

SYNTHESIS AND CHARACTERIZATION OF SURFACE-ACTIVATED  
MULTIWALLED CARBON NANOTUBES-POLYMER COMPOSITE  
ELECTROSPUN NANOFIBER

FATIRAH BINTI FADIL

UNIVERSITI TEKNOLOGI MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF SURFACE-ACTIVATED  
MULTIWALLED CARBON NANOTUBES-POLYMER COMPOSITE  
ELECTROSPUN NANOFIBER

FATIRAH BINTI FADIL

A thesis submitted in fulfilment of the  
requirements for the award of the degree of  
Doctor of Philosophy (Chemistry)

Faculty of Science  
Universiti Teknologi Malaysia

APRIL 2016

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ  
**Bismillah Hir-Rahman Nir-Rahim.**

**In the name of Allah, the Beneficent, the Merciful.**

### *Dedication*

To my parents:

The reason of what I become today. Thanks for your great support and continuous care.

To my husband:

Thanks for everlasting support and unconditional love my dear soulmate.

To my siblings:

I am really grateful of having both of you in my life. There is no better friend than a sister. Love you guys.

## ACKNOWLEDGEMENTS

### **In the name of Allah, the Most Gracious, the Most Merciful,**

Alhamdulillah. With His blessing on me, I have completed my PhD research journey toward the end. My thanks are due first to my amazing supervisor, Assoc. Prof. Dr. Nor Aziah Buang for her guidance and encouragement, for always making time to offer me advice, from the beginning and until to the very end. Special thanks go also to Prof. Seeram Ramakrishna and Dr. Molamma P. Prabhakaran from National University of Singapore (NUS) for their invaluable help, knowledge, given me opportunity to work in an international environment at their place. Many thanks to all the people I have work and collaborated with, especially Mr. KH Ang from Nanolab Instrument (M) Sdn. Bhd for providing industrial instrument training. I owe many thanks to all the past and present lab members of Inorganic Laboratory for the enjoyable experience of working and having good time with them. I would like to thank all the people who I have met over this four years, who have enriched me in so many different ways. Thanks to Dr. Fatiha Ismail for her lasting friendship and support, constant guidance despite the distance and also my other colleagues; Azizul, Amin, Syikin, Johari, Akmaliah, Syafiq, Khairullah, Rijal and Amirul. Lastly, my really heartfelt thanks to my dear husband, Mohd Firdaus A.Aziz, Ibu, Ayah, Along and Adik for their love and support through my years of studying. Many thanks to all of you. Alhamdulillah.

## ABSTRACT

The major problem in the development of polymer nanofiber composites with the infusion of multiwalled carbon nanotubes (MWCNTs) is to ensure good dispersion of the MWCNTs within the polymer matrix. This study reports an effective approach to activate the surface of MWCNTs by a non-covalent binding strategy, and incorporation of MWCNTs in poly ( $\epsilon$ -lactide-co- $\epsilon$ -caprolactone) (PLCL) using electrospinning process. The debundling of the MWCNTs aggregates through the non-covalent surfactant attachment on their outer layers was studied using surfactants with different ionic characters, which were sodium dodecyl sulphate (anionic, SDS), cetyltrimethyl ammonium bromide (cationic, CTAB), and polysorbate 80 (non-ionic, Tween-80) surfactants. Results obtained from the Atomic Force Microscopy (AFM) analysis of surface roughness of the surfactant-MWCNTs aggregates show different contours which were assigned to the size of the aggregates, distribution and orientation of the deposited surfactants on the surfaces of MWCNTs. The dispersion behavior of the respective surfactant molecules studied showed that the non-ionic surfactant molecules of Tween-80 have better adsorption coverage on MWCNTs surface due to the hydrophobic interactions between the liquid-solid interfaces, rather than the ionic surfactants of SDS and CTAB. The orientation of the adsorbed surfactants on the surfaces of MWCNTs was found to be strongly associated with the surfactant affinity, which was contributed by the surfactants head groups ionization. The surface morphology of each adsorbed surfactant molecule onto MWCNTs surface was determined by the Field Emission Scanning Electron Microscopy (FESEM) analysis. Furthermore, the infusion of the Tween-80-MWCNTs usability as the nanofiller component to produce electrospun polymer nanofiber composites was conducted using a customized electrospinning reactor system. The inclusion of Tween-80-MWCNTs resulted in superior electrospun MWCNTs-PLCL nanofiber composite with tensile stress value of 5.82-15.95 MPa, with the incorporation of MWCNTs ranging from 0.1wt% to 1.0wt%. Characterization by Transmission Electron Microscopy (TEM) depicted the homogenous distribution of MWCNTs within the polymer matrix. The manipulation of the electrospinning operational parameters in producing different structural features of the polymer nanofibers from PLCL was successful in producing both solid and porous structured nanofibers through the variation of solvent composition used. The solid PLCL nanofibers were formulated from the optimized polymer solution of 11wt% (w/v) of PLCL in dichloromethane/ dimethyl formamide (DCM/DMF) (70:30) at an applied voltage of 14kV with spinning solution flow rate of 1.0 mL/hr. While the porous PLCL nanofibers were formulated from the optimized polymer solution of 11wt% (w/v) of PLCL in DCM/acetone (70:30) at an applied voltage of 14kV with spinning solution flow rate of 1.0 mL/hr. The substitution of DMF to acetone in binary solvent system has resulted in highly-porous PLCL nanofibers. The AFM characterization revealed the differences in the surface roughness and pore depths of both dense and porous PLCL electrospun nanofibers fabricated.

