Polymer Nanocomposites: Characterization and Applications

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ABSTRACT

Organic polymeric composite materials are useful in applications sucgh as light emitting diodes, electrochromic displays, smart windows, and field transistors, electromagnetic interference shielding devices, energy storage products such as batteries, super capacitors and fuel cells. Nanoparticles of conducting polymers are formed by chemical or electrochemical synthesis by precipitation, crystallization, sol–gel transformation, emulsion polymerization. Molecular template nucleation is a method to design specific size, morphology and control. These reactions are important in design of wires, tubes, globules and discs. Conducting polymer nanowires are alternatives to silicon nanowires and carbon nanotubes due to their tunable conductivity, flexibility, chemical diversity, and ease of processing. The paper reports the characterization of nanocomposites, templated electrochemical conductance, and applications. The main challenges are to build and control engineered polymeric materials at the nanometer (nm) scale important for current and future development of nanomaterials for a wide range of applications. The 'phenomenal effect' of these nanoparticles combined with bulk material makes them lighter, stronger, with high ductility in bioapplications. The size of the nanoparticle grains displayed specific properties in the bulk material. We describe easier processing, mixtures with other polymeric /non polymeric matrices to develop conducting polymer based nanocomposites or nanoconducting polymers.

Key words: energy storage tanks, storage polymers, nanocomposites, synthesis

1 INTRODUCTION

Organic polymer with electrical, electronic, magnetic and optical properties of a metal/metal oxide "intrinsically conducting polymer" (ICP) or "synthetic metal" (i.e., nano-rods, -tubes, -wires, and -fibers). Chemical and electrochemical synthesis of conjugated polymer nanotubes and nano-wires: polyaniline(PANI) ,polypyrole (PPy), polyn-methylpyrrole (PNMPy), polythiophene (PTh) and polyethylenedioxythiophene (PEDOT) in the form of nano-arrays, nano-tubes and nano-fibers) is a "**conjugate polymer nanomaterial**". As example, polyaniline (PANI) is explored in this paper.

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2 WHAT MAKES NANOCOMPOSITES VALUABLE?

The following process parameters affect fiber structure:
viscosity, concentration, net charge density (conductivity), surface tension of the polymer fluid, molecular weight, molecular weight distribution, topology (branched, linear etc.) of the polymer, electric potential, flow rate of the polymer solution, distance between the capillary-end and target/ collection screen, ambient parameters (temperature, humidity and air velocity in the chamber), motion of target screen, Internal diameter of the nozzle/capillary.

3 CHARACTERIZATION TECHNIQUES

X-ray diffraction (XRD) and transmission electron microscope (TEM) are choice in process kinetics, monitoring the position, shape, but poor spatial distribution of the clay layers. Some techniques are cited here in table 1.

3.1.Mechanical Properties

The mechanical behavior of nanocomposites **is** based on the nature of the polymer matrix, particularly crystalline or amorphous nature of the polymer, and the interaction between the filler and matrix. The elastic modulus, filler–matrix interaction.

3.1.1.Viscoelastic Properties

Inter particle distance in nanocomposites explains elastic modulus and strength of these materials at micron-sized particles.

3 CONDUCTION IN NANOCOMPOSITES

Polymers can be electrically conductive when doped with oxidizing or reducing agents.

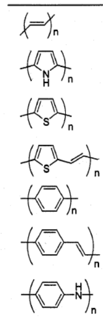
$P_n \Leftrightarrow [P_n^{+} A^{-}] \quad [P_n^{+}A^{-}] \Leftrightarrow [P_n^{2+}2A^{-}], \quad [P_n^{\bullet +}A^{-}]+P_m \rightarrow [(P_n P_m)^{\bullet +}A^{-}]$
(reduction oxidation) (reduction oxidation)

Polyconjugated structures if treated with an oxidizing or a reducing agent (doping) makes polymer salts with electrical conductivities. *P-type doping:* removal of electrons from the valence band by the oxidizing agent, leaving the polymer with a positive charge. *N-type doping:* it encompasses donation of an electron to the empty conduction band by a reducing agent. Polyconjugated structures if treated with an oxidizing or a reducing agent (doping) makes polymer salts with electrical conductivities. *P-type doping:* removal of electrons from the valence band by the oxidizing agent, leaving the polymer with a positive charge. *N-type doping:* it encompasses donation of an electron to the empty conduction band by a reducing agent.

