposite measuring in nanometer. Very often one of the components is of nano size, however, even final composite products may also be of nano-size, especially for their application in biosystems.

One of the best examples of composite materials used in our daily life includes plywood which is composite

wood, masonry, fiberglass, ceramic matrix composite, metal matrix composite, and many more advanced composites.

Nanocomposites of CNF is a multiphase solid material less than 100 nm which is created to design and form new materials with unprecedented flexibility and improved structural, chemical, and physical properties. It encompasses large varied systems such as one dimensional, two dimensional; three-dimensional and amorphous materials made up of distinctly different components and mixed at the nanoscale level. The properties of nanocomposite materials not only depend on their components but also their interfacial and morphological characteristics. CNF is synthesized from

both biogenic sources such as bagasse and Karanja oil (Figure 1) or chemical precursors e.g. Plastic and Ethanol (Figure 2).

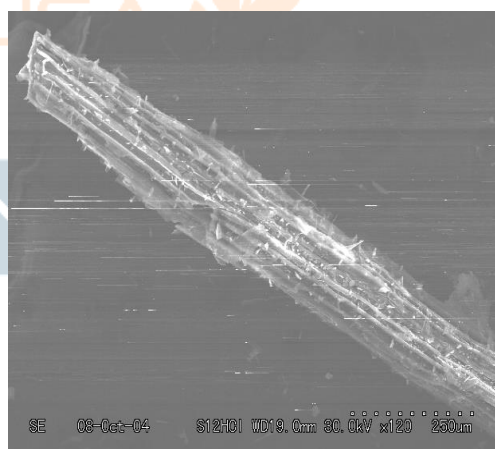
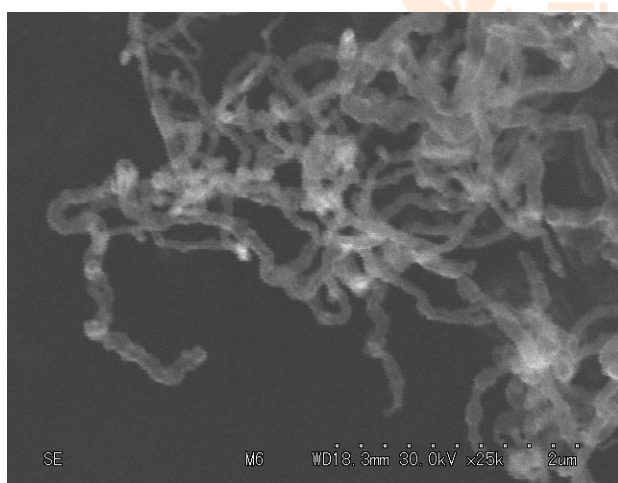
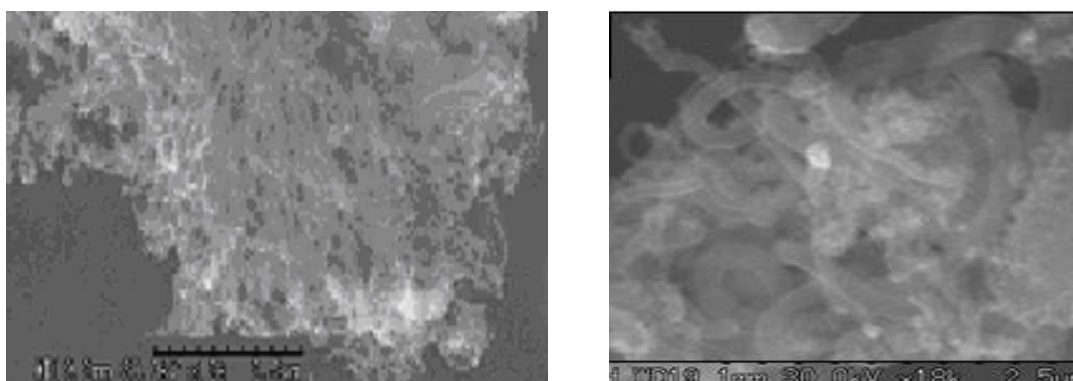


Figure -1: CNF synthesized from Biogenic sources (Left) Sugar cane fiber-Bagasse (Right) Karanja oil

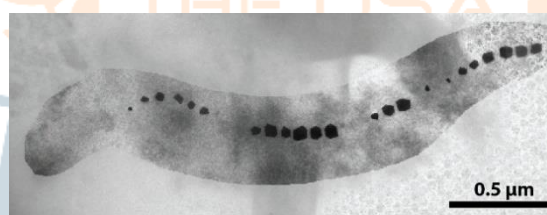


**Figure -2: CNF synthesized from chemical hydrocarbon sources (Left) Plastic and (Right) Ethanol**

In nature nanocomposites are found in the bones, shells, etc. there are many natural organic and inorganic nanocomposites which exist at different levels depending on their level of complexity.

The first level is the simplest level in which the mineral phase is simply deposited into or within the organic structure. For example:

1. Magnetic bacteria that have an internal chain of magnetite  $\text{Fe}_3\text{O}_4$  nanocrystals running down their long axis.
2. Many species of Grasses precipitate  $\text{SiO}_2$  within their cellular structures.



**Figure 3: Magnetic bacteria containing magnetic nanoparticles (Credit Andy Tay, Source: Magnetic bacteria and their unique superpower attract researchers [1])**

The second level is the medium level in which the structure of the mineral phase is determined by the organic matrix. For example, the Bacteria S layer (surface layer) serves as a protein template for the formation of a thin film of mesostructured gypsum.

The third level is the highest level in which the structure of the mineral is intimately associated with the organic phase to create a structure with properties superior to those of either the mineral or the organic phase. For example (i) Sea urchin spine in which a single crystal is composed of calcite containing about 0.02%

glycoprotein trapped within the crystal lattice of the spine (ii) Bone having a complex structure and function, (iii) Nacreous (mother of pearl) layer of abalone shell consists of alternating layers of 500nm thick aragonite platelets and approx. 30nm thick sheets of an organic matrix etc.

## NANOCOMPOSITES

Nanocomposites depending on their size limit are used for different activities e.g., nanocomposites <5 nm for catalytic activity, < 20 nm for making hard magnetic material soft, < 50nm for refractive index changes, and <100nm for superparamagnetism.

Nanocomposites are preferable to conventional composites owing to their following properties:

- High surface to volume ratio
- Nanoparticle properties
- Multifunctional capabilities
- Chemical functionalization
- Huge interface zone
- Mechanical properties
- Increased ductility with no decrease in its strength and scratch resistance
- Optical properties (Light transmission characteristics depend on particle size)

## Types of Nanocomposites

Nanocomposites are either (i) Polymer-based i.e., Polymer/Polymer, Polymer/Metal, Polymer/Ceramic, Polymer/Clay, or Polymer and CNM such as CNT and CNF; or (ii) Non-polymer based such as Metal/Metal, Metal/Ceramic, Ceramic/Ceramic, Polymer/Clay.

Based on the polymer chain ratio, the Lamellar nanocomposites are categorized as:

- Intercalated Nanocomposites have the polymer chains alternate with the inorganic layers in a fixed compositional ratio and have a well-defined number of polymer layers in the intra-lamellar space. The intercalated nanocomposites are also more compound-like because of the fixed polymer/layer ratio, and they are interesting for their electronic and charge transport properties
- Flocculated Nanocomposite here the flocculation of intercalated and stacked layers, to some extent takes place due to hydroxylated edge-edge interactions of the clay or polymer layer.
- Exfoliated Nanocomposites in this the number of polymer chains between the layers is almost continuously variable and the layers stand >100 Å apart. The exfoliated nanocomposites are more interesting for their superior mechanical properties (Figure 4).



	plasticizing corn starch and reinforcing it with cellulose nanofibers bagasse using alkali steam explosion coupled with high shear homogenization	3. To improve mechanical & barrier properties of nanocomposite	
Poly-Lactic Acid (PLA)	1. PLA derived from starch was reinforced into CNF.  2. It is a biodegradable plastic having a lower rate of crystallization	1. To control <i>in vitro</i> degradation of CNF-reinforced PLA composites, for human bone fixation 2. CNF/PLA increases the crystallization rate of PLA by acting as a nucleating agent.	1. Zhang et al 2018 [16]  2. Shazleen et al 2021[76]
Cellulose	CNF pre-dispersed in plasticizer before nanofibrillation and then included in starch, obtaining thin films	to improve mechanical and barrier properties of polymeric films	Granda et al 2020 [28]
Chitosan	1. CNF-doped CS colloidal solution formed a robust CNF-CS. The procedure included simple solution-casting evaporation; Cross-linking casting evaporation; Surface deposition cross-linking; Electro-deposition and Covalent grafting; 2. CNF & Chitosan nanofiber (ChNF) prepared by isolating ChNF using the aqueous counter collision (ACC) method and CNF by the combination of TEMPO oxidation and ACC method, 3. Cs/CNF	1. This nanocomposite film is used for the immobilization and to-sensing of K562 cells on an electrode  2. For food packaging as it exhibits improved mechanical properties and antioxidant activity.  3. For tunable self-healing hydrogel to be used as injectable for tissue regeneration	Chen et al 2007 [29]  2. Hai et al 2020 [77]  3. Cheng et al 2019 [78]
Alginate	1. Thin film of aq. Soln. of Na alginate & CNF was prepared by solvent evaporation; films were then cross-linked with	2. As antiviral and antimicrobial alginate sheet	Sanmartín-Santos et al 2021 [30]

	<p>divalent cations of calcium and vacuum dried.</p> <p>2. Using the casting method a multiphase CNF+Ca-alginate membrane having sufficient mechanical strength was prepared</p>	<p>2. For selective mass transfer, showing potential for selective separation of molecules such as glucose that can be applicable in downstream processing in food-chemical engineering</p>	<p>2. Nakayama et al 2020 [79]</p>
Collagen	<p>1. CNF+ Collagen hydrogel (CS) decreases gelation time</p> <p>2. Reinforcement of carboxylated CNF for homogeneous collagen film, based on inter-/intra-molecular electrostatic interaction between cationic acid-swollen collagen fiber and anionic carboxylated CNF, was fabricated.</p>	<p>1. SEM illustrated larger and porous morphology and denser nanofibrous structure than pure collagen; having more water retention ability, lower hydrolytic degradation rate, higher stability of CNF composite hydrogels than pure CS, and enhanced mechanical strength and fracture strain. MTT assay revealed no change in cell viability for CS/CNF scaffold as CSLive-dead assay demonstrated the excellent capability of CNF nanocomposite for cell 3D culturing.</p> <p>2. It has promising applications in the meat industry</p>	<p>1. Sajedeh et al 2020 [80]</p> <p>2. Wang et al 2018 [81]</p>
Gelatin	<p>1. Gelatin film enforced CNC is also used as a nanocomposite. Both CNC and CNF are nanoscale cellulose fibers having reinforcing effects in polymer nanocomposites;</p>	<p>1. It was used as a nanocomposite matrix for Trichoderma harzianum KUEN 1585 spores as seed coating material. Which has shown increased seed</p>	<p>Dogaru et al 2021 [82]</p>

	<p>though CNC and CNF are different in shape, size and composition.</p> <p>2. Using casting procedure G/CNF/ZnO nanocomposite was prepared</p>	<p>germination time, percentage, and roots length of the corn seeds.</p> <p>2. Used for active packaging of the chicken fillet to increase shelf life</p>	<p>2. Ahmadi et al 2020 [83]</p>
Fibrin	<p>A hemostatic patch material, fabricated using a superhydrophobic surface with immobilized CNFs.</p>	<p>To promote rapid blood coagulation through quick fibrin growth for rapid blood clotting. It reduces blood loss, enables subsequent facile wound-dressing removal, without clot tears and secondary It reduces blood loss, enables subsequent facile wound-dressing removal, without clot tears and secondary bleeding, and drastically reduces bacteria attachment. As verified within vivo and in vitro analysis in rats</p>	<p>Li et al 2019 [41]</p>
PVA	<p>1. C-Confined PVA-Derived Silicon/Silica/CNF Composites</p> <p>2. PVA blended with CNF</p>	<p>1. As anode or high-energy lithium-ion batteries</p> <p>2. To improve the thermal stability and lower the degradation rate of PVA.</p>	<p>1. Dirican Mahmut et al2014 [44]</p> <p>2. Miao et al 2016 [85]</p>
PEG		<p>As a carrier with high adsorption and fast electron-transfer exchange properties on the edges of nanofiber surface</p>	<p>Takahashi et al 2010 [45]</p>
PCL	<p>1. CNF amalgamated 3D PCL scaffold having porous-nanoarchitecture</p>	<p>1. For human meniscal tissue engineering, as it showed biocompatibility both In vitro and in vivo in rabbit</p>	<p>1. Gopinathen et al 2018, [51]</p>
PLGA	<p>1. Poly(lactic-co-glycolic acid)&amp; CNF composites</p> <p>2.CNFs aligned in PLGA composites</p>	<p>1. For myocardial tissue engineering applications</p>	<p>1. Stout et al (2011) [84]</p> <p>2. Asiri et al (2014)[86]</p>