## ABSTRAK

Masalah utama dalam pembangunan gentian nano polimer komposit dengan penyatuan tiub nano karbon dinding berlapis (MWCNTs) adalah untuk memastikan penyebaran yang baik MWCNTs di dalam matriks polimer. Kajian ini melaporkan pendekatan efektif untuk mengaktifkan permukaan MWCNTs dengan menerokai strategi pengikatan bukan kovalen, dan penggabungan MWCNTs ke dalam poli ( $\epsilon$ -lactid-co- $\epsilon$ -kaprolakton) (PLCL) menggunakan proses pemintalan elektro. Penyahgumpalan agregat MWCNTs dengan melekatkan surfaktan secara bukan kovalen pada lapisan luarnya telah dikaji dengan menggunakan surfaktan yang berbeza sifat ionik iaitu natrium dodesil sulfat (anionik, SDS), setiltrimetil ammonium bromida (kationik, CTAB), dan polisorbitat 80 (bukan ionik, Tween-80). Keputusan yang diperoleh daripada analisis mikroskop daya atom (AFM) terhadap kekasaran permukaan agregat surfaktan-MWCNTs menggambarkan perbezaan bentuk kontur yang merujuk kepada saiz agregat, taburan dan orientasi surfaktan yang terenap pada permukaan MWCNTs. Perilaku penyerapan bagi setiap molekul surfaktan yang dikaji menunjukkan bahawa molekul surfaktan bukan ionik Tween-80 mempunyai liputan penyerapan yang lebih baik pada permukaan MWCNTs disebabkan oleh interaksi hidrofobik antara muka cecair-pepejal, berbanding surfaktan ionik SDS dan CTAB. Orientasi surfaktan terjerap pada permukaan MWCNTs didapati berkaitan rapat dengan afiniti surfaktan, yang disumbangkan oleh pengionan kumpulan kepala surfaktan. Morfologi permukaan bagi setiap molekul surfaktan terjerap di permukaan MWCNTs telah ditentukan oleh analisis mikroskopi pengimbasan elektron pancaran medan (FESEM). Tambahan pula, kebolegunaan gabungan Tween-80-MWCNTs sebagai komponen bahan pengisi nano bagi menghasilkan pintalan elektro komposit gentian nano polimer telah dijalankan menggunakan sistem reaktor pintalan elektro yang ditempah khas. Perangkuman Tween-80-MWCNTs telah menghasilkan pintal elektro gentian nano MWCNTs-PLCL komposit terbaik dengan nilai tegasan tegangan 5.82-15.95 MPa, dengan julat penggabungan MWCNTs antara 0.1wt% hingga 1.0wt%. Pencirian menggunakan mikroskopi penghantaran elektron (TEM) menunjukkan taburan MWCNTs yang sekata dalam matriks polimer. Manipulasi terhadap parameter operasi pemintalan elektro untuk menghasilkan gentian nano polimer daripada PLCL dengan ciri struktur yang berbeza telah berjaya menghasilkan gentian nano yang berstruktur padat dan berliang melalui penggunaan pelbagai komposisi pelarut. Gentian nano PLCL padat telah diformulasikan daripada larutan polimer 11wt% (w/v) PLCL yang dioptimumkan dalam diklorometana/ dimetilformamida (DCM/DMF) (70:30) pada voltan gunaan 14kV dengan kadar aliran 1.0 mL/jam. Manakala gentian nano PLCL berliang telah diformulasi daripada larutan polimer 11wt% (w/v) PLCL yang dioptimumkan dalam DCM/aseton (70:30) pada voltan gunaan 14kV dengan kadar aliran larutan pemintalan 1.0 mL/jam. Penggantian DMF dengan aseton dalam sistem pelarut dedua telah menghasilkan gentian nano PLCL yang amat berliang. Pencirian AFM telah mendedahkan perbezaan kekasaran permukaan dan kedalaman liang bagi kedua-dua pintalan elektro gentian nano PLCL padat dan berliang yang telah difabrikasi.

## TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	<b>DECLARATION</b>	ii
	<b>DEDICATION</b>	iii
	<b>ACKNOWLEDGEMENTS</b>	iv
	<b>ABSTRACT</b>	v
	<b>ABSTRAK</b>	vi
	<b>TABLE OF CONTENTS</b>	vii
	<b>LIST OF TABLES</b>	xiii
	<b>LIST OF FIGURES</b>	xiv
	<b>LIST OF ABBREVIATIONS</b>	xix
	<b>LIST OF APPENDICES</b>	xxi
<b>1</b>	<b>INTRODUCTION</b>	<b>1</b>
	1.1 Nanofibers technology	1
	1.2 Biodegradable polyester in nanofibers technology	2
	1.3 Composite fabrication process	5
	1.4 Synthetic composite	5
	1.5 Carbon nanotubes as multifunctional filler	6
	1.6 Surfactant assisted dispersion of carbon nanotubes	7
	1.7 Electrospinning in nanofibers technology	8
	1.8 Problem statement	9
	1.9 Objectives of the research	11
	1.10 Scope of the research	11
	1.11 Significance of the research	13

<b>2</b>	<b>LITERATURE REVIEW</b>	<b>15</b>
2.1	Carbon nanotubes in polymer composite application	15
2.2	Carbon nanotubes structure and its properties	18
2.3	Current approaches for the dispersion of carbon nanotubes	21
2.3.1	Role of surfactant in assisting the dispersion of carbon nanotubes	23
2.3.2	Types of surfactant and their characteristics	24
2.3.3	Fluid surfaces and interface	26
2.4	Electrospun polymer nanofibers composite	29
2.5	Structure formation in polymer nanofibers	32
2.6	Electrospinning processing parameters	35
2.6.1	Needle diameter	35
2.6.2	Flow rate	35
2.6.3	Applied voltage	36
2.6.4	Spinneret tip-to-collector	37
2.6.5	Collector	37
2.6.6	Spinning solution	38
<b>3</b>	<b>EXPERIMENTAL</b>	<b>42</b>
3.1	Experimental outline	42
3.2	Preparation of surfactant activated MWCNTs	43
3.3	Preparation of surfactant solutions	44
3.4	Characterization of surfactant activated MWCNTs	46
3.4.1	Surface topography of surfactant-MWCNTs by atomic force microscope (AFM)	46
3.4.2	Surface morphology of surfactant-MWCNTs by field emission scanning electron microscope (FESEM)	47
3.4.3	Diffraction pattern of surfactant-MWCNTs by X-Ray diffraction (XRD)	47
3.4.4	Thermodynamic properties of surfactant-MWCNTs by differential scanning	

	calorimeter (DSC)	48
3.4.5	Chemical properties of surfactant-MWCNTs by Fourier transform infra-red (FTIR)	49
3.4.6	Graphitization of surfactant-MWCNTs by Raman spectroscopy	49
3.4.7	Thermal stability of surfactant-MWCNTs by thermal gravimetric analysis (TGA)	50
3.4.8	Dispersion test of surfactant-MWCNTs by dynamic light scattering (DLS) analysis	50
3.5	Fabrication of custom-built electrospinning unit	51
3.6	Optimization of spinning solution	53
3.7	Electrospinning of nanofibers and MWCNTs composite nanofibers of PLCL	54
3.8	Characterization of electrospun nanofibers	55
3.8.1	Surface morphology of electrospun nanofibers by scanning electron microscope (SEM)	55
3.8.2	Structural morphology of electrospun nanofibers by transmission electron microscopy (TEM)	56
3.8.3	Chemistry properties of electrospun nanofibers by attenuated total reflectance Fourier transform infra-red (ATR-FTIR)	56
3.8.4	Tensile measurement of electrospun nanofibers by tensile analyzer	56
3.8.5	Electrical conductivity of electrospun nanofibers by electrical impedance spectroscopy (EIS)	57
3.9	Research flow chart	58
<b>4</b>	<b>SURFACE ACTIVATION OF MWCNTs THROUGH NON-COVALENT ATTACHMENT OF SURFACTANT</b>	<b>59</b>

4.1	Chapter overview	59
4.2	AFM analysis of surfactant-MWCNTs aggregates	60
4.3	FESEM analysis of surfactant-MWCNTs aggregates	69
4.4	XRD analysis of surfactant-MWCNTs aggregates	73
4.5	Raman spectroscopy analysis of surfactant-MWCNTs aggregates	75
4.6	Non-covalent interaction between surfactant and MWCNTs	77
4.7	DSC thermogram of surfactant-MWCNTs aggregates	79
4.8	TGA analysis of surfactant-MWCNTs aggregates	81
4.9	Dispersion stability of surfactant-MWCNTs aggregates	85
4.10	Surface tension of surfactant-MWCNTs solution	89
4.11	Chapter summary	92
<b>5</b>	<b>OPTIMIZATION OF ELECTROSPINNING OPERATIONAL PARAMETERS FOR THE FABRICATION OF POLY (<math>\epsilon</math>-CAPROLACTONE)-CO- (<math>\epsilon</math>-CAPROLACTONE) NANOFIBERS</b>	<b>94</b>
5.1	Chapter overview	94
5.2	Optimization of solvent	95
5.2.1	Electrospun PLCL nanofibers in single solvent	96
5.2.2	Electrospun PLCL nanofibers in DMF/acetone solution	99
5.2.3	Electrospun PLCL nanofibers in DCM/DMF solution	101
5.2.4	Electrospun PLCL nanofibers in DCM/acetone solution	103
5.3	Influence of dielectric constant and boiling point of solvents in electrospinning	105
5.4	Optimization of polymer concentration	112