Table.1. Common characterization techniques for clay based polymer nanocomposites.

Techniques	Characteristics and properties
XRD/WAXRD	Degree of swelling and interlayer distance of clays Dispersion degree of clay platelets Morphology (conventional, intercalated, exfoliated or mixed) Kinetics of intercalation process
SEM	Surface roughness and morphology Dispersion degree of clay particles
TEM/HRTEM	Morphology and its development Microstructure (intercalated vs exfoliated) Spatial distribution of clay platelets Structural heterogeneities Defect structure and atomic arrangement
AFM	Crystallization behavior of polymer Surface roughness Particle size and distribution Morphology and microstructure
FTIR	Component identification and analysis Interfacial interactions Crystallization and orientation of polymer
NMR	Local dynamics of polymer chains Morphology and dispersion of clay particles Surface chemistry
SAXS	Dispersion of nanoscale clay platelets Morphology (intercalated, exfoliated or mixed) and its development Phase behavior and structure evolution Lamellar texture and thickness
TGA	Thermal stability
DSC	Melting and crystallization behavior Local dynamics of polymer chains
Cone calorimetry	Flame retardancy, such as heat release rate and carbon monoxide yield Thermal stability
Rheometry	Nanorheology
Mechanical test	Young's modulus Tensile strength Elongation at break Viscoelastic properties

The first step is the formation of a cation (or anion) radical, which is called a soliton or a polaron. The p-type or n-type doping, electrons concept is changed now after discovery of polyacetylene(PA) polyparaphenylene (PPP), and polypyrrole (PPy)~ can display conductivity (no need of unpaired electrons but spin less charge carriers) for conduction. So, molecule geometry distortion in the ionized state or elastic energy E_{dis} leads to an upward shift ΔE of the highest occupied molecular orbital (HOMO) and a downward shift of the lowest unoccupied molecular orbital (LUMO). In nanocomposite, ionization energy $\Delta E > E_{dis}$, makes polaron (radical ion spin) associated with a lattice distortion $\Delta E - E_{dis}$ (E_{rel}) polaron binding energy. Second electron removal makes polymer chain a bipolaron (pair of like charges associated with a strong local lattice distortion) shown in Figure 1. $E_{dis} > E_{dis}$ for the polaron. The p-(n-) type doping show bipolaron empty gap(fully occupied or spin less) and show two optical transitions below the band gap transition: for p-type doping, from the VB to the lower bipolaron level and from the VB to the upper bipolaron level.



structure	polymer	π−π* bandgap (eV)	condcutivity (s/cm)
	polyacetylene	1.5	10^3 - 1.7×10^5
	polypyrrole	3.1	10^2 - 7.5×10^3
	polythiophene	2.0	10-10^3
	poly(thienylene vinylene)	1.6	40
	poly(*para*-phenylene)	3.0	10^2 -10^3
	poly(*p*-phenylene vinylene)	2.5	3-5×10^3
	polyaniline	3.2	0-200

Fig.1. The bipolarons are thus spin less. The presence of bipolarons on polymer chains result in the possibility of two optical transitions below the band gap transition: for p-type doping, from the VB to the lower bipolaron level and from the VB to the upper bipolaron level.

4 GENRAL APPLICATIONS

4.1 Luminescence

Electronic excitation of the polymer from π to π* states, and π* to π states show: fluorescence, phosphorescence, or radiation less decay (rotational or vibrational motion within the polymer and its surroundings). Absorption - emission maxima (Stokes shift) occurs when emission from the lowest vibrational excited state relaxes to various vibrational levels of the electronic ground state. Emission efficiency of the polymer is quantum yield of luminescence Φpl or the ratio of the number of photons emitted to the number of photons absorbed, as shown:

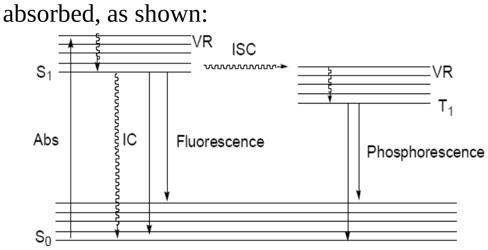


Figure 2. Emission mechanism.

$$\Phi_{PL} = \frac{Photons_{EM}}{Photons_{ABS}} \qquad \Phi_{PL} = \frac{\tau_r}{\tau_r + \tau_{nr}}$$

The Φpl is related to the rates of radiative (τr) and non-radiative (τnr) decays. Electroluminescence (EL) in polymer as Light Emitting Diodes (LED) is shown in Fig.3 made of Indium Tin Oxide (ITO) and polymer), with low work function metal cathode such as calcium. Light emitting diodes are bipolar devices, where holes (*h*+) and electrons (*e*-) are transported in the polymer is revolution.