		2. For increased cardiomyocyte density as assessed in vitro	
PGS	poly (glycerol Sebacate-Urethane) and cellulose nanocrystal composite	Exhibits shape memory effect suitable for a minimally invasive medical device.	Wu et al 2014 [87]
PANI	CNF–PANI composite paper synthesized by rapid-polymerization of aniline monomers on the CNF paper, which has pristine flexibility.	Showed improved electrical conductivity and electrochemical performances as compared with the paper composed of only CNF	Yan et al 2010 [89]
PF(Phenol-Formaldehyde)	1. CNF + PF Composite 2. CNF reinforced PF Composite	For re-entry frames in space-craft. 2, CNF incorporation influenced mechanical properties, better thermal stability, and better adhesion of the phenolic resin to the fabric under fracture surface study	1. Chou TW et al 1989 [59] 2. Joshi & Bhattacharya 2004 [58]
EPOXY	1. & 2. CNF/epoxy and CNF/CF/epoxy nanocomposites 3. CNF/GNP Hybrid Nanofillers with Epoxy Resin: Nanocomposites.	1. To enhance mechanical and electrical functionality. 2. To reduce thermal residual stresses (TRS) i.e. thermo-mechanical properties 3. To counteracts the effect of surfactants and increase the fracture toughness and glass transition of the CNF/GNP hybrid	1. Bal and Saha et al [63] 2. Ghasemi et al 2015[73] 3. Muhammad et al 2019 [40]
PEEK	CNF homogeneously dispersed& aligned in PEEK nanocomposite	Gave the product a linear increase in tensile and bending stiffness and tensile yield stress and strength without negatively affecting the matrix ductility	Sandler et al 2002 [8]
PPy	CNF/PPy nanocomposite	As a toxic gas sensor for NH <sub>3</sub> and HCl.	Jang and Bae et al. 2007 [67]

## APPROACHES INVOLVED IN SYNTHESIZING CNF AND POLYMERS NANOCOMPOSITES FOR VARIOUS APPLICATIONS

The structure of various forms of CNF is well explained by Sharon and Sharon [6]. CNF is generally fabricated either by catalytic chemical vapor deposition growth using chemical or biological precursor or by electrospinning. The overall performances of the CNF/polymer composites are largely governed by the dispersion of the CNF in the polymer matrix. Therefore, the dispersion technique plays a key role in the synthesizing of CNF composites. In the preceding paragraphs, a few commonly used fabrications techniques of CNF-Polymer nanocomposites are described. Different methods of synthesis are used to suit the applications, for which these nanocomposites are synthesized. In preparation of any composite, there are three main material constituents

- The Matrix
- The re-enforcement material i.e., CNF
- The interfacial region

The dispersion of CNFs in the polymer matrix is realized by three approaches:

1. Melt-Mixing Process which is the most widely used method due to its low cost, simplicity, and availability. Processes like extrusion or roll mill [7, 8]; Haake torque rheometer [9], and mini-max molder [10,11] all belong to the melt mixing method.
2. Sonication Process in low viscosity solutions. In this method, to obtain a good dispersion condition for CNF in a polymer matrix, a high shear mixing condition is usually required.

Although the high shear mixing leads to relatively good dispersion of the CNF, the aspect ratio, which is another key parameter governing the overall performances of the CNF/polymer composites, gets decreased during the mixing process. It was found that the decrease of the aspect ratio results in the degradation of some properties [12, 13]. Therefore, the investigation of the relatively low shear mixing approach without sacrificing the dispersion is still a challenge for the preparation of CNF/polymer composites by the melt mixing approach

3. Chemical Surface Treatment of CNFs method helps the dispersion of CNF in the polymer matrix. The compatibility between the grafting functional groups and the polymer matrix is the main factor that decides the CNF dispersion and performances of the composites. In this process, the CNF surface is oxidized by soaking it in sulfuric/nitric acid at various temperatures followed by acylation. And then the functional group is grafted onto the surface of the CNF by the reaction between the oxidized CNF and the functional groups. Li et al [14] have prepared and characterized the surface-treated CNF by using diamines or triamines as linker molecules. The amine group acts as a bridge connecting the CNF and the  $-NH_2$  to form the CNF-C(O)-NH- structure.

Using these three approaches and different chemical and biological polymers; CNF+Polymer composites have been prepared by different scientists for various applications. The method of synthesis, CNF content, fabrication temperature, and the polymer selected, has helped in producing composites of different properties.

CNF composites have been investigated for both fundamental scientific research and applications in many fields, such as electrical devices, sensors, electrode materials for batteries, and supercapacitors. For these uses, electrical conductivity is an important consideration. The electrical property of CNF composites counts on the dispersion and percolation status of CNFs in the matrix. The thermal conductivity and mechanical properties of CNF composites also decide their applications as sensors and electrode materials.

CNF is used as a reinforcement material in composites especially reinforced plastic (CFRP) composites because it offers a higher strength-to-weight ratio, stiffness-to-weight ratio, lightweight, high-strength, and high-stiffness composite materials, which are crucial for the development of an energy-efficient transportation industry, enabling vastly improved power generation, new mechanisms for storing and transporting reduced carbon fuels, enhancing renewable power production, in wind turbines, aerospace (commercial and military aircraft, space launch vehicles), pressure vessel industries for increased strength to weight and stiffness, in sports & leisure composites e.g. skis and snowboards, bicycles and hockey sticks and in aviation and automotive industries.

The properties of CNF composites are governed by the dispersion condition of the CNFs in the matrix materials. The electrical property of the CNF composites largely depends on the dispersion and percolation condition of the CNFs in the matrix, therefore the method of dispersing CNF plays a very important role. The main electrical transport mechanism is the tunneling effect. Therefore, the surface treatment methods, the dispersion approaches, and the polymer types are extremely

important for the enhancement of electrical properties.

It has been found that nanocomposites are more advantageous and offer improvements over conventional composites, especially in their thermal, mechanical, electrical, and barrier properties; hence possibility of a variety of industrial applications such as in automotive, construction, aerospace, food packaging, electrical and electronics, etc. is envisaged.

### **CNF AND BIO-POLYMER NANO-CONJUGATES AND THEIR APPLICATIONS**

Good dispersion of CNF in a polymer is the prerequisite for the fabrication of advanced multifunctional polymeric nanocomposite. There have been many trials of dispersing biopolymers as well as synthetic polymers; mostly using CNT and some also using CNF.

#### **Polysaccharide**

##### **Starch-CNF Nanocomposite**

Starch. (Figure 5a) is a complex Polysaccharide having many monomeric sugar molecules linked together by glycosidic bonds, especially glucose ( $C_6H_{12}O_6$ ). Starch is an organic white, tasteless, insoluble in cold water, alcohol, or other solvents. Starch is found in all plant seeds, tubers, and other plant-derived foods such as bread, potatoes, pasta, and rice. Apart from being consumed as food; the starch is used for making cotton and linen. This complex polysaccharide is mostly present as amylose and amylopectin, arranged in linear or branched form. The simplest form of starch is the linear polymer amylose; amylopectin is the branched form. This polysaccharide is produced by most green plants as an energy storage material. Poly-Lactic Acid derived from starch has been used as a conjugating polymer.

Starch and CNF nanocomposites have been used for electrochemical and food storage applications. Due to their unique properties use of porous carbon material as an electrode for electrochemical applications has been tried by many authors. One of the requirements for developing electrodes for enhanced electrochemical applications is to control the porosity of carbon. Jeong et al [15] have developed mesoporous CNT-CNF electrodes by heat-treatment of electrospun starch with CNT and then applied them as a binder-free electrochemical electrode for a lithium-ion battery. For this purpose, they conjugated starch, with mesoporous CNT- CNF, and their pore structures were controlled by manipulating the heat-treatment conditions. They have exhibited that the activation process greatly increased the volume of micropores and mesopores of CNF by etching carbons with CO<sub>2</sub> gas. The specific area increased as recorded by Brunauer-Emmett-Teller (BET) was found to be about 982.4 m<sup>2</sup> •g<sup>-1</sup>. Moreover, this activated CNT-CNF exhibited a high specific capacity (743 mAh•g<sup>-1</sup>) and good cycle performance (510 mAh•g<sup>-1</sup> after 30 cycles) due to their larger specific surface area, which had increased adsorption sites of lithium ions, and higher electrical conductivity, compared with CNF without CNT. They have concluded the pore structure of the CNF made from starch could be controlled by the heat-treatment conditions and activation process thus providing a CNF conjugate for various applications.

#### PLA-CNF Nanocomposite

Recently CNF has been reinforced in Poly-lactic acid (PLA)[16] as a strategy to control degradation in vitro of CNF-reinforced PLA composites, by combining fiber modification and pulsed electromagnetic fields. PLA is biodegradable and bioactive thermoplastic aliphatic polyester. It is derived from corn starch, cassava roots, chips or starch, sugarcane, etc. It is used in food

handling and medical implants that slowly biodegrade within the body. Since CNF/PLA composites are a human bone-fixation material, which controls the degradation of materials, Zhang et al [16] studied CNF/PLA both in modified and unmodified forms. During the subsequent degradation process, they selectively applied a pulsed electromagnetic field (PEF) and found that the interfacial ester bonding between modified CNF and PLA matrices significantly affected degradation in vitro of C/PLA composite. However, PEF affected the degradation performance of C/PLA composites and, after PEF treatment, the material's water absorption, mass retention, bending, and shearing strengths were changed to varying degrees.

#### Cellulose-CNF Nanocomposites

Cellulose is also a Polysaccharide consisting of a linear chain of several hundred to many thousands of  $\beta$  linked D-glucose units (Figure 5b) This organic compound with the formula (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>, the molar mass of 162.1406 g/mol, and density 1.5 g/cm<sup>3</sup>; is an important structural component of the primary cell wall of all green plants, algae and oomycetes; and also fibers of plants. Some species of bacteria secrete cellulose to form biofilms.

Conventional food packaging systems passively protect the food packed in them, to act as a barrier between the food and the surrounding environment. On the other hand, an active food packaging system that not only acts as a passive barrier but also interacts with the food in some desirable way, e. g. by releasing desirable compounds (antimicrobial or antioxidant agents), or by removing some detrimental factor (such as oxygen or water vapor). The consequences of such interactions are usually related to improvements in food stability. Antimicrobial food packaging systems have received considerable attention since they help to control the growth of pathogenic and spoilage

microorganisms on food surfaces. Antimicrobial nanocomposite systems are particularly interesting since materials in the nanoscale range have a higher surface-to-volume ratio when compared with their microscale counterparts. Nanomaterials are thus more efficient because they can attach more copies of microbial molecules and cells[17]. Nanoscale materials have been investigated for antimicrobial activity as growth inhibitors [18], killing agents [19], or antibiotic carriers.

CNF composites in the food packaging system are at the initial stage of development. Rather than using CNF derived from chemicals or plant metabolites; attention is focused on cellulose nanofibers [20]. Instead of synthetic plastics use of biodegradable polymers appears a more lucrative packaging solution as it is decomposable and are also derived from renewable sources [21, 22, 23].

To improve biopolymer packaging performance addition of nanoscale materials to the biopolymer is being tried, as nanoscale materials have a larger contact surface area per weight of material than macroscale, allowing greater interaction with the polymer matrix of the film and leading to better performance of the material. Cellulose-derived nanofibers are one such nanomaterial having great potential as a reinforcing material in polymeric matrices. Cellulose is a component of plant fiber. It is obtained from cotton, eucalyptus, wood, flax, sugarcane bagasse, sugar beet, etc.[24]. Apart from being economic, its hydrophilic nature, it has a high affinity with protein-based polymer formulations and also with most natural polymers [25]. When added to packaging CNF are capable of imparting high rigidity,

vapor permeability, and water solubility reduction [26, 27].

Recently, cellulose nanofiber reinforced starch films is prepared by Granda et al [28] to upgrade mechanical properties and barrier character. A new form of CNF i.e. Nano fibrillated cellulose has attracted scientists to its sustainability and its capacity to improve the mechanical and barrier properties of polymeric films. They [28] have used cellulose to optimize the dispersibility of CNF in a thermoplastic starch. They realized that CNF needs a hydrophilic dispersant to be included in the matrix, and the starch needs a hydrophilic plasticizer to obtain a thermoformable material, so they have used Glycerol to fulfill both targets at once. CNF was pre-dispersed in the plasticizer before nanofibrillation and later on was included in starch, obtaining thin films. Nanofibrillated cellulose reinforced starch films upgraded not only the mechanical properties ((tensile strength, elongation at break, and Young's modulus)) but also the barrier character. The tensile strength of these CNF–starch composite films was 60% higher than the plain thermoplastic starch at a very low 0.36% w/w percentage of CNF. The films showed a noticeable correlation between water uptake, temperature, and humidity. Regarding permeability, a ca. 55% oxygen and water vapor permeability drop was found by CNF loading.