5.5	Relation of electrospinning jets and nanofibers structure	117
5.5.1	Branched jet	118
5.5.2	Single jet	119
5.5.3	Lateral jet	119
5.5.4	Pendant droplet jet	121
5.6	Optimization of electrospinning operational parameters	122
5.6.1	Optimization of applied voltage	122
5.6.2	Optimization of distance spinneret tip-to-collector	124
5.6.3	Optimization of flow rate	126
5.6.4	Optimization of needle diameter	128
5.7	Chapter summary	129
<b>6</b>	<b>CHARACTERISTIC OF PLCL NANOFIBERS COMPOSITE INFUSED WITH MWCNTs</b>	<b>131</b>
6.1	Chapter overview	131
6.2	SEM analysis of MWCNTs-PLCL nanofibers composite	132
6.2.1	Solid MWCNTs-PLCL nanofibers composite	132
6.2.2	Porous MWCNTs-PLCL nanofibers composite	135
6.3	Fragmentation of electrospun MWCNTs-PLCL nanofibers composite	139
6.4	TEM analysis of solid MWCNTs-PLCL nanofibers composite	143
6.5	ATR-FTIR analysis of solid MWCNTs-PLCL nanofibers composite	145
6.6	Mechanical characteristic of solid MWCNTs-PLCL nanofibers composite	147
6.7	Electrical conductivity of solid MWCNTs-PLCL	

		xiii
	nanofibers composite	150
6.8	Reinforcement and ballistic behavior of MWCNTs- polymer nanofibers	152
6.9	Chapter summary	154
<b>7</b>	<b>CONCLUSION AND RECOMMENDATIONS</b>	<b>155</b>
7.1	Conclusion	155
7.2	Recommendations	158
	<b>REFERENCES</b>	<b>160</b>
	Appendices A-F	177-193

**LIST OF TABLES**

<b>TABLE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
2.1	Chemical oxidation process of carbon nanotubes	22
2.2	Typical surface and interfacial tensions of liquids at 20°C (Myers, 2006)	27
2.3	Properties table of common solvents (Reichardt, 1990)	41
3.1	Preparation of surfactant solution	44
4.1	Enthalpy changes in surfactant-MWCNTs aggregates	79
5.1	Spinning solution parameter for PLCL	96
5.2	Properties table of DCM, acetone and DMF (Reichardt, 1990)	105
5.3	Calculated dielectric constant value of binary solvent composition	110
5.4	Nanofibers form and diameter size at different PLCL concentration	112
6.1	Tensile properties of PLCL and MWCNTs-PLCL nanofibers composite	148
6.2	Electrical conductivity of PLCL and MWCNTs-PLCL nanofibers composite	150

**LIST OF FIGURES**

<b>FIGURE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
1.1	Molecular structures of $\epsilon$ -caprolactone monomer, L-lactide monomer and PLCL copolymer	3
1.2	The degradation mechanism of PLCL by hydrolysis process	4
1.3	(a) Illustration model of carbon nanotubes by rolling sheets of graphene into a cylinder of nanometer size diameter (b) The structure of CNTs explored by high-resolution transmission electron microscopy. This figure is adapted from Endo (2010)	6
1.4	(a) Photograph of spider web (b) electrospun nanofiber web	9
2.1	Illustration of (a) carbon black (b) carbon fiber (c) carbon nanotubes dispersion in polymeric matrix.	16
2.2	The molecular dynamics model of carbon nanotubes subjected to ballistic impact (a) initial model (b) a deformed carbon nanotubes at its maximum energy absorption. This figure is adapted from Mylvaganam and Zhang (2007)	17
2.3	Illustration of carbon atom in hexagonal framework arrangement	20
2.4	Simplified surfactant structure	23
2.5	Cohesive forces between water molecules	26
2.6	The development of the critical micelle concentration (CMC). This figure is adapted from Emmert (2015)	28

2.7	MWCNTs composited nanofibers at different MWCNTs loading of (a) 1 wt% (b) 3 wt% (c) 5wt% and (d) 10 wt%. This figure is adapted from Keulder (2013)	31
2.8	Electrospinning design in (a) vertical upward, (b) vertical downward and (c) horizontal arrangement. This figure is adapted from Sahay et al., (2011)	33
2.9	Jet formations in the electrospinning process. This figure is adapted from Ramakrishna et al., (2005)	34
2.10	Material for collector cover (a) Aluminium foil (b) plastic (c) metal mesh and (d) wipe tissue	38
3.1	(a) The schematic diagram and (b) photograph of the fabricated custom-built electrospinning unit	51
4.1	AFM images of purified MWCNTs	61
4.2	AFM image of CTAB-MWCNTs aggregates	61
4.3	AFM images of SDS-MWCNTs aggregates	62
4.4	AFM images of Tween-80-MWCNTs aggregates	62
4.5	AFM surface contour measurement and the illustration of adsorbed surfactant orientation on MWCNTs solid surface (a) CTAB-MWCNTs (b) SDS-MWCNTs and (c) Tween-80-MWCNTs	63
4.6	Molecular modeling of the material arrangement (a) dome surface contour (b) pointy surface contour (c) horizontal positioning (d) upward positioning. This figure is adapted from Della Pia <i>et al.</i> (2012)	65
4.7	Molecular structure of SDS	66
4.8	SDS arrangement on hydrophobic surface. This figure is adapted from De Aguiar <i>et al.</i> (2011)	66
4.9	Molecular structure of CTAB	67
4.10	Molecular structure of Tween-80	68
4.11	FESEM micrograph of Tween-80-MWCNTs aggregates at magnification of 50000x	70
4.12	FESEM micrograph of SDS-MWCNTs aggregates at magnification of 50000x	71