Nanotechnology is currently enabling the production of high-efficiency organic photovoltaics (OPVs). Conducting nanowires poly(propylene) PP, PANI, and PEDOT (~100–200 nm in diameter), Al_2O_3-based masks with nanopores show considerable promise for use as nanoemitters in emission displays in field-effect transistor (FET) configuration shown in Fig 4 and *I–V* characteristics of these transistor structures are nonlinear, as are the *I–V* curves of individual PANI fibrils shown in Fig. 4(b). The field mobility of carriers in a polymer fibril μFET *I–V* curve of a traditional MOSFET is shown in Fig.4(c). The carrier mobility μFET from the transistor conductance *gm:*

$$g_m = \partial I_{ds}/\partial V_g|_{V_{ds} = \text{const}} = -(Z/L)\mu_{FET} C_i V_{ds},$$

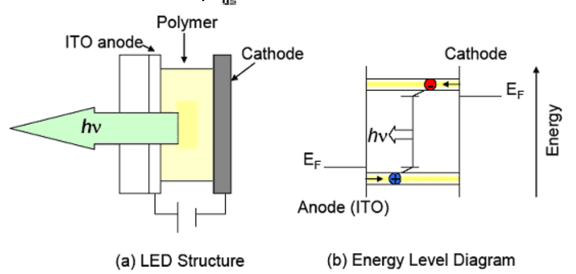


Figure 3 LED structure and its energy level diagram.

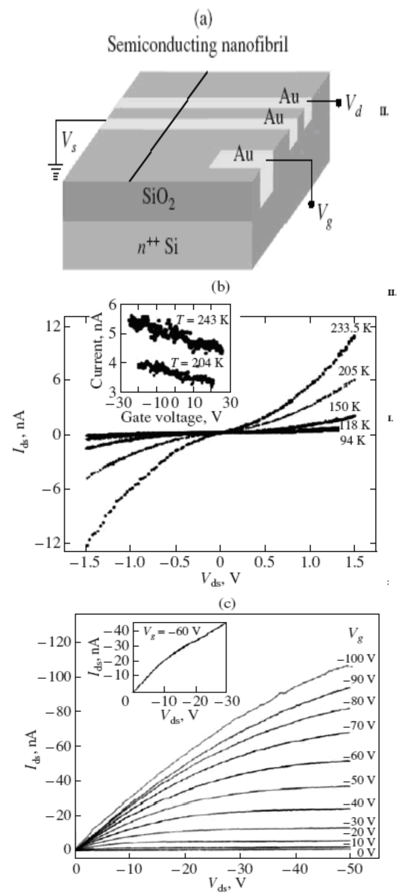


Figure 4: (a) Field effect transistor (FET) based on individual PANI fibril(b) IV characteristics of FET based on polyaniline fibril(20 nm) (c) IV characteristics of P3HT fibril.

4.2 Photovoltaics

Organic photovoltaics are nanostructured thin films composed of layers of semiconductor organic materials (polymers or oligomers). CNT devices hold promise to revolutionize solar energy harvesting, ink-jet or screen printing, enabling rapid mass-production while scaling down cost. In recent years, bulk hetero-junction polymer photovoltaic devices and photodiodes have been constructed with composite films of CPs as electron donors and CNs as electron acceptors. Optical and photovoltaic properties of a composite based on MWNTs and PPV to make stable LEDs high conductivity, good quantum efficiency (1.8% at 2.9–3.2 eV).CP/SWNTs composites are hybrid organic semi-conducting material promise for organic photovoltaic cells as organic light emitting diodes (OLEDs) and photovoltaic cell. Dispersion of SWNTs in a host polymer(*m*-phenylene-vinylene-*co*-2,5-dioctoxy-*p*-phenlene-vinylene) (PmPV) (hole conducting) traps the holes, depending on the applied voltage, in a double emitting organic light emitting diode (DE-OLED). SWNTs dispersed in PEDOT is *p*-type semi-conductor. Devices made with SWNTs dispersed in PEDOT emit green light at 2.37 eV with significant decrease in the electroluminescence (EL). OLEDs with the structure of ITO-coated glass/PEDOT:PSS/SWNTs-PVK (poly-carbazole) nanocomposite /(4-(dicyano methylene)-2-methyl-6-(p-dimethyl aminostryryl)-4H-pyran (DCM)-doped) Alq3-Li Al.SWNTs are emerging SWNTs-PVK nano- composites with spin-coated on the PEDOT:PSS-ITO-coated glass with high quantum efficiency improved by a factor of 2–3 for SWNTs concentration up to 0.2 wt%.