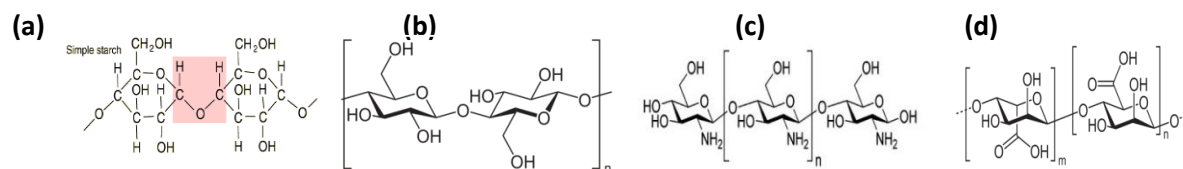


Figure - 5: Molecular structure of Some polysaccharides (a) Starch, (b) Cellulose (c) Chitosan, and (d) Alginate

### Chitosan and CNF Nanocomposites

Chitosan is a linear Polysaccharide composed of randomly distributed  $\beta$ -linked D-glucosamine and N-acetyl-D-glucosamine (Fig. 8). It is synthesized commercially from the deacetylation of chitin shells of shrimp and other crustaceans and also cell walls of some fungi, with sodium hydroxide for many biomedical uses. Chitosan is water-soluble and acts as a bioadhesive by readily binding to negatively charged surfaces such as mucosal membranes.

Comparatively more efforts have been directed toward synthesizing chitosan conjugated CNT than with CNF. Many research efforts have been devoted to chitosan bio-composite reinforcements using CNT. However, such findings with CNT have opened a vista for trying CNF with is comparatively less expensive and has some unique properties. Chitosan and CNF nanocomposites are successfully prepared by (i) Simple solution-casting evaporation method; (ii) Cross-linking casting evaporation methods; (iii) Surface deposition cross-linking; (iv) Electro-deposition method; (v) Covalent grafting; (vi) Electrostatic interaction; (vii) Layer by layer self-assembly; (viii) Freeze-drying ; (ix) Wet-spinning; (x) Electro-spinning. The incorporation of CNF increases the mechanical properties such as tensile modulus strength. Chitosan is a biocompatible compound. Hence, doping CNF with chitosan has many applications in biosensors. Chen et al [29] have used the biocompatibility of chitosan (CS) and conductivity of carbon nanofiber (CNF) and with

the help of controllable electrodeposition of soluble CNF-doped CS colloidal solution formed a robust CNF-CS nanocomposite film for the immobilization and cyto-sensing of K562 cells on an electrode. The adhesion of K562 cells on the nanocomposite film-modified electrode was followed by electrochemical impedance spectroscopy and cyclic voltammetry. The presence of CNF facilitated the electrochemical behavior of K562 cells. It was found that the impedance of electronic transduction was related to the amount of the adhered cells, producing a highly sensitive impedance sensor for K562 cells ranging from  $5 \times 10^3$  to  $5.0 \times 10^7$  cells mL<sup>-1</sup> with a limit of detection of  $1 \times 10^3$  cells mL<sup>-1</sup>.

### Alginate and CNF Nanocomposites

Alginate is a Polysaccharide. In nature, brown algae occur in the range of 30 to 60% (on a dry weight basis). Alginic acid accumulates in brown seaweeds and forms a structural component of their cell walls.

Sodium alginate is a US-FDA-approved biopolymer allowed for human biomedical applications due to its excellent properties such as biodegradability, renewability, cost-effectiveness, non-toxicity, and biocompatibility. Sanmartín-Santos et al [30] have demonstrated that as low as 0.1% w/w of CNF can significantly enhance the antiviral activity of calcium alginate. Alginate-based nanocomposites possess antiviral activity and enhanced physical and biological properties also which render them great potential in

biomedical applications with antimicrobial requirements.

Since Ca-alginate hydrogels have poor mechanical properties that restrict their applications in biomedical fields such as skin tissue engineering; Llorens-Gómez et al [31] have prepared alginate-based films reinforced with different amounts (0, 0.1, 0.5, 1 and 2% w/w) of CNFs, which had similar biological properties as neat alginate hydrogels. They were not cytotoxic and neither showed cell adhesion on the films. Water sorption at the body temperature did not suffer strong changes with the incorporation of CNFs into the alginate matrix. The dynamic mechanical and tensile/compressive properties of calcium alginate significantly improved with the addition of even a very low amount of CNFs. The tensile and compression modulus of the calcium alginate + 2% w/w CNF films in the dry and hydrated state increased up to three and six times, respectively.

## Protein

### Collagen and CNF Nanocomposites

Collagen is the main structural protein made up of amino acids: glycine, proline, hydroxyproline, and arginine (Figure 6a). It is found in skin, hair, nails, gut, and connective tissues. Collagen is the most abundant protein present in mammals, making 25% to 35% of the whole-body protein content. The abundance of three amino acids: glycine, proline, and hydroxyproline of collagen that has Hydrogen bonds linking the peptide bond NH of a glycine residue with a peptide carbonyl (C=O) group in an adjacent polypeptide help hold the three chains together; CH gives it a triple-helical structure of collagen (Figure 6b).

CNF has received less attention in regenerative medicine than its cousin CNT. Tissue engineering is a

discipline that is in its infancy but has emerged rapidly and received extensive attention [32, 33]. It involves the replacement of the anatomic structure of the damaged, injured, or missing tissue or organs by agglomerating biomaterials, cells, and biologically active molecules [34]. Biomaterials are three-dimensional scaffolds that provide mechanical support to the growing cells or tissue, guiding them in a microenvironment mimicking the biological system. These can then be transplanted into the system. Earlier tissue engineers were mostly focused on the investigations of macro-level structures. However, the present-day need is to engineer functional units of the subcellular scale structures and nanostructures to control cell molecular and cell-cell interactions. Thus, engineering tissue for the miniaturization at the nano level to precisely design mimicry of the native tissue structures is one of the most promising directions for the tissue fabricators for most researchers.

The principal task of a scaffold is to direct cell behavior such as migration, proliferation, differentiation, maintenance of phenotype, and apoptosis, by facilitating sensing and responding to the environment via cell-matrix communications and cell-cell communications. Such scaffold should have the capacity to give highly porous surfaces allowing seeding of cells at high densities as well as providing spatial signals to actuate the organization of the cell as well as that of the extracellular matrix derived from them. Scientists in their study have found that both CNT and CNF possess very fascinating properties as a scaffolding agent such as ordered structures with high aspect ratio, ultra-lightweight, high mechanical strength, high electrical and thermal conductivity, metallic or semi-metallic behavior, and high surface area. These properties have made CNTs a favorite material for nanofabrication of compatible

biomaterials which can act as a scaffold for engineering tissues.

Collagen and CNT composite have been used for many applications in biological systems such as scaffolds in tissue engineering [35]; to improve cell alignment, the performance of cardiac constructs, and as injectable biomaterials to deliver cell or drug molecules for cardiac regeneration following myocardial infarction shortly [36]. In bone tissue regeneration and engineering [37] have tried using CNT. Comparatively less attention has been paid to CNF and collagen nanoconjugates. However, recently Samadian et al [38] have reported osteoconductive and electroactive CNF/hydroxyapatite nanocomposite tailored for bone tissue engineering: in vitro and in vivo studies.

## 5.2.2 Gelatin and CNF Nanocomposite

Gelatin is derived from collagen taken from animal body parts. Gelatin is a heterogeneous mixture of single or multi-stranded Polypeptides (Figure 6c), each with extended left-handed proline helix conformations. It is a translucent, colorless, flavorless polymer that is used as a food ingredient. It is brittle when dry and gel-like when moist. The hydrolyzed form of gelatin is also referred to as hydrolyzed collagen, collagen hydrolysate, gelatin hydrolysate, hydrolyzed gelatin, and collagen peptides as it contains 50 - 1000 amino acids. In food, it is commonly used as a gelling agent, also in beverages, medications, drug and vitamin capsules, photographic films, papers, and cosmetics.

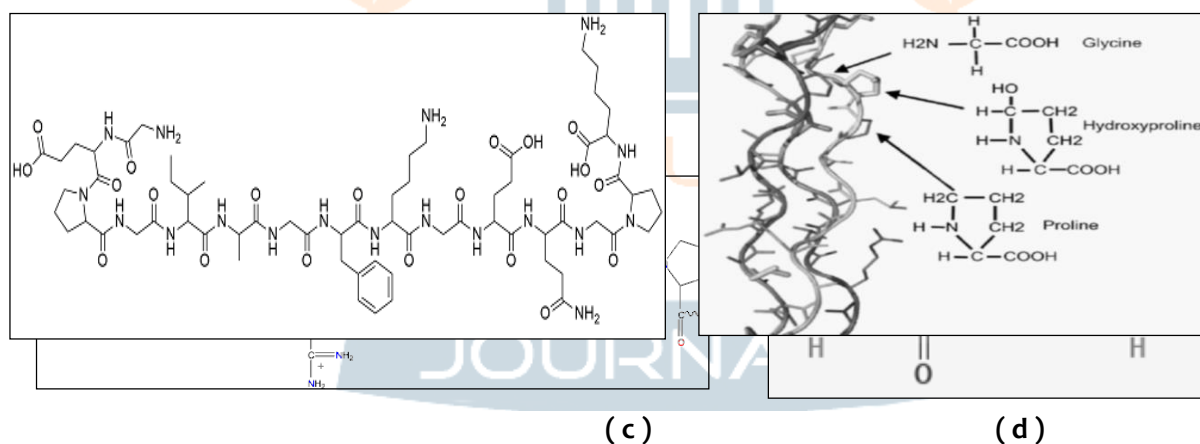


Figure-6: (a) Molecular structure of (a) Type II-Collagen; (b) Triple-helical structure of Collagen; (c) Molecular structure of Gelatin and (d) Molecular structure of Fibrin

Gelatin, a cost-effective animal protein, has been used as a highly efficient bio-surfactant to functionalize CNFs. Gelatin-CNF nanocomposite exhibits high mechanical, electrical, and processing properties.

Dispersion of Gelatin-CNFs in the epoxy resin and good interfacial adhesion between them were found to be due to gelatin modification. The electrical percolation threshold of the gelatin-CNFs/epoxy decreased from

0.33 wt.% to 0.21 wt.%, whereas the flexural strength and modulus increased by 29.1 % and 27.1 % with 0.25 wt.% nanofiller addition, which was proved by nanoindentation test. The wettability of nanocomposite with gelatin treated CNFs is also improved with decreased contact angle. Thus, promising a method to be applied in the fabrication of multifunctional polymeric matrix for fiber-reinforced plastic composites [39]. Earlier Muhammad et al [40] have shown that the addition of surfactant alone to epoxy reduces the fracture toughness, elongation at break, and glass transition temperature whereas the addition of CNF to it counteracts the effect of surfactants and increases the fracture toughness and glass transition of the CNF/GNP hybrid.

### Fibrin and CNF Nanocomposites

Fibrin (C<sub>5</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>) as the name suggests is a fibrous, non-globular protein (Figure 6d). It is formed by the polymerization of fibrinogen (an insoluble protein) by the action of protease thrombin during the clotting of blood. It forms a fibrous mesh that stops the flow of blood.

Fibrin is formed is by polymerization of the soluble plasma protein fibrinogen when there is a blood flow from a wound and is an integral part of the blood-clotting cascade, hemostasis, and tissue repair. Fibrin has been used as a tissue sealant. Hemostatic materials are of great importance in medicine. Using CNF, a hemostatic patch material was developed by Li et al[41] Successful implementation of hemostatic material needs to achieve rapid blood coagulation before significant blood loss, and enable subsequent facile wound-dressing removal, without clot tears and secondary bleeding. To target these two attributes, when a superhydrophobic surface with immobilized CNFs was used, it promoted quick fibrin growth and caused rapid clotting, and severely limited blood

wetting to prevent blood loss and drastically reduced bacteria attachment/infection. The bonus part is the minimal contact between the clot and the superhydrophobic CNF surface that yielded an unforced clot detachment after clot shrinkage. These attributes were verified in vitro as well as in vivo rat experiments.