4.13	FESEM micrograph of CTAB-MWCNTs aggregates at magnification of 50000x	72
4.14	XRD pattern of (a) purified MWCNTs, (b) SDS-MWCNTs (c) Tween-80-MWCNTs and (d) CTAB-MWCNTs	74
4.15	Raman spectra of (a) purified MWCNTs (b) SDS-MWCNTs, (c) Tween-80-MWCNTs and (d) CTAB-MWCNTs	76
4.16	TG and DTG thermogram of purified MWCNTs	82
4.17	TG and DTG thermogram of SDS-MWCNTs	83
4.18	TG and DTG thermogram of CTAB-MWCNTs	84
4.19	TG and DTG thermogram of Tween-80-MWCNTs	85
4.20	The illustration of the type of polydispersion of the particle distribution in suspension	86
4.21	Distribution of (a) Tween-80-MWCNTs, (b) CTAB-MWCNTs and (c) SDS-MWCNTs aggregates with mono-modal, bi-modal and poly-modal histogram	88
4.22	Graph of surface tension measurement versus surfactant concentration of surfactant-MWCNTs mixture in (a) SDS, (b) CTAB and (c) Tween-80 solution	89
4.23	Resonance of sulphate ion	91
5.1	SEM micrographs of PLCL nanofibers in single solvent of DMF (a1) (a2), acetone (b1) (b2) and DCM (c1) (c2) at magnification of 1000x and 5000x, respectively	98
5.2	SEM micrographs of electrospun PLCL nanofibers in DMF/acetone binary solvent ratio of 7:3 (a1) (a2), 1:1 (b1) (b2) and 3:7 (c1) (c2) at magnification of 1000x and 3000x respectively	100
5.3	SEM micrographs of electrospun PLCL nanofibers in DCM/DMF binary solvent ratio of 7:3 (a1) (a2), 1:1 (b1) (b2) and 3:7 (c1) (c2) at magnification of 1000x and 3000x respectively	102
5.4	SEM micrographs of electrospun PLCL nanofibers in DCM/acetone binary solvent ratio of 7:3 (a1) (a2), 1:1	

	(b1) (b2) and 3:7 (c1) (c2) at magnification of 1000x and 3000x respectively	104
5.5	The electrospinnability of PLCL in series of binary solvent consisting of DCM, DMF and acetone	111
5.6	SEM micrograph of 10 wt% (a), 11 wt% (b), 12 wt% (c) and 13 wt% (d) of electrospun PLCL nanofibers at magnification of 3000x	113
5.7	PLCL nanofibers thickness	115
5.8	PLCL nanofibers diameter size distribution and nanofibers web thickness in (a) 10 wt% (b) 11 wt% (c) 12 wt% (d) 13 wt%	116
5.9	(a) multiple branches jet (b) solidified jet branches at needle end of branched jet	118
5.10	(a) primary jet (b) solidified jet at needle end of single jet	119
5.11	(a) multiple jet (b) solidified jet at needle end of lateral jet	120
5.12	(a) droplet jet (b) solidified jet at needle end of pendant droplet jet	121
5.13	SEM micrograph of PLCL nanofibers at (a) 11 kV (b) 12 kV (c) 13 kV (d) 14 kV (e) 15 kV (f) 16 kV at magnification of 3000x	123
5.14	SEM micrographs of PLCL nanofibers collected at distance tip-to-collector of 10 cm (a1) (a2), 8 cm (b1) (b2) and 6 cm (c1) (c2) with magnification of 1000x and 3000x, respectively	125
5.15	SEM micrograph of PLCL nanofibers at (a) 0.8 mL/hr, (b) 1.0 mL/hr (c) 1.2 mL/hr (d) 1.4 mL/hr of spinning solution flow rate at magnification of 3000x	127
5.16	SEM micrograph of PLCL nanofibers produced using a (a) 0.45 mm (b) 0.5 mm (c) 0.7 mm (d) 0.8 mm of needle internal diameter at magnification of 10000x	129
6.1	SEM micrograph of electrospun solid nanofiber (a) PLCL (b) MWCNTs-PLCL with (0.1 wt%) (c) (0.2 wt%) (d) (0.3 wt%) (e) (0.4 wt%) (f) (0.5 wt%) and (g) (1.0 wt%) of MWCNTs at magnification of 20000x	133