4.3 Solar Cells

Solar cells are devices, which operate inversely to OLEDs, transform radiation from the optical range into electricity. Under illumination, a transfer of electrons to the acceptors takes place and the holes transported through the CP/NC (photo-induced charge transfer). SWNTs-doped polymer composites demonstrate low percolation threshold, composite reinforcement, mechanical stability (tensile strength ca.20 GPa), thermal management in large area thin film array. Photovoltaic systems incorporate nanostructure-SWNT complexes into the polymer.

4.4 Biosensors

Recently, CN-based gas sensors of the field effect- transistor at room temperature due to a drastic change in the electrical conductivity upon the adsorption of various gases, have received a great deal of attention. SWNTs used for gas sensors must be semiconducting. CN/CP nanocomposites based on a SWNTs/PPY showed n-type behavior. SWNT/PPy nanocomposite towards NO_2 show with high surface area of the coated PPy and high sensitivity due to synergetic effect of the steric hindrance of the substituents on the aromatic rings and the presence of MWNTs inside the polymer matrix. Electrochemical biosensors can be intimate coupled with biomolecule (enzyme) and generates electrical signal. It needs immobilization of the biomolecule as well as its affinity for and accessibility towards the target analyte. Many amperometric biosensors are oxidase-based require a use of charge-transfer mediators or electro catalysts. CNT act as transducers, stabilizer and mediators for biosensor applications (immobilized enzyme-nanotube surface) to enhance redox reaction and the electron transfer in HEME proteins. Hydrogen Storage-New technology makes 8 wt% (reversible) hydrogen gas storage in doped 3 forms of the organic conducting polymers such as polyaniline and polypyrrole.

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4.5 BIOMEDICAL APPLICATIONS

DNA Hybridization Analysis-A revolution- MWNTs offer CPs-based biosensors (PPy based glucose oxidase system for detection of glucose, DNA-doped PPy film coated on the CN modified electrode) for free DNA hybridization detection by impedance measurements. Problem: DNA duplex formation not related with change in redox signal. CPs, PPy, allow biological recognition element associated with potential reporter polymer chain for direct electrochemical detection of DNA hybridization by AC impedance measurement. For example, MWNTs functionalized with carboxylic group (MWNTs-COOH) can be modified on the glassy carbon electrode (GCE) and the oligo-nucleotide probes were doped with the electro polymerized PPy films as the sole counter anion during the growth of the conducting films. It decreases impedance before and after hybridization reaction with the complementary DNA sequencesdue to low electrode resistance (a reagent less DNA hybridization analysis).