### Whey Protein Isolates (WPI) and CNF Nanocomposites

CNF conjugated with whey protein isolates (WPI) are being used in food packaging. The use of proteinaceous WPI in packaging material offers an excellent barrier to oxygen, which protects food by avoiding the oxidation process, it acts as a barrier to aromas, has high transparency and film-forming ability, and can be used as active packaging for transporting food additives, antioxidants, antimicrobial agents and nutrients, etc. Moreover, due to the presence of the amino acid chain, these biopolymers are hydrophilic, which directly influences the water vapor barrier and solubility properties [42]. Celin de Carvalho et al, [43] have shown that depending on the quantity of CNF added to WPI films caused a reduction in thickness of the film, the composite was more resistant to water; the mechanical properties of films were improved making the films more resistant and elastic. The addition of 4% (w/w) of CNF decreased the permeability by about 30%. The addition of the 6% w/w CNF did not change the mechanical properties and water vapor permeability; this was related to nanoparticle agglomeration when added to the polymer matrix in excess. When 2 or 4% (w/w) CNF was added to WPI the transmittance of the films decreased

### CNF AND SYNTHETIC POLYMER NANO-CONJUGATES AND THEIR APPLICATIONS

CNFs gained much interest in the last few years due to their promising electrical, chemical, and mechanical

characteristics. We now discuss a new nanocomposite composed of CNF conjugated with synthetic polymers that have found many applications.

### Poly Vinyl Alcohol (PVA)+CNF Nanocomposites

PVA (Figure 7i) is a white, odorless, water-soluble synthetic polymer  $\text{CH}_2\text{CH}(\text{OH})_n$ . Generally, other vinyl polymers are prepared by polymerization of its corresponding monomer but PVA is synthesized by partial or complete hydrolysis of polyvinyl acetate to remove acetate groups. It has many applications such as in papermaking, textiles, and a variety of coatings. It is used in smart textiles as it has a Melting point of  $200^\circ\text{C}$  and a Boiling point of  $228^\circ\text{C}$ .

PVA is used in papermaking, textile warp sizing, as a thickener and emulsion stabilizer in PVA adhesive formulations, and a variety of coatings. A nanocomposite composed of CNF hosted by PVA and both integrated into one electrospun nanofiber web; shows that electrical conductivity of the formed nanofibers has been improved up to  $1.63 \times 10^{-4} \text{ S/cm}$  for CNFs of weight 2%. The peak temperature of mass loss through TGA measurements has been reduced by 2.3%. The homogeneity of the formed PVA and CNF in one web, with stretched CNFs after the electrospinning process offers a wide variety of applications including nanoelectronics, nanomedicine, and gas adsorption. One of the uses of PVA is to use it as a precursor for synthesizing carbon nanofiber by electrospinning and subsequently heating a mixture of PVA + TEOS (tetraethyl orthosilicate) + Si to carbonize at a high temperature and make a novel composite of silicon/silica/carbon (Si/SiO<sub>2</sub>/C). These Si/SiO<sub>2</sub>/ CNF composites were then coated with amorphous carbon by chemical vapor deposition (CVD) technique to achieve good cycling performance. Si/SiO<sub>2</sub>/ CNF composite anode materials were developed for lithium-ion batteries. The CVD carbon-coated CNF

composites formed freestanding, conductive nonwoven mats that were used directly as binder-free anodes in lithium-ion batteries. The SiO<sub>2</sub> component of the CNF composites provided sufficient buffering function to accommodate the volume expansion of the Si nanoparticles during the repeated charging and discharging cycles, whereas amorphous carbon coating helped to maintain the Si nanoparticles within the CNF structure, resulting in improved cycling performance. Electrochemical studies showed Si/SiO<sub>2</sub>/ CNF composites exhibited large capacity retention of 91% and high coulombic efficiency of 97.4% at the 50th cycle; declaring it a promising anode material for next-generation, high-energy lithium-ion batteries [44].

### Poly Ethylene Glycol (PEG) +CNF Nanocomposites

PEG ( $\text{C}_2\text{nH}_4\text{n}+2\text{n}+1$ ) is a Polyether compound (Figure 7ii) also known as polyethylene oxide or poly (oxyethylene), depending on its molecular weight. It is water soluble with a Molar mass of  $18.02 + 44.05n$  g/mol and 1.125 density. It is used in medicine to industrial manufacturing.

Like PVA, PEG has also been used as a precursor to CNF. But here instead of electrospinning; pyrolytic conversion of PEG is done using Ni as a catalyst. Takahashi et al [45] showed that three types of CNF (herring-bone CNF, platelet CNF, and cup-stacked CNF) can be synthesized by the thermal decomposition of a mixture of poly(ethylene glycol) (PEG) and nickel chloride (NiCl<sub>2</sub>). Following the same procedure, Ko et al [46] prepared a PEG/Ni membrane on a silicon wafer surface by heating it at  $7500^\circ\text{C}$  for 15 min. Before use silicon wafer was heated to  $4000^\circ\text{C}$  and kept at that temp. for one hour and then heated to  $7500^\circ\text{C}$ . This formed the CSCNF microsphere, which was dispersed in an aqueous solution of 0.5% Nafion. This CSCNF microsphere works as a sophisticated carrier with high

adsorption and fast electron-transfer exchange properties on the edges of the nanofiber surface.

In amphiphilic copolymers from poly(ethylene glycol)mono-acrylate (PEGMA), designed via Reversible Addition Fragmentation chain Transfer (RAFT) polymerization; CNFs were dispersed and their stability and dispersion capacity has been investigated and found to be very suitable [47].

## Poly Caprolactone (PCL)+CNF Nanocomposites

Poly Caprolactone (C<sub>6</sub>H<sub>10</sub>O<sub>2</sub>)<sub>n</sub> is biodegradable Polyester(Figure 7iii)with a low melting point of around 60 °C and a glass transition temperature of about –60 °C. In the human body, PCL is degraded by hydrolysis of its ester linkages in physiological conditions. PCL is a very suitable material for the production of specialty polyurethanes; therefore, it has received a great deal of attention for use as a long-term implantable biomaterial and controlled drug release

PCL – this biodegradable polymer has been explored for its use and application in biological systems for nearly two decades. PCL has been used as a source of nanofiber. Some of the experimental successes incorporating CNF and PCL nanocomposites include:

As early as 2005 Ma et al [48] modified the surface of electrospun poly(caprolactone) (PCL) derived nanofibers by grafting gelatin to improve Endothelial Cell (EC)spreading and proliferation and control cell orientation and show their compatibility with ECs and to show the PCL nanofibers as a blood vessel tissue-engineering scaffold.

Developing a biologically mimetic and functional nanofiber for tissue scaffold by coaxial electrospinning of (Fluorescein Isothiocyanate-Conjugated Bovine Serum Albumin)-Encapsulated Poly(ε-caprolactone)

nanofibers for sustained release of bioactive protein [49].

Poly(ε-caprolactone) (PCL) nanofibers, conjugated with levofloxacin (a drug used to treat bacterial infection) and mesoporous silica nanoparticle, has been used for the slow release of levofloxacin [50].

Further advancing the use of PCL nanofiber in tissue scaffolds; Gopinathan et al [51] have developed a biocompatible (both in vivo and in vitro) CNF amalgamated 3D poly-ε-caprolactone scaffold functionalized porous-nanoarchitecture for human meniscal tissue engineering. In vivo rabbit, bio-toxicity studies revealed scaffold's non-toxicity and it also indicates that the incorporation of CNF in the polymer matrix may be optimized based on mechanical properties of the patient meniscus and it may help in developing the customized patient-specific 3D constructs with improved multifunctional properties.

Another use of PCL-derived nanofiber is shown by Kaviannasab et al [52]. The core-shell nanofibers from Poly(ε-caprolactone) (PCL) and Polyvinylpyrrolidone (PVP) consist of PCL at the core and shell of PVP. Using this core shell, the drug release dynamic was assessed by spectroscopy.

Recently Nasari et al [53] have shown the use of loading Poly (ε-caprolactone)/poly (N-vinyl-2-pyrrolidone) core-shell nanofibers by multi-walled carbon nanotubes (MWCNT) and 5-fluorouracil to deliver this anticancer. This opens the way to use comparatively cheaper CNM i.e., CNF instead of MWCNT,

## Poly Lactic-co-Glycolic Acid (PLGA)+CNF Nanocomposites

PLGA is a copolymer that is synthesized using ring-opening co-polymerization of two different

monomers, the cyclic dimers of glycolic acid and lactic acid (Figure 7iv). PLGA is naturally amorphous. Though separately both poly (lactic) and poly(glycolic) acid are poorly soluble in most solvents, PLGA dissolves in many solvents including tetrahydrofuran, acetone, ethyl acetate, and chlorinated solvents. Being biocompatible and biodegradable, it has found applications in many drug deliveries, and food administration and is approved for therapeutic devices.

Most of the work done is on the use of MWCNT conjugated with PLGA for targeted delivery of an anticancer drug (Doxorubicin, pro-apoptotic protein caspase-3 (CP3). Preparation of PLGA/MWCNT composite Nanofibers has been easily achieved by Airflow Bubble-Spinning. However, electrospun PLGA nanofibers have also been used for the same purpose. There have not been many efforts in replacing CNT with CNF; so far as conjugating with PLGA has been reported.

Stout et al (2011) [84] have tried to in vitro study to investigate cardiac tissue cell functions (specifically cardiomyocytes and neurons) on (PLGA) (50:50 wt.%)–CNF) composites to ascertain their potential for myocardial tissue engineering applications. CNF was added to the pure PLGA to increase its conductivity and cytocompatibility of cardiomyocytes and neurons. Assessment using SEM, XRD, and Raman spectroscopy analysis confirmed that PLGA: CNF materials are conductive and that the conductivity increases with an increase in amounts of CNF added to PLGA. The results also indicated that both neuron and cardiomyocyte density increase with the increase in the amount of CNF in PLGA. This composite also promoted the adhesion and proliferation of both cell types important for myocardial tissue engineering applications. Later Asiri et al (2014) [86], instead of randomly embedding CNF in PLGA; used CNFs aligned in PLGA composites,

and compared it with CNF +PLGA results. It was noted that anisotropic mechanical and electrical properties and significantly improved cardiomyocyte density for up to 5 days on CNFs aligned in PLGA compared with being randomly oriented in PLGA.

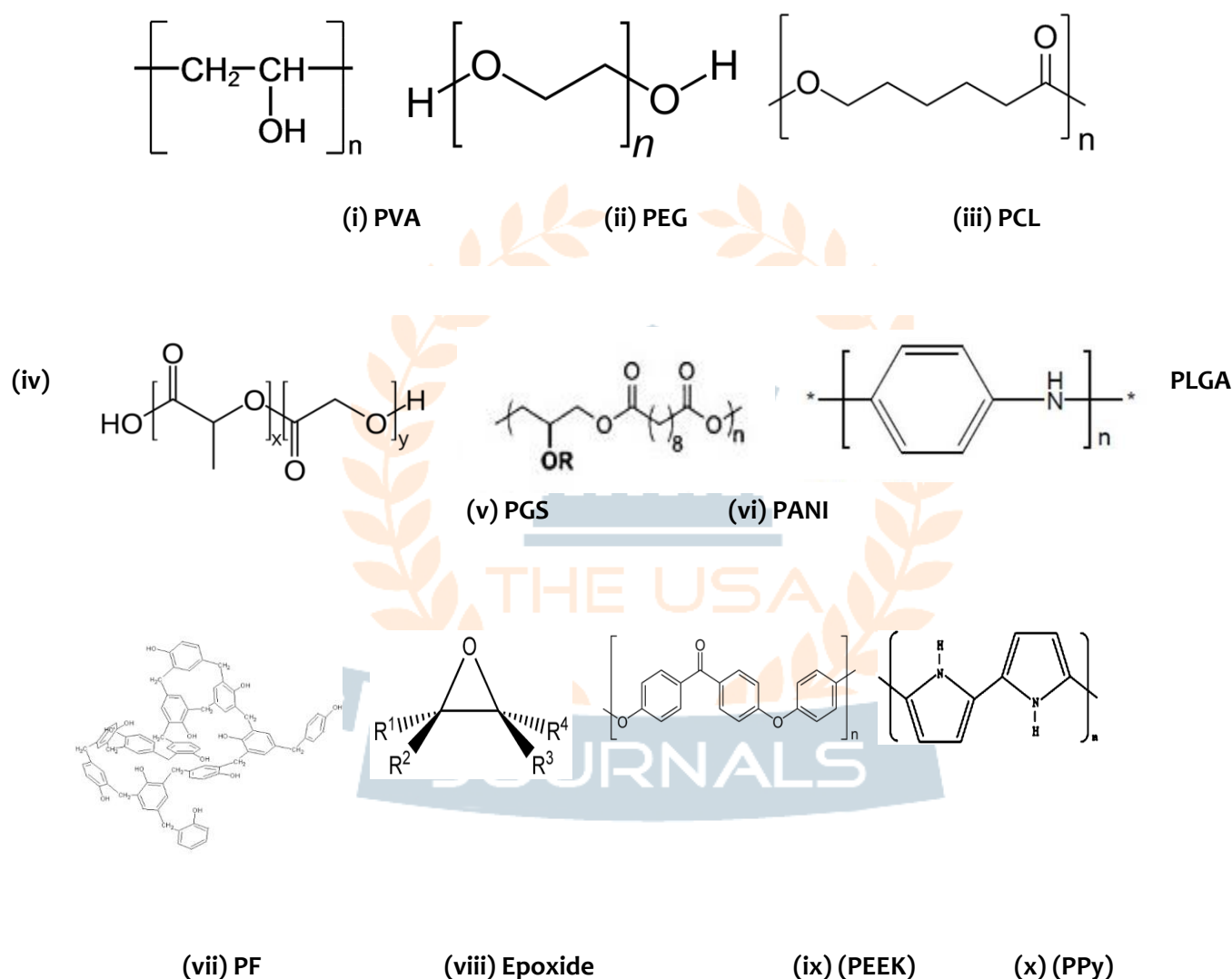
### Poly Glycerol Sebacate (PGS)+CNF Nanocomposites