6.2	SEM micrograph of electrospun porous nanofibers (a) PLCL (b)/MWCNTs-PLCL with (0.1wt%) (c) (0.2 wt%) (d) (0.3wt%) (e) (0.4wt%) (f) (0.5wt%) and (g) (1.0 wt%) of MWCNTs at magnification of 10000x	136
6.3	Simulated electrospun fibers from the spinneret (top) to the collector plate (bottom) with reference of the phase diagram where (i), (ii) and (iii) represent the elongation of fluids during the spinning. Electrospun fibers in dark regions represent solvent-rich regions and bright regions represent polymer-rich regions. This figure is adapted from Dayal <i>et al.</i> (2007)	138
6.4	SEM micrographs of solid MWCNTs-PLCL nanofibers composite with the occurrence of fibers cut off at magnification of (a) 20000x, (b) 40000x and (c) 80000x	139
6.5	SEM micrographs of porous MWCNTs-PLCL nanofibers composite with the occurrence of fibers cut off at magnification of (a) 3000x, (b) 5000x and (c) 10000x	140
6.6	Illustration of the proposed mechanism of the jet's axial stress and entanglement before (dashed line) and after (solid line) the jet break. This figure is adapted from Dayal <i>et al.</i> (2007)	141
6.7	AFM 3D images of the fragmented solid MWCNTs-PLCL nanofibers composite	142
6.8	TEM micrograph of electrospun PLCL nanofibers composite at scale bar of (a1) 100 nm (a2) 20 nm (a3) 10 nm and MWCNTs-PLCL nanofibers composite at scale bar of (b1) 100 nm (b2) 20 nm (b3) 10 nm	144
6.9	ATR-FTIR spectra of MWCNTs, PLCL nanofibers and MWCNTs-PLCL nanofibers composites of 0.1-1.0 wt%	146
6.10	Stress-strain curves of MWCNTs-PLCL nanofibers composite	148
6.11	Molecular dynamic simulation of CNTs under axial compression, a-d is the possible buckling of CNTs morphology changes corresponding to strain. This figure is adapted from Yakobson <i>et al.</i> (1996)	152

**LIST OF ABBREVIATIONS**

PLCL	-	Poly $\epsilon$ -caprolactone co- L-lactide
CFRP	-	Carbon Fiber Reinforced Polymer
CNTs	-	Carbon nanotubes
MWCNTs	-	Multiwalled carbon nanotubes
FTIR	-	Fourier Transform Infrared
TGA	-	Thermal Gravimetric Analysis
XRD	-	X-ray Diffraction
FESEM	-	Field Emission Scanning Electron Microscope
AFM	-	Atomic Force Microscopy
DCM	-	Dichloromethane
DMF	-	Dimethyl Formamide
TEM	-	Transmission Electron Microscope
SWCNTs	-	Singlewalled Carbon Nanotubes
PS	-	Poly Styrene
PMMA	-	Poly Methyl Methacrylate
HCl	-	Hydrochloric acid
STM	-	Scanning Tunnelling Microscope
CCVD	-	Catalytic Chemical Vapor Deposition
H <sub>2</sub> SO <sub>4</sub>	-	Sulphuric acid
HNO <sub>3</sub>	-	Nitric acid
H <sub>2</sub> O <sub>2</sub>	-	Hydrogen peroxide
SOCl <sub>2</sub>	-	Thionyl chloride
SLS	-	Sodium lauryl sulphate
SDS	-	Sodium dodecyl sulphate
CV	-	Cyclic voltammetry
DA	-	Dopamine
NaDDBS	-	Sodium dodecyl benzene sulfonate

PVA	-	Poly vinyl alcohol
DMAcAM	-	Dimethylacetamide
THF	-	Tetrahydrofuran
DMSO	-	Dimethyl sulfoxide
Tween-80	-	Polyoxyethylene (20) sorbitan monooleate
CTAB	-	Cetyl trimethylammonium bromide
CMC	-	Critical micelle concentration
KBr	-	Potassium bromide
DTA	-	Differential thermal analysis
DLS	-	Dynamic light scattering
ATR-FTIR	-	Attenuated Total Reflection- Fourier Transform Infrared
D-band	-	Defect band
G-band	-	Graphite band
Z-average	-	Cumulant size
PU	-	Polyurethane

**LIST OF APPENDICES**

<b>APPENDIX</b>	<b>TITLE</b>	<b>PAGE</b>
A	FESEM micrograph and EDX value of purified MWCNTs	177
B	DSC profile of Tween-80-MWCNTs aggregates	178
C	DSC profile of CTAB-MWCNTs aggregates	179
D	DSC profile of SDS-MWCNTs aggregates	180
E	Publications and presentations	181
F	Awards	183

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Nanofibers technology**

Nanofiber technology is one of the nanotechnology divisions where fibrous materials are fabricated at nano-scale dimension. Electrospun polymer nanofibers were formed from the highly charged polymer solution that which electrically heated, extruded, evaporated and cooled upon exposed in air through a technique called electrospinning. Electrospinning is a powerful technique in producing polymeric based fibers at nano to sub-micron level range of fibers diameter. They have attracted significant attention across multiple fields of chemistry, biochemistry and engineering because of the uniqueness rheological, mechanical and biomedical properties that are inaccessible from the casting polymers (Cameron and Shaver, 2011). The electrospun nanofibers from biopolymer based have offered new avenue in the field of tissue regeneration by producing scaffolds with the critical similarities to the native tissue based on the interconnectivity and its dimensions.