Nanomedicine- is 'the monitoring, repair, construction, and control of human biological systems at the molecular level, using engineered nanodevices and nanostructures' by nanoscale manipulation for clinical application, diagnosis, prevention, and treatment of disease and disease mechanisms. Examples: 1. Nanodevices (eg, Q-dots, dendrimers), nanoparticles, drug delivery systems, emulsions, carriers for delivering vaccines and nanomaterials(high strength, hardness, reduced friction, and improved biocompatibility), nanomachines (move through the body, troubleshooting and repairing tiny brain or cardiovascular lesions). 2.Growth factor or enzymes combine as dopant with biosensor CPs. Biocompatible CP can catalyze a bioreaction and enzyme can measure concentration of metabolites (e.g. glucose, cholesterol, penicillin). Emeraldine (EM), nigraniline (NA), and leucoemeraldine (LM), polypyrrole coated woven fabrics (Context TM) are biocompatible with lower conductivity (103 ~104Ω/ square) and better cellular response. *In vitro* applications of conducting CP polymer redox state effect electrical stimulation of cell growth by protein adsorption (fibronectin), DNA synthesis and enhanced neurite length. 3.Poly-Lactic acid and carbon nanotubes stimulate osteoblasts growth(increased proliferation, concentration of calcium in extra cellular matrix, and up regulation of mRNA expression for collage type I) upon cells exposed to 10μA at 10Hz electric stimulation. 4. Nanodrug delivery at nanometer scale is interest for controlled drug delivery and biomedical devices. Electrochemical actuators-Conducting polymer's response to electrochemical oxidation or reduction changes its conductivity, color and volume, electron transport in and out between polymer and electrolyte (Piezoelectronics-expands or contracts). Polymers doped with bioactive drugs can be used as micro fluidic pumps. 5. Controlled release of anti-inflammatory drug response of neural prosthetic devices, conducting-polymer nanotubes decrease the impedance and increase the charge capacity of the recording electrode sites on micro fabricated neural prosthetic devices. 5.Microelectrode neural probes for single neuron (central nervous system and peripheral nervous system). 7.Polymers polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) reduce impedance over large surface area for ionic-to-electronic charge transfer in neural prosthesis applications. 8. The reposne of dexamethasone by external electrical stimulation of PEDOT nanotubes. 9. Nanofibers of poly(L-lactide) (PLLA) or poly(lactide-*co*-glycolide) (PLGA) or PLLA/ PLGA are dexamethasone-incorporated PLGA nanoscale fibers.10. Nanowire Immunosensor act as field-effect transistors that change conductance upon binding of charged macromolecules to receptors linked to the device surfaces as biosensors. 11. Bioreceptor (antibody)-functionalized nanowires for label-free, real-time, rapid, sensitive and cost-effective detection of multiple pathogens in water. 12.Functionalized polypyrrole nanowires- high controllability, high-density for biosensor arrays of poliovirus, hepatitis-A virus and rotarvirus by electrostatic charges from binding of the pathogens to the antibodies show sensitivity, selectivity and durability of poliovirus, HAV and rotavirus antibodies.13.Enzyme nanomotors- encapsulation act as 'electronic nose' biosensor arrays for breath alcohol levels, automotive exhaust safety inspection, and identification of toxic gases using chip chemical sensing and signal processing on enzyme nanosensors 'stripes' (lithographically patterned sensor arrays), example: proteins (avidin, streptavidin, catalase), biotin to polymer-bound avidin opens possibility of bio-friendly fuels such as glucose to power these nanoscale motors.14.Nanopackaging Systems-packaging films are moisture absorbent sachets, oxygen scavengers, transport shock resistant materials, time and temperature detectors for thawed frozen goods, antimicrobial coatings, conducting polymers (artificial metals) for transistors and semi-conducting devices. Thermochromic, electrochromic and chemo chromic inks, optical patterns (holograms and other optical variable devices (OVDs).Example-PANI can detect changes in meat and dairy products, polyaniline, ammonia in meat and milk industry. 15. Energy Actuators- Polypyrrole, Si/SiO2/Ti/Al, PANI, CP and CNT converse electrical energy to mechanical energy with a material response to applied electrical voltage. Eamples: artificial muscle robotics, optical fibre switches, optical displays, prosthetic devices, microscopic pumps and anti-vibration systems. 16. Nanotoxicology- health and environmental impacts, disease detection, imaging, and treatment, immune system, reuse ultrafine particles, industrial pollution to cause pulmonary toxicity. MWNTs,TiO_2 crystals can do oxidative DNA damage. SWNTs-C-nanotubes, C-fullerenes as 'green' nanomaterial show concern of surface area, oxidative stress, and pro-inflammatory effects of nanoparticles in the lung.

5 CONCLUSION

Nano conducting polymers: Biodegradable polymer-based nanocomposites are useful in aerospace, automotive, food packaging, solar cells, electrical and electronic goods, inkjet markets, cosmetics, and body moldings, engine covers and catalytic converts, batteries, computer chips, memory devices, biosensors for diagnostics. Bio-nanotechnology is in infancy. Reference: http://scribd.com/doc/25799862/Biotechnology-and-Nanotechnology/