PGS (Figure 7v) is a comparatively newly discovered [3] synthetic biodegradable, thermoset, and tough polymer that is used in making many composites. According to Wang it is cheap, bio-resorbable, biodegradable, and has a non-toxic degradation product. Due to its many unique desired properties such as having surface degradation and elastomeric behavior, Physico-chemical, mechanical, thermal, and morphological properties; PGS and its composite forms have been researched for both in-vitro and in-vivo studies for numerous tissue engineering applications; especially the combination of PGS with  $\beta$ -tricalcium phosphate ceramics is recently proposed by Tevlek et al [4] for guided bone regeneration in our previous study. In another study Wu et al (2014) [87] have shown that poly (glycerol Sebacate-Urethane and cellulose nanocrystal composite are a biodegradable biocompatible material that exhibits shape memory effect and can be used as a minimally invasive medical device. Though poly (glycerol Sebacate) conjugated with graphene is suitable for piezoresistive sensors. CNF otherwise has shown effectivity in piezoelectric sensitivity. (Sengupta et al 2020)[88]

PGS has been mostly conjugated with CNTs because CNT-based nanocomposites often possess properties such as high stiffness, electrical conductivity, thermal stability, and utilizing CNTs as physical filler. Such composites have been studied for various biomedical, piezoresistive sensors, and biotechnological applications. MWCNT-PGS exhibits a highly stretchable elastomeric nature, hence, being very suitable for

piezoresistive sensors. However, the use of CNF instead of CNTs has not yet attracted much attention.

Though many of these synthetic polymers have been used as a precursor for spinning them into nanofibers.



**Figure –7: Molecular structures of (i) Poly Vinyl Alcohol (PVA); (ii) Poly Ethyl Glycol (PEG); (iii) Poly Caprolactone (PCL); (iv) Poly Lacto Glycolic Acid (PLGA); (v) Poly Glycerol Sebacate (PGS); (vi) Polyaniline (PANI); (vii) Phenol Formaldehyde (PF) Resin; (viii) Epoxide (ix) (PEEK) and (x) Polypyrrole (PPy).**

#### Polyaniline (PANI)+CNF Nanocomposites

Polyaniline (PANI) is a conducting polymer. Owing to high capacitance, good environmental stability, and

low cost combined with the easiness of preparation, PANI materials have been widely studied as Supercapacitors[5]. PANI is prepared by the oxidation of aniline with ammonium peroxydisulfate in various aqueous media. When the polymerization is carried out in the solution of strong sulfuric acid, a granular morphology of PANI is obtained (Figure 7vi).

Nanotechnology being a promising field of interdisciplinary research has opened up opportunities in various applications of PANI in many fields including agriculture and natural resources management also. For instance, a hydrogel-based Nano-clay for use as a growth media additive in pot plants and small-scale cultivation [54, 55]. For natural resources, nanotechnology has numerous applications such as stabilizing sandy soil, maintaining soil water, and controlling soil erosion [56]. The study of the effect of different levels of PANI on soil penetration force showed that soil penetration force increased exponentially. None of the PANI polymer levels reduced soil penetration force below the control. On the other hand, the addition of sulfonated polyaniline (SPANI) (Figure 8) has been shown to have an adverse

effect on the soil penetration force. 0.678%, of SPANI, gave the lowest values of the soil resistance to penetration. Hence, a 100% germination of corn seeds was obtained within 5 days as compared to the control, which provided 100% germination after 12 days. Toxicity test showed that the concentration of a substance that is (LC<sub>50</sub>) lethal to 50% of the earthworm was 1.13%. This indicates that using sulfonated polyaniline (SPANI) at 0.678%, the rate would be safe for earthworms. Whereas, for mice, the orally fed SPANI LD<sub>50</sub> of SPANI was 206.64 mg/kg body weight, which is classified as moderately toxic. The data shows that more work is needed to be done for obtaining the absorbing rate of SPANI in the plant to determine the rate of toxicity to plants and humans.

Most of the newly reclaimed lands are located in arid and semi-arid regions that suffer from crusting. Controlling soil surface crust formation using Nanosized sulfonated polyaniline has been a good promise [57].

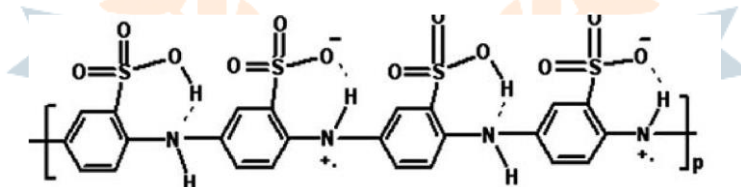


Figure 8: Sulfonated polyaniline (SPANI)

PANI-derived nanowire is an electrically conducting polymer, hence that can be used as an active layer for sensors whose conductivity change can be used to detect chemical or biological species. PANI has been considered to promote the electrochemical capacitance of flexible CNT and graphene papers. Researchers have used electro-spinning to produce

flexible CNF paper. This electrospinning process is simple and fast, and the CNFs are relatively inexpensive compared with CNTs or graphene. More importantly, the preparation of a freestanding CNF-PANI composite paper by a simple rapid-mixture polymerization of aniline monomers on the CNF paper has been demonstrated; which maintains the pristine flexibility of the CNF paper and displays improved

electrical conductivity and electrochemical performances compared with the CNF paper (Yan et al 2010) [89].

### Phenolic Resin or Phenol-Formaldehyde (PF) Resin+CNF Nanocomposites

Phenolic resins or Phenol formaldehyde resins (Figure 7vii) are synthetic polymers. It is obtained by reacting phenol or substituting phenol with formaldehyde. Phenolic resins are the first commercial synthetic resins known as plastic, which is used as the basis for Bakelite, production of molded products such as

laboratory countertops, billiard balls, coatings, adhesives, etc. Earlier it was used as the primary material for the production of circuit boards but now it has been largely replaced with epoxy resins, and fiberglass cloth, as with fire-resistant FR-4 circuit board materials.

Joshi and Bhattacharya [58] used dispersed CNF into the phenolic resin (prepared by condensing phenol and formaldehyde and then refluxing them at 70°C, by three different processes i.e., sonication, mechanical stirring with 0.2% non-ionic surfactant and stirring followed by sonication. The surfactant helps in the proper dispersion of the CNF into the matrix. Finally, dipping the fabric in the resin composite and then drying overnight completes the process. The fiber impregnated composite is compression-molded at a curing temperature of 150°C, for 2 hours using 3 metric tons of force. Textile structured CNT/CNF composites help in the preparation of carbon-carbon composites [59], This composite has found application in spacecraft re-entry frames. The incorporation of Carbon nanomaterial enhances the mechanical properties of the composites and gives better thermal stability. CNF reinforced polymeric matrix composites

with CNF reinforcement are examples of unique three-phase nanocomposite systems.

### Epoxy Resin+ CNF Nanocomposites

Epoxy word is used for any of a class of adhesives, plastics, or other materials that are polymers of epoxides. It is one of the plastic families. This thermoset polymer is made from a monomer that contains at least two epoxide groups. The epoxide is an organic compound, a cyclic ether whose molecule contains a three-atom ring involving an oxygen atom and two carbon atoms (Figure 7 viii). This ring approximates an equilateral triangle, which makes it strained, and hence highly reactive, much more than other ethers. They are produced on a large scale for many applications. As compared to phenolic resin, epoxy coating resin has relatively shorter processing times, epoxy coating is more resistant to mechanical influence. Epoxy coating is suitable on rougher surfaces and is water-resistant. Epoxy resins are used in the manufacture of adhesives, plastics, paints, coatings, primers and sealers, flooring, and other products and materials used in building and construction.

Pervin et al [60] using the sonication method, fabricated nanocomposites composed of SC-15 epoxy and CNF. The mixing process was carried out through a high-intensity ultra-sonication of the CNF and SC-15 epoxy. Once the sonication was completed, the hardener was added to the mixture, followed by high-speed mechanical stirring, and then cured at room temperature

Simultaneously in another attempt Kellarakis and co-workers [61] prepared CNF/ethylene/propylene (EP) random copolymer composite using a similar process i.e. oxidizing the CNF surface with H<sub>2</sub>SO<sub>4</sub> and then

reducing it with sodium borohydride in absolute ethanol to form the CNF–OH structure. After that, the hydroxylated CNF was dispersed in dichlorobenzene and a polypropylene-graft-maleic anhydride polymer to form the CNF–O– structure. Apart from the melt mixing processing for the CNF/thermoplastic polymers, the dispersion of the CNF in thermosetting polymers to prepare the CNF/thermosetting polymers (mostly epoxy resins) composites mainly counts on the solution approach with the help of sonication. In this process, the CNFs were dispersed in the liquid epoxy form by sonication before being mixed with the hardener. Usually, acetone or other solutions are needed to help the effect of sonication. In addition, to avoid the increasing temperature during the sonication process, external cooling devices are necessary in most cases.

The preparation of the CNF/epoxy nanocomposite by Choi et al [62] showed that ozone surface treatment of the CNF is helpful for its dispersion in the epoxy matrix. The CNFs were dispersed in acetone by sonication and stirring at room temperature.

Bal and Saha [63] studied the influence of the amount of CNF (1.5, 2, and 2.5 wt.% of CNFs) on the mechanical and viscoelastic behavior of epoxy-based nanocomposites. The composite synthesis was done at room temperature (27 °C) and at a low temperature of 4 °C. It was found that flexural modulus was improved to 50% and 25% for composites containing 1.5 wt. % CNF and 83% and 79% for 2 wt. % CNF respectively for all the room temperature cured composites. And low temperature cured composites; maximum improvement in flexural modulus was 83% & 128%. According to the authors improved Storage modulus and Glass Transition. The temperature of these specimens was too good for interfacial adhesion. No further improvement at higher CNF content of 2.5 wt.

% was observed which was due to the appearance of aggregated phases in the composites.

MWCNT grown on CNF reinforced epoxy has been used to improve physical and electrical properties. An improvement in sizing-sensitive mechanical and physical properties, such as the interfacial adhesion, shear properties, and handling of the fibers, whilst retaining resin-infusion capability has been observed [64]. The CNT-modified carbon fiber composite offers improvements of 146 % increase in Young's modulus; 20% increase in ultimate shear stress; 74 % increase in shear chord modulus and an 83 % improvement in the initial fracture toughness. Moreover, it is found that the addition of CNTs imparts electrical functionalization to the composite, with 400% enhancements in the surface direction, thus it may be a suitable route for developing sizing-free composites with enhanced mechanical and electrical functionality.

### **Poly Ether Ether Ketone (PEEK)+ CNF Nanocomposites**

Polyether ether ketone (PEEK) is a colorless, semicrystalline organic thermoplastic polymer (Figure 7ix). It has excellent mechanical and chemical resistance properties that are retained to high temperatures. Its Young's modulus is 3.6 GPa and its tensile strength is 90 to 100 MPa. PEEK has a glass transition temperature of around 143 °C (289 °F) and melts at around 343 °C. The thermal conductivity increases nearly linearly with temperature between room temperature and solidus temperature [6]. It is highly resistant to thermal degradation. Resists attack by both organic and aqueous environments. Its fine powder or thin film is soluble in concentrated sulfuric acid at room temperature, although dissolution can take a very long time. Moreover, it has high resistance to biodegradation. It is used in engineering applications such as fabricating bearings, piston parts,

pumps, high-performance liquid chromatography columns (HPLC), compressor plate valves, and electrical cable insulation, in aerospace, automotive, electronic, and chemical industries. PEEK seals and manifolds are commonly used in fluid applications. It is also used where continuous high temperatures (up to 500 °F/260 °C) are required. Because of this and its low thermal conductivity, it is also used in FFF printing to thermally separate the hot end from the cold end. It has increasing applications in medical implants, e.g. high-resolution magnetic resonance imaging (MRI), for creating a partial replacement skull in neurosurgical applications, used in spinal fusion devices and reinforcing rods. It offers optimal bone growth and is radiolucent, but it is hydrophobic causing it to not fully fuse with the bone.