Electrospun polymer nanofibers were commonly produced from variety of polymers including, natural or synthetic polymer source, with or without filler, in melt or with solvent, on condition that the polymer solution was conductive enough to be drawn as fibrous form. Polymer based liquid precursor from high molecular weight polymers and high polymer concentrations are advantageous for the electrospinning process since polymer chain entanglements and overlapping are important for the formation of uniform nanofibers (Celebioglu and Uyar, 2012). On the other hand, the use of solvent in preparing the spinning solution is basically to

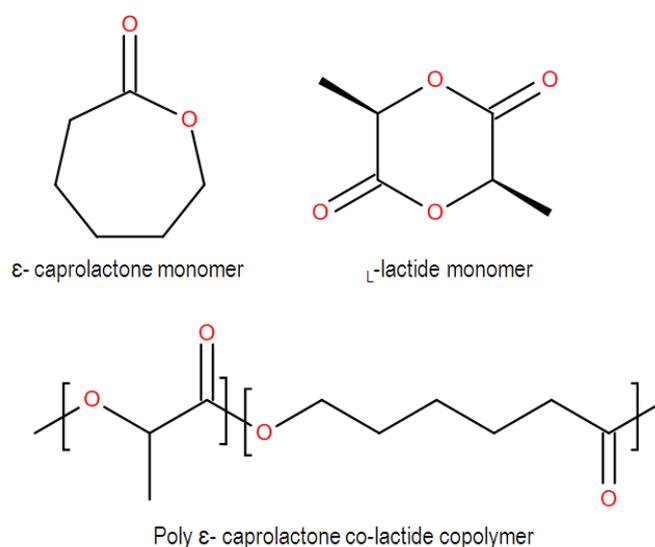
induce the polymer solution transformation process from droplet into fibrous form under high voltage atmosphere (Leach *et al.*, 2011). The values of the applied high voltage used during the electrospinning process which are normally within the range of 10-30 kV, managed to draw electrospun nanofibers with the fibers diameter size ranging from 100-1000 nm (Ramakrishna *et al.*, 2005).

## 1.2 Biodegradable polyester in nanofibers technology

The synthetic biodegradable polymers offer an alternative over the non-degradable polymer materials which mostly used in the biomedical applications. The solution of biodegradable polymers can be processed into different solid forms through electrospinning technique. For instance, they can either be processed into multi- or nanofilaments for surgical sutures or exhibit porous scaffolds with desired pore morphology, which is specifically conducive for implants and tissue growth. Besides, they can also be spun into the micro/nanospheres form for controlled drug delivery process application (Makadia and Siegel, 2011, Kulshrestha and Mahapatro, 2008).

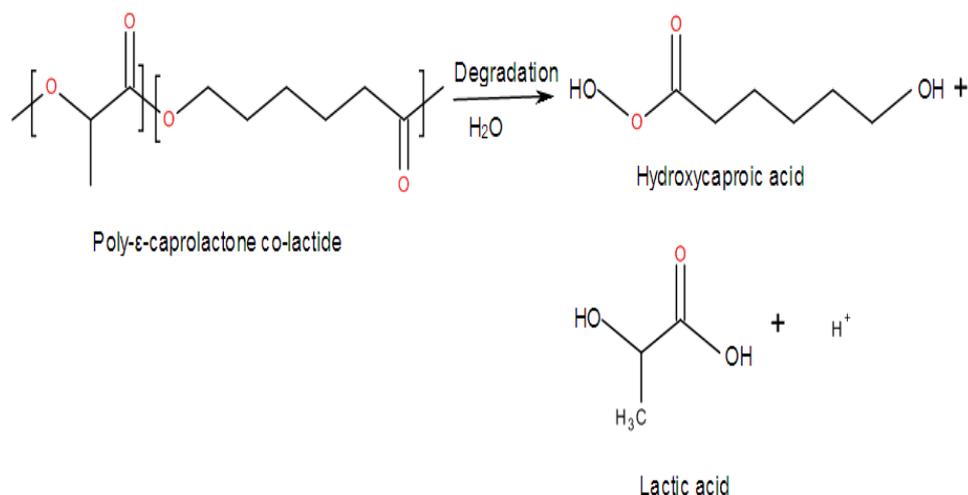
Polyester is a category of synthetic biodegradable polymers which contain ester functional groups in their main chain. Polyester is widely used as cushioning and insulating materials in pillows, comforters and padding. Nowadays, polyester is the main family of synthetic biodegradable polymers that is used as commodity plastics packaging materials and even in the biomedical field application. The ring opening polymerization of cyclic esters provides an access to biodegradable, bioassimilable and renewable materials that made from the polyester polymer. In the previous study, most biomedical applications and investigation were now concerned on the polyglycolide, polylactide, poly ( $\epsilon$ -caprolactone) and their others copolymers (Ulery *et al.*, 2011, Diaz *et al.*, 2014). These are the most common of the synthetic polyester polymers that have been used intensively as their consumption was approved by the health authorities in various countries (Rentsch *et al.*, 2012, Vroman and Tighzert, 2009, Chen *et al.*, 2012).

On the other hand, poly (*L*-lactide)-co-  $\epsilon$ -caprolactone) (PLCL) is a polyester copolymer which has exhibited an intermediate strength of its mechanical properties. PLCL was synthesized by ring-opening copolymerization of *L*-lactide and  $\epsilon$ -caprolactone using coordination catalysts. PLCL is one of the compatible synthetic polymers for medical use as referred from its biocompatibility and slow biodegradability properties (Fernández *et al.*, 2012, Baimark and Molloy, 2004, Garkhal *et al.*, 2007, Jeong *et al.*, 2004). Figure 1.1 illustrates the molecular structure of  $\epsilon$ -caprolactone monomer unit, *L*-lactide monomer unit and PLCL copolymers.



**Figure 1.1** Molecular structures of  $\epsilon$ -caprolactone monomer, *L*-lactide monomer and PLCL copolymer

The advantage of PLCL properties over both poly caprolactone (PCL) and poly lactide (PLA) is that PLCL combines the desirable mechanical properties of PCL, with higher degradation and biocompatibility of PLA. The degradation process of PLCL proceeds via simple hydrolysis of random polymer chain scission nucleated on the ester part. For *L*-lactide-rich fragments, hydrolysis process is continues until *L*-lactic acid is formed.  $\epsilon$ -caprolactone-rich fragments on the other hand were hydrolyzed to produce  $\epsilon$ -hydroxycaproic acid as shown in Figure 1.2. Both *L*-lactic acid and  $\epsilon$ -hydroxycaproic acid will then metabolized and excreted from human body without any adverse toxicological effects (Baimark and Molly, 2004).



**Figure 1.2** The degradation mechanism of PLCL by hydrolysis process

There are variety of PLCL available which differ in their ratio of lactide to caprolactone (LA: CL) which are (1:99), (30:70) and (50:50) (Joeng *et al.*, 2004, Sanna *et al.*, 2011, Lim *et al.*, 2004). Since PLCL is composed of the soft matrix of  $\epsilon$ -caprolactone monomer units and the hard domains of the additional L-lactide monomer units, PLCL has the tendency to exhibit merely stiff or rubber-like elasticity in its physically cross-linked structure (Inai *et al.*, 2005). The mechanical strength and elasticity of PLCL is likely varied accordingly to the (LA: CL) co-monomers ratios. Hence, the use of PLCL with specific (LA: CL) co-monomers ratio were depend on its specific applications. For example, the use of PLCL with higher lactide composition is preferred for slow delivery of drugs instead of PLCL with lower lactide composition (Makadia and Siegel, 2011).

Even so, there are methods that can be done to modify the PLCL mechanical properties. An alternative way for enhancing the mechanical properties of the polymer is known as composite fabrication process.

### **1.3 Composite fabrication process**

Composite fabrication process is described as a technique used for the formation of blended materials which composed of two or more constituent materials which known as composite materials (Malhotra *et al.*, 2012, Klaus *et al.*, 2005). A composite material is composed from the primary phase which is the polymer matrix materials, while the secondary phase is the reinforcing materials which is used to fortify the matrix in terms of strength and stiffness. These combined materials work together to give the superior properties to the properties of the individual components (Heinrich and Vilgis, 2002).

### **1.4 Synthetic composite**

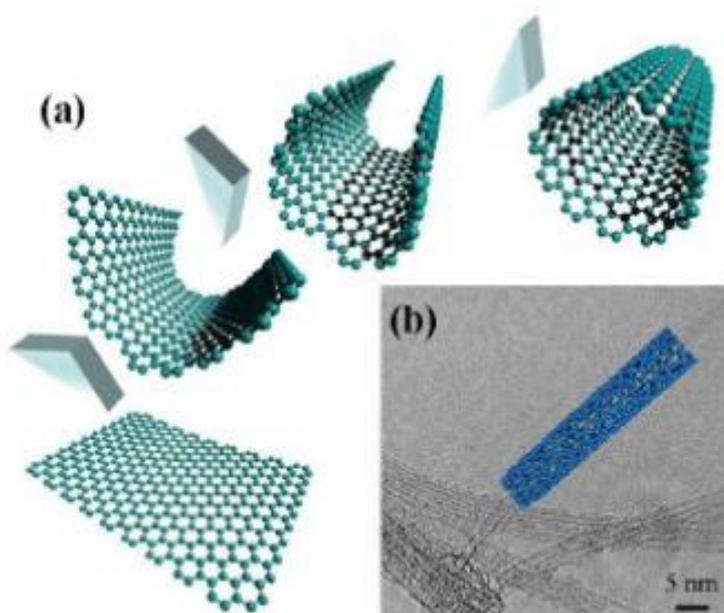
The synthetic composite is a part of man's technology which has been produced thousands of years before, for examples mud bricks and concretes. One of the examples of the first modern man-made composite is fiberglass. The primary phase in the fiberglass is plastic, whereas the secondary phase