CNF (Vapor grown) + Poly (Ether Ether Ketone) nanocomposite is a high-temperature semi-crystalline polymer nanocomposite. CNF was homogeneously dispersed and aligned in a thermoplastic matrix using standard polymer processing techniques the extrusion and injection molding. They were evaluated for their mechanical properties, which revealed a linear increase in tensile stiffness and strength with nanofibers loading fractions up to 15 wt.% while matrix ductility was maintained up to 10 wt.%. Differential scanning calorimetry showed that an interaction between matrix and the CNF occurs during processing that changes the polymer morphology due to the presence of nanoscale filler. The addition of low CNF contents resulted in a linear increase in tensile and bending stiffness and tensile yield stress and strength without negatively affecting the matrix ductility at loadings up to 10 wt.%. The intrinsic stiffness of vapor-grown CNF was very low [8].

### Polypyrrole (PPy) + CNF Nanocomposites

This organic polymer PPy is produced by oxidative polymerization of pyrrole (Figure 7. x). It is a solid with the formula  $H(C_4H_2NH)_nH$ . It is an intrinsically conducting polymer, used in electronics, optical, biological, and medical fields.

PPy is used as RADAR absorbing material. Radar absorbing materials require resistive or magnetic materials that will convert electromagnetic energy into heat. The electrical properties of PPy make it a suitable candidate for a radar absorbing material. There are several simple ways to make the polymer with controlled conductivity, and many strategies to process it into a robust material.

Microwave absorbers are in use both in civil and military applications on account of their ability to eliminate electromagnetic wave pollution and to reduce RADAR signatures. The first electromagnetic wave absorber came into light in the mid-1930s to improve front to back ratio of a 4GHz antenna [65, 66]. With the development of radar, there has been a growing and widespread interest in radar-absorbing material technology.

The microwave absorbers are categorized into various forms such as Resonant Absorber, Broad-Band Absorber, and Magnetic Absorber. Dielectric Absorber and Metal Absorber.

Recently nanostructured materials have attracted attention as an absorber in microwave frequency regions due to their unique chemical and physical properties.

Therefore, the nano-size ferromagnetic particles having properties different than bulk materials or large particles are selected as a microwave absorbers. Unfortunately, these materials need a thick coating to meet practical demands.

Research studies reveal that in microwave absorbers, the volume to weight ratio of absorber material is very important for lightweight and strong absorption properties that can be achieved using carbon nano absorbers such as CNF. It is possible to construct synthetic materials from such carbon that can have tailored conductivity, from very poor (insulated grains of carbon black) to very high (connected chains of graphite). Therefore, the carbon-based absorbers essentially follow the electric field loss mechanism. Also, a stimulating result of CNF suggests fabricating its polymer composites which can be useful for various applications as it is well established that shielding effectiveness and absorption capability of a conductive composite are related to its conductivity.

Jang and Bae [67] have exhibited the suitability of CNF/PPy nanocomposite for their self-sensing function is due to the variation in their electrical properties caused by the change in the external conditions, such

as stress/strain and the gas environment. The electrical conductivity of the CNF composites reversibly changes by several orders of magnitude with the reversible change of the external conditions. fabricated CNF/ PPy coaxial nano cable toxic gas sensor for detecting NH<sub>3</sub> and HCl. This sensor was prepared by a one-step vapor deposition polymerization method, it had an ultrathin and uniform PPy layer on the surface of CNF (Fig 11). When this sensor is exposed to the NH<sub>3</sub> or HCl, there is a change in the oxidation level of the PPy layer resulting in the reaction between the PPy and the NH<sub>3</sub> or HCl, and the electrical conductivity due to the decrement in the charge carrier density.

Though there has been the use of CNF composites CNF for sensing strain/stress or gas, there is a need to investigate the possibility of use of CNF composites for sensing temperature, humidity, magnetic field, and light also.

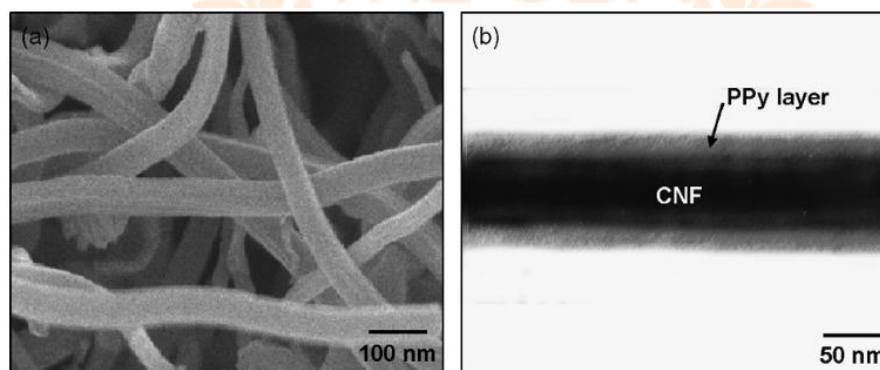


Figure 11. SEM & TEM images of the PPy-coated CNF as a toxic gas sensor [Jang, J.; Bae, J. Carbon nanofibers/polypyrrole nano cable as a toxic gas sensor. *Sens. Actuators B Chem.* 2007, 122, 7–13.]

VARIOUS APPLICATIONS OF CNF WITHOUT  
CONJUGATING WITH ANY POLYMER.

In Cosmetics

The cosmetic industry was among the first to implement nanotechnological principles in product development. Nanomaterials are being used in cosmetic products for various effects. Fronza has [68] defined nanocosmetic as “a cosmetic formulation that carries active or other nanostructured ingredients, which has superior properties regarding its performance if compared with conventional products”.

In India Kajal or Kohl, a black color cosmetic for decorating eyes is an age-old tradition. Since ancient times kajal is prepared at home from the soot collected on a plate from burning herbal extract-soaked cotton in presence of vegetable oil (mustard oil or coconut oil) or ghee and camphor. The synthesis of kajal is mentioned in epics like the Ramayana and the Mahabharata. Prof. Sharon of IIT Bombay produced kajal by burning mustard oil (soaked in the cotton piece) and, using a scanning electron microscope showed that the raw soot has an extensive network of CNTs. He suggested that being a tubular structure the CNTs do not pierce or irritate the eyes. The FESEM image of the sample prepared exhibits carbon nanoparticles of width to be less than 50 nm. Among his communications.

It has been found that the carbon-based graphitic CNF in the field of cosmetics because when the size of carbon particles decreases into the nanoscale range, the antibacterial action increases due to the large surface area and presence of several atoms near the surface. Carbon nanoparticles damage the membranes in bacteria due to photo-oxidation [69]. However, still, a question remains about its impact on the body in the long run. several studies have concluded that it is safe for external use or digesting it is fine in small quantities, but inhaling CNF is not safe. CNF is not metabolized, adsorbed, or absorbed by the body, but it can be used

to treat some poisonous bites and disinfect some wounds. CNF can adsorb oil hence, are ideal for an oily face mask to help in controlling oil and acne problem. CNF can be used in shampoo for oil-free hair that is soft without turning the hair black. Like charcoal, i.e. is still used in villages in India for cleaning teeth, CNF is also safe for teeth. It's not acidic, and it's quite soft, it is a passive agent and it isn't harmful to teeth. It has been tried to add CNF to toothpaste that has pH balanced and is sulfate-free and was found to make teeth pearly white as well as help maintain healthy gums.

### For Gas Storage

CNF due to their high free porous volume, structural regularity, robustness, hydrothermal stability, and functional variety are emerging into the advanced materials field. They present high gas uptake capacities and the presence of stabilized active functions in the framework. A significant technical challenge has been recognized as the development of a viable method to efficiently trap hydrogen, methane, and carbon dioxide gas molecules in a confined space for various applications. CNF has shown great promise for the adsorptive storage of hydrogen, methane, and carbon dioxide in clean energy applications.

Dwindling stock of fossil fuel in nature and the present-day level of generation of energy is unable to cope with the galloping increase in demand for fuel. Hydro-energy and nuclear energy have their inherent drawbacks. Hence, it has become a requirement to explore the various new and renewable sources of energy.

Hydrogen is expected to be the future source of energy. The technology to store enough hydrogen in a small package to be carried easily has diverted the attention to the use of CNF or CNT because it provides

porous material having a high specific surface area (SSA) (either gravimetric or volumetric) for physisorption. Moreover, reports of very high and reversible adsorption in carbon nanomaterials have stimulated many experimental works and theoretical calculations worldwide. But owing to the low apparent density of CNTs and CNFs, doubts have been raised about whether their volumetric hydrogen storage capacity could meet the volumetric target value set by the US DOE hydrogen plan. So far, the best possible option for hydrogen storage material has not been achieved, though, CNF obtained from plant fibers promises to be a strong contender at ambient temperature. The hydrogen storage capacity recorded has varied in the range of 0.1 wt% to 68 wt%. Hence, the adsorption of hydrogen by CNF needs a thorough investigation to understand the factors, which control the hydrogen adsorption to give required and reproducible results.

#### For Photo-Voltaic Solar cell

A device that directly converts solar light energy into electrical energy through the process of photovoltaics is called a solar cell. It needs a photovoltaic effect via an electrode in a conductive solution exposed to light. Many efforts to improvise the electrode and a search for alternative materials have led to carbon because it is expected to have similar properties as silicon and would be highly stable; especially metallic/semi-metallic graphitic carbon such as CNT and CNF that also show many interesting physical and chemical properties. The use of CNF that contains carbon with configuration  $sp^3$  as well as  $sp^2$  and the ratio of these carbons decides whether CNF will behave like metal or a semiconductor. But under no condition, either of these two types of carbon ( $sp^3$  or  $sp^2$ ) will be absent in a CNF structure. If that is so then the carbon of  $sp^2$  configuration in CNF will act as a trapping center for

the photo-generated carriers (electrons or holes). Hence, the efficiency of solar cells developed will depend on whether these trapping centers have been neutralized by some external doping or not.

Dmytro et al[70] and Fan and Javey[71] have suggested that a solar cell that was assembled on a carbon fiber with a diameter of  $\sim 5\text{--}10\text{ }\mu\text{m}$  served as a core electrode; inorganic CdS nanowire crystals and the organic dye or polymer layers were successively deposited on the carbon fiber as active components resulting in a core-shell photovoltaic structure. The development of this technology may lead to a major step toward photovoltaics.

#### For Removal of Dyes

CNF synthesized from biogenic materials offers unique morphologies with a very high surface area for adsorbing dyes from the aqueous medium. The structure of CNFs is more conducive than many other nanoforms of carbon in aiding the removal of various species from different effluents by adsorption. In one of our trials, we have found that the adsorption capacity of activated carbon reduces drastically after the first two to three minutes of action, whereas CNFs continue to be active beyond this period up to ten minutes due to their selectiveness, which ensures that their active sites are still not fully saturated.

Apart from the structural advantage, the surface chemistry of CNFs enhances their ability to be used as adsorbents. The surface charge, hydrophobicity and chemical reactivity of CNFs can be modified which is a boon to researchers working on the selectivity of adsorbents.

#### In Batteries



Sharon et. al. (1998) has been making efforts to find out suitable plant-derived precursors to synthesize carbon nanomaterials. Camphor was a very successful precursor during this course of study. They have synthesized carbon nanobeads (CNB) from camphor and have also [72] studied the intercalation of lithium with carbon. It was found that almost 65% of the theoretical value could be obtained by carbon nanobeads. The intercalation of Li-ion with carbon depends upon various factors such as pore size (either the size of the diameter of the CNT or pore size of channels present in fibrous carbon materials), density, surface area, and activation of CNM, etc. The examination of the literature as discussed earlier, suggests that the capacity and reversibility of lithium interaction depends largely on the surface area, pore size, and morphology of carbon nanomaterials, it was thought to pyrolyze various parts of the plants like seed, stem, and fibers of the different plant to examine which part of the plant and its pyrolysis conditions gives better lithium intercalation. Because the structure of carbon fibers obtained by pyrolysis of plant precursors depends upon the structure of the seed and stem. Moreover, for such precursors, no catalyst is needed for the formation of CNM. It is also expected that carbon obtained from the pyrolysis of seeds or stems of the plant would produce porous fibers of a type difficult to produce otherwise. Thus it would be interesting to examine the role of such natural porous materials as the anode in lithium batteries.

## CONCLUSION

This review concludes that Carbon nanofiber (CNF), is accepted as an important nano form of carbon and it is competing with CNT in many applications in both fundamental scientific research and practical applications. Furthermore, it is a promising material as

an additive in polymers for its applications in many fields. The electrical property of CNF composites largely counts on the dispersion and percolation status of CNFs in matrix materials. The properties and applications of CNF nanocomposites are dependent on many factors such as fabrication methods of CNF composites, types of polymer, polymer to CNF ratio, etc.

## REFERENCES

1. Andy Tay, Magnetic Bacteria; High-Throughput Microfluidic Sorting of Live Magnetotactic Bacteria; Appl Environ Microbiol.; 84(17): e01308-18, 2018. DOI: 10.1128/AEM.01308-18
2. Denault J, Labrecque, Technology Group on Polymer Nanocomposites – PNC-Tech. Industrial Materials Institute. National Research Council Canada, 75 de Mortagne Blvd. Boucherville, Québec, J4B 6Y4.2004.
3. Wang Y, Ameer GA, Sheppard BJ, Langer R.A tough biodegradable elastomer, *Nature Biotechnology*. 20(6): 602-606, 2002. DOI: 10.1038/nbt0602-602.
4. Tevlek Atakan, Halil Murat Aydin. Poly(Glycerol-Sebacate) Elastomer: A Mini Review. *Orthoplastic Surgery & Orthopedic Care International Journal*. 1(2), 2017, DOI: 10.31031/OOIJ.2017.01.000507
5. Kim C, Choi YO, Lee WJ, Yang KS, Supercapacitor performances of activated carbon fiber webs prepared by electrospinning of PMDA-ODA poly(amic acid) solutions, *Electrochim. Acta*, 50: 883, 2004
6. Madhuri Sharon & Maheshwar Sharon (Ed) An Introduction to Carbon Nanofiber, Wiley Scrivener Publisher the USA, 2021, <https://doi.org/10.1002/9781119769149.ch1>



7. Sanchez M, Rams J, Campo M, Jiménez-Suarez A, Urena A (2011) Characterization of carbon nanofiber/epoxy nanocomposites by the nanoindentation technique, *Compos Part B Eng* 42:638–644
8. Sandler J., Werner P., Shaffer M.S.P., Demchuk V., Altstädt V., Windle A.H. Carbon-nanofibre-reinforced poly (ether ether ketone) composites, *Compos. Part A Appl. Sci. Manuf.*; 33:1033–1039, 2002. doi: 10.1016/S1359-835X(02)00084-2..
9. K. Lozano, J. Bonilla-Rios and E. V. Barrera, A Study on Nanofiber-Reinforced Thermoplastic Composites (II): Investigation of the Mixing Rheology and Conduction Properties, *J. Applied Polymer Science*, 80(8):1162-1172, 2001  
<http://dx.doi.org/10.1002/app.1200>.
10. Tibbetts G.G., Finegan I.C., Kwag C, Mechanical and electrical properties of vapor-grown carbon fiber thermoplastic composites, *Mol. Cryst. Liq. Cryst.*; 387:129–133, 2002.  
<https://doi.org/10.1080/10587250215229>
11. Yang, B.; Sato, M.; Kuriyama, T.; Inoue, T. Improvement of a gram-scale mixer for polymer Blending, *J. Appl. Polym. Sci.*, 99: 1–5, 2006.
12. Al-Saleh, M.H.; Sundararaj, U. A review of vapor grown carbon nanofiber/polymer conductive composites, *Carbon*, 47: 2–22, 2009
13. Lee B.O.; Woo W.J.; Park H.S.; Hahm H.S.; Wu J.P.; Kim M.S. Influence of aspect ratio and skin effect on EMI shielding of coating materials fabricated with carbon nanofiber/PVDF, *J. Mater. Sci.* 37: 1839–1843, 2002.
14. Li, J.; Vergne, M.J.; Mowles, E.D.; Zhong, W.H.; Hercules, D.M.; Lukehart, C.M. Surface functionalization and characterization of graphitic carbon nanofibers (GCNFs). *Carbon*, 43: 2883–2893, 2005
15. Jeong Yong jin, Kyuhong Lee, Kinam Kim, and Sunghwan Kim, Pore-Structure-Optimized CNT-Carbon Nanofibers from Starch for Rechargeable Lithium Batteries. *Materials*, 9: 995; 2016 doi:10.3390/ma9120995
16. Zhang D, Qi J, Qiao S, Liu L, Wang P, Zhao Z. A strategy for controlling degradation in vitro of carbon fiber reinforced polylactic acid composite (by combining fiber modification and pulsed electromagnetic fields). *J. Biomaterial Sc. Polymer Edition*, 29: 16, 2018
17. Luo PG, Stutzenberger FJ. Nanotechnology in the Detection and Control of Microorganisms, *Adv App Microbiol.* 63: 145 - 181 2008; DOI: 10.1016/S0065-2164(07)00004-4.
18. Cioffi Nicola, Luisa Torsi, Nicoletta Ditaranto, Giuseppina Tantillo, Lina Ghibelli, Luigia Sabbatini, Teresa Bleve-Zacheo, Maria D'Alessio, P. Giorgio Zambonin, Enrico Traversa. Copper Nanoparticle/Polymer Composites with Antifungal and Bacteriostatic Properties, *Chem. Mater.* 17: 5255 – 5262, 2005,
19. Kumar R, Howdle S, Münstedt H. Polyamide/silver antimicrobials: Effect of filler types on the silver ion release, *Jour. Biomed Mater Res B Appl Biomater.* 75(2): 311- 319, 2005.  
<https://doi.org/10.1002/jbm.b.30306>
20. Carvalho Raissa Alvarenga, Taline Amorim Santos, Viviane Machado de Azevedo, Pedro Henrique Campelo Felix, Marali Vilela Dias, Soraia Vilela Borges. Bio-nanocomposites for food packaging applications: effect of cellulose nanofibers on morphological, mechanical, optical, and barrier properties. *Polym. Int*, 67(4): 386-392, 2018.DOI 10.1002/pi.5518
21. Peelman N, Ragaert P, De Meulenaer B, Adons D, Peeters R, Cardon L Applications of

- bioplastics for food packaging, Trends in Food Sci Technol. 32:128–141, 2013
22. Siracusa V, Rocculi P, Romani S, Rosa MD. Biodegradable polymers for food packaging: a review, Trends Food Sci Technol. 19: 634 – 643, 2008.
23. Tang DW, Yu SH, Ho YC, Huang BQ, Tsai GJ, Hsieh HY Characterization of tea catechins-loaded nanoparticles prepared from chitosan and an edible polypeptide, FoodHydrocoll. 30: 33–41, 2013
24. Margarita MAM, Delia RTB, Florencia CM. Bio-nanocomposites for food packaging applications, Rev Espec Ing Procesos Aliment Biomater5:11–28, 2011
25. Eichhorn SJ, cellulose nanowhiskers: promising materials for advanced applications, Soft Matter.; 7:303–315, 2011.
26. Azeredo HMC, Mattoso LHC, Avena-Bustillos RJ, Filho GC, Munford ML, Wood D Nanocellulose reinforced chitosan composite films as affected by nanofiller loading and plasticizer content. Journal of Food Science, 75:1–7, 2010.
27. Santos TM, Souza Filho MSM, Caceres CA, Rosa MF, Morais JPS, Pinto AMB, Fish gelatine films as affected by cellulose whiskers and sonication, FoodHydrocoll, 41:113–118, 2014.
28. Granda Luis Angel, Helena Oliver-Ortega, Maria José Fabra, Quim Tarrés, Maria Àngels Pèlach, José Maria Lagarón, José Alberto Méndez. Improved Process to Obtain Nanofibrillated Cellulose (CNF) Reinforced Starch Films with Upgraded Mechanical Properties and Barrier Character. Polymers ( Special Issue Nanocellulose-Reinforced Composites: Challenges and Opportunities), 12(5):1071, 2020  
<https://doi.org/10.3390/polym12051071>
29. Chen Hao, Lin Ding, Xueji Zhang, Huangxian Ju. Biocompatible Conductive Architecture of Carbon Nanofiber-Doped Chitosan Prepared with Controllable Electrodeposition for Cytosensing. Anal. Chem., 79(12): 4442–4447, 2007. <https://doi.org/10.1021/ac062344z>
30. Sanmartín-Santos Isaías, Sofía Gandía-Llop, Beatriz Salesa, Miguel Martí, Finn LillelundAachmann, Ángel Serrano-Aroca. Enhancement of Antimicrobial Activity of Alginate Films with a Low Amount of Carbon Nanofibers (0.1%w/w). Appl. Sci., 11(5): 2311, 2021; <https://doi.org/10.3390/app11052311>
31. Llorens-Gámez M, BeatrizSalesa, ÁngelSerrano-Aroca, Physical and biological properties of alginate/carbon nanofibers hydrogel films. International Journal of Biol. Macromolecules. 151: 499-507, 2020. <https://doi.org/10.1016/j.ijbiomac.2020.02.213>
32. Toshiaki Takezawa, Aya Nitani, Tadashi Shimo-Oka, Yoshiharu Takayama. A protein-permeable scaffold of a collagen vitrigel membrane is useful for reconstructing crosstalk models between two different cell types. Cells Tissues Organs;185(1-3):237-41. 2007 DOI: 10.1159/000101325.
33. Vats A, N.S. Tolley, J.M. Polak, J.E. Gough. Scaffolds and biomaterials for tissue engineering: a review of clinical applications. Clinical Oncology and Allied Subjects. 28(3): 165-172, 2003
34. Lanza Robert, Langer Robert. Joseph Vacanti Eds. Principles of Tissue Engineering, 2nd Edition. eBook ISBN: 9780080539676, Academic Press, 2000
35. MacDonaldRebecca A, Brendan F Laurenzi, Gunaranjan Viswanathan, Jan P Stegemann. Collagen-carbon nanotube composite materials as scaffolds in tissue engineering.

- Journal of Biomedical Materials Research Part A 74(3):489-96, 2005.  
DOI: 10.1002/jbm.a.30386
36. Sun Hongyu, Jing Zhou, Zhu Huang, Linlin Qu, Ning Lin, Chengxiao Liang, Ruiwu Dai, Lijun Tang, and Fuzhou Tian. Carbon nanotube-incorporated collagen hydrogels improve cell alignment and the performance of cardiac constructs. *Int J Nanomedicine*; 12: 3109–3120, 2017. DOI: 10.2147/IJN.S128030
37. Pei Baoqing, Wei Wang, Nicholas Dunne, Xiaoming Li. Applications of Carbon Nanotubes in Bone Tissue Regeneration and Engineering: Superiority, Concerns, Current Advancements, and Prospects *Nanomaterials*, 9: 1501, 2019; doi:10.3390/nano9101501
38. Samadian Hadi, Hamid Mobasheri, Mahmoud Azami, Reza Faridi-Majidi. Osteoconductive and electroactive carbon nanofibers/hydroxyapatite nanocomposite tailored for bone tissue engineering: in vitro and in vivo studies, *Scientific Reports*, 10, Article number 14853, 2020
39. Zeng Lijian, Xianrong Huang, Xueling Li, Renfu Li, Yichao Li, Yi Xiong, A gelatin-treated carbon nanofiber/epoxy nanocomposite with significantly improved multifunctional properties. *Materials Today communication*, 24: 101006, 2020  
<https://doi.org/10.1016/j.mtcomm.2020.101006>
40. Muhammad A. S. Anwer, Jintian Wang, Hani E. Naguib. 1D/2D CNF/GNP Hybrid Nanofillers: Evaluation of the Effect of Surfactant on the Morphological, Mechanical, Fracture, and Thermal Characteristics of Their Nanocomposites with Epoxy Resin. *Ind. Eng. Chem. Res.* 58(19): 8131–8139, 2019.  
<https://doi.org/10.1021/acs.iecr.9b0095>
41. Li Zhe, Athanasios Milionis, Yu Zheng, Marcus Yee, Lukas Codispoti, Freddie Tan, Dimos Poulikakos, Choon Hwai Yap. Superhydrophobic hemostatic nanofiber composites for fast clotting and minimal adhesion. *Nat. Commun.*; 10: 5562. 2019a  
DOI: 10.1038/s41467-019-13512-8
42. Kokoszka S, Debeaufort F, Lenart A, Voilley A. Water vapor permeability, thermal and wetting properties of whey protein isolate based edible films, *International Dairy Journal*. 20:53–60, 2010
43. Celine de Carvalho Furtado; Império Lombardi Jr2. Whey Protein Supplementation as a Strategy to Preserve Muscle Mass and Increase Protein Synthesis in the Elderly: a Review of Literature. *International Journal of Aging Research*, 2(2), 34, 2019  
<https://doi.org/10.28933/ijoar-2019-03-1805>
44. Dirican Mahmut, Meltem Yanilmaz, Kun Fu, Ozkan Yildiz, Huseyin Kizil, Yi Hu, Xiangwu Zhang. Carbon-Confined PVA-Derived Silicon/Silica/Carbon Nanofiber Composites as Anode for Lithium-Ion Batteries. *Journal of The Electrochemical Society*, 161 (14): A2197-A2203, 2014
45. Takahashi Yusuke, Hirotaka Fujita, Wan-Hua Lin, Akiyoshi Sakoda. Synthesis of carbon nanofibers from poly(ethylene glycol) with controlled structure. *Adsorption* 16(1):57-68, 2010. DOI: 10.1007/s10450-010-9204-7
46. Ko, Yusuke Takahashi, Akiyoshi Sakoda, Yasuyuki Sakai, Kikuko Kimori. Direct Synthesis of Cup-Stacked Carbon Nanofiber Microspheres by the Catalytic Pyrolysis of Poly(ethylene glycol). *Langmuir*, 28(23): 8760–8766, 2012 <https://doi.org/10.1021/la3010745>
47. Yu Zhiwei, Kai Xu, Zien Fu, Xin Liu Youxiong Zhang, Jun Peng, Mingcai Chen. AFT synthesis



- of polyethylene glycol (PEG) and amino-functionalized amphiphilic copolymers for dispersing carbon nanofibers. RSC Adv., 5: 23683-23690, 2015
48. Ma Zuweri, Wei He, Thomas Yong, S. Ramakrishna. Grafting of Gelatin on Electrospun Poly( $\epsilon$ -caprolactone) Nanofibers to Improve Endothelial Cell Spreading and Proliferation and to Control Cell Orientation. Tissue Engineering. 11(7-8): 1149-1158, 2005, <https://doi.org/10.1089/ten.2005.11.1149>
49. Zhang Y. Z., X. Wang, Y. Feng, J. Li, C. T. Lim, S. Ramakrishna. Coaxial Electrospinning of (Fluorescein Isothiocyanate-Conjugated Bovine Serum Albumin)-Encapsulated Poly( $\epsilon$ -caprolactone) Nanofibers for Sustained Release. Biomacromolecules, 7(4): 1049–1057, 2006 <https://doi.org/10.1021/bm050743>
50. Javid Jalvandi, Max White, Yuan Gao, Yen Bach Truong, Rajiv Padhye, Ilias Louis Kyratzis. Slow-release of levofloxacin conjugated on silica nanoparticles from poly( $\epsilon$ -caprolactone) nanofibers, International Journal of Polymeric Materials and Polymeric Biomaterials, 66(10): 507-513, 2017  
DOI: 10.1080/00914037.2016.1252350
51. Gopinathan Janarthanan, Mamatha Muraleedharan Pillai, Kumari, Singaram Gnanapoongothai, Beliyur Krishna Dinakar Rai, Kulasekaran Santosh Sahanand, Rajendran Selvakumar, Amitava Bhattacharyya. Carbon nanofiber amalgamated 3D poly- $\epsilon$ -caprolactone scaffold functionalized porous-nano architectures for human meniscal tissue engineering: In vitro and in vivo biocompatibility studies. Nanomedicine, 14(7): 2247 - 2258, 2018, DOI: 10.1016/j.nano.2018.07.012
52. Kaviannasab Elham, Dariush Semnani Saied Nouri Khorasani, Jaleh Varshosaz, Shahla Khalili, Faezeh Ghahreman. Core-shell nanofibers of poly ( $\epsilon$ -caprolactone) and Polyvinylpyrrolidone for drug delivery system. Materials Research Express, 6(11): 115015, 2019
53. Nasari Mina, Dariush Semnani, Mehdi Hadianfar, Saeid Amanpour. Poly ( $\epsilon$ -caprolactone)/poly (N-vinyl-2-pyrrolidone) core-shell nanofibers loaded by multi-walled carbon nanotubes and 5-fluorouracil: an anticancer drug delivery system. Journal of Materials Science; 55, 10185–10201; 2020
54. Boroghani, M.; Mirnia, S. K.; Vahhabi, J.; Ahmadi, S. J.; Charkhi, A. Nanozeolite Synthesis and the Effect of on the Runoff and Erosion Control under Rainfall Simulator. Australian Journal of Basic & Applied Sciences; 5(12) 156, 2011.
55. Ram Prasad, Vivek Kumar, Kumar Suranjit Prasad. Nanotechnology in sustainable agriculture: present concerns and future aspects. African Journal of Biotechnology. 13 (6), 705 – 713, 2014
56. Öztas, T., A.K. Özbek and E.L. Aksakal, Structural developments in soil treated with Polyvinylalcohol. International Conference on Sustainable Land Use and Management, Soil Sci. Soc. of Turkey Int. Symp., pp: 143-148, 2002.
57. Zein El-Din A.M., Hammed H. A. M. Hassan2, M.M. Abou El-Kheiri and R.M. Youssef Controlling soil surface crust formation using Nanosized sulfonated polyaniline. Journal of Soil and Water Conservation, 1(1):001-009, 2016. <http://www.unifiedjournals.org/jswc>
58. Joshi MM, Bhattacharya A. Carbon Nanofiber Reinforced Carbon/Polymer Composite. NSTI-Nanotech 2004, www.nsti.org, ISBN 0-9728422-9-2 Vol. 3, 2004

59. Chou TW, Ko FK. Editors: Textile structural composites; Elsevier, Amsterdam (1989), pp. 209–263, 1989
60. Pervin F.; Zhou Y.; Rangari V.K.; Jeelani S. Testing and evaluation on the thermal and mechanical properties of carbon nano fiber-reinforced SC-15 epoxy. *Mater. Sci. Eng.*, 405: 246–253, 2005
61. Kellarakis A., Yoon K., Somani R.H., Chen X., Hsiao B.S., Chu B., Polymer, Rheological study of carbon nanofiber induced physical gelation in polyolefin nanocomposite melt. *Polymer*, 46:11591–11599, 2005.
62. Choi Y.K.; Gotoh, Y.; Sugimoto, K.I.; Song, S.M.; Yanagisawa, T.; Endo, M. Processing and characterization of epoxy nanocomposites reinforced by cup-stacked carbon nanotubes. *Polymer*, 46, 11489–11498, 2005.
63. Bal S, Saha S. Fabrication and characterization of carbon nanofibre(CNF)based epoxy composites IOP Conf. Ser.: Mater. Sci. Eng. **75**: 012018, 2015
64. Pozegic TR, Jayawardena K DGI, Chen J-S, Anguita JV, Balocchi P, Stolojan VS. Ravi, Silva P, Hamerton I. Composites Part A: Applied Science and Manufacturing, 90, 306–319, 2016 <https://doi.org/10.1016/j.compositesa.2016.07.012>
65. Abbas Qaisar, Rizwan Raza, Imran Shabbir, A.G.Olabi. Heteroatom doped high porosity carbon nanomaterials as electrodes for energy storage in electrochemical capacitors: A review. *Journal of Science: Advanced Materials and Devices*, 4 (3): 341-352, 2019
66. Emerson, W. H. Electromagnetic wave absorbers and anechoic chambers through the years, *IEEE Trans. On Antennas and Propagation*, 21(4): 484-490, 1973
67. Jang J, Bae J. Carbon nanofiber/polypyrrole nano cable as toxic gas sensor *Sens. Actuators B Chem.* 122: 7–13, 2007, <https://doi.org/10.1016/j.snb.2006.05.002>
68. BM Fronza ,IY Rad, Shah PK, Barros MD, Giannini M., Stansbury JW. Nanogel-based filler matrix interphase for polymerization stress reduction, *Journal of dental research* 98(7):779-785,2019.
69. Madhuri Sharon, S. Datta, S. Shah, Maheshwar Sharon, T. Soga & R. Afre. Photocatalytic degradation of *E. coli* & *S. aureus* by Multi-Walled Carbon Nanotubes. *Carbon Letters*, 8 (3): 184 – 190, 2007
70. Dmytro A. Grynko, Alexander N. Fedoryak, Petro S. Smertenko, Oleg P. Dimitriev, Nikolay A. Ogurtsov, and Alexander A. Pud. Hybrid solar cell on carbon fiber. *Nanoscale Res Lett.*; 11: 265, 2016   
doi: 10.1186/s11671-016-1469-7
71. Fan Z Y, Javey A. Photovoltaics Solar cells on curtains. *Nature Materials*, 7(11): 835–836, 2008. DOI: 10.1038/nmat2312.
72. Sharon M, W.K. Hsu, H.W.Kroto, D.R.M. Walton, A. Kawahara, T. Ishihara, Y. Takita. Camphor-based carbon nanotubes as an anode in lithium secondary batteries. *Journal of Power Sources*, 104 (1): 148-153, 2002
73. Ghasemi AR, MohammadiMM, Mohandes M. **The role of carbon nanofibers on thermo-mechanical properties of polymer matrix composites and their effect on reduction of residual stresses. Composites Part B: Engineering**; **77**: 519-527, 2015
74. Kasinee Prakobna, Sylvain Galland, Lars A. Berglund. High-Performance and Moisture-Stable Cellulose–Starch Nanocomposites Based on Bioinspired Core-Shell Nanofibers.



- Biomacromolecules* 2015, 16, 3, 904–912.  
<https://doi.org/10.1021/bm5018194>
75. Anuradha Rani, Sheetal Monga, Monica Bansal, Anupama Sharma. Bionanocomposites reinforced with cellulose nanofibers derived from sugarcane bagasse. *POLYM. COMPOS.*, 39: E55–E64, 2018.
76. Shazleen SS, Yasim-Anuar TAT, Ibrahim NA, Hassan MA, Ariffin H. Functionality of Cellulose Nanofiber as Bio-Based Nucleating Agent and Nano-Reinforcement Material to Enhance Crystallization and Mechanical Properties of Polylactic Acid Nanocomposite. *Polymers (Basel)*. 27;13(3):389, 2021. DOI: 10.3390/polym13030389.
77. Hai LV, Zhai L, Kim HC, Panicker PS, Pham DH, Kim J. Chitosan Nanofiber and Cellulose Nanofiber Blended Composite Applicable for Active Food Packaging. *Nanomaterials (Basel)*. 10(9):1752, 2020. doi:10.3390/nano10091752
78. Cheng, KC., Huang, CF., Wei, Y. et al. Novel chitosan–cellulose nanofiber self-healing hydrogels to correlate self-healing properties of hydrogels with neural regeneration effects. *NPG Asia Mater* 11: 25, 2019. <https://doi.org/10.1038/s41427-019-0124-z>
79. Nakayama, Ri, Takamatsu Y, Namiki N. Multiphase calcium alginate membrane composited with cellulose nanofibers for selective mass transfer. *SN Appl. Sci.* 21:799, 2020. <https://doi.org/10.1007/s42452-020-03532-1>
80. Sajedeh Lohrasbi, Esmaeil Mirzaei, Ayoob Karimizade, Sara Takallu, Anita Rezaei. Collagen/cellulose nanofiber hydrogel scaffold: physical, mechanical and cell biocompatibility properties; *Cellulose*; 27(2), 927-940. 2020
81. Wang W, Zhang X, Li C, Du G, Zhang H, Ni Y. Using carboxylated cellulose nanofibers to enhance mechanical and barrier properties of collagen fiber film by electrostatic interaction. *J Sci Food Agric.*; 98(8):3089-3097, 2018. doi: 10.1002/jsfa.8809
82. Bianca-Ioana Dogaru, Vasile Stoleru, Gabriela Mihalache, Sems Yonsel, Maria-Cristina Popescu, Gelatin Reinforced with CNCs as Nanocomposite Matrix for *Trichoderma harzianum* KUEN 1585 Spores in Seed Coatings. *Molecules*, 26: 5755, 2021. <https://doi.org/10.3390/molecules26195755>
83. Ahmadi A, Ahmadi P, Ehsani A. Development of an active packaging system containing zinc oxide nanoparticles for the extension of chicken fillet shelf life. *Food Sci Nutr.*; 8(10):5461-547, 2020. doi:10.1002/fsn3.1812
84. David A. Stout, Bikramjit Basu, Thomas J. Webster. Poly (lactic-co-glycolic acid): Carbon nanofiber composites for myocardial tissue engineering applications. *Acta Biomaterialia*; 7(8,): 3101-3112, 2011
85. Xiaran Miao, Feng Tian, Jinyou Lin, Hui Li,<sup>c</sup> Xiuhong Li, Fenggang Bian, Xiangzhi Zhang. Tuning the mechanical properties of cellulose nanofibrils reinforced polyvinyl alcohol composites via altering the cellulose polymorphs. *RSC Adv.*, 6: 83356-83365, 2016. DOI <https://doi.org/10.1039/C6RA14517E>
86. Asiri AM, Marwani HM, Khan SB, Webster TJ. Greater cardiomyocyte density on aligned compared with random carbon nanofibers in polymer composites. *Int J Nanomedicine*. 28;9: 5533-5539, 2014. DOI: 10.2147/IJN.S71587.
87. Tongfei Wu, Martin Frydrych, Kevin O'Kelly, Biqiong Chen. Poly(glycerol sebacate

urethane)-cellulose nanocomposites with water-active shape-memory effects. Biomacromolecules, 15(7):2663-71, 2014  
DOI: 10.1021/bm500507z

88. Sengupta D, Chen SH., Michael A, Chee Yee Kwok, Sean Lim, Yutao Pei, Ajay Giri, Prakash Kottapalli. . Single and bundled carbon nanofibers as ultralightweight and flexible piezoresistive sensors. no Flex

Electron 4:9,2020.  
<https://doi.org/10.1038/s41528-020-0072-2>

89. Xingbin Yan. Zhixin Tai, Jiangtao Chen, QunjiXue. Fabrication of carbon nanofiber-polyaniline composite flexible paper for supercapacitorNanoscale 3(1):212-6, 2010.  
DOI: 10.1039/conr00470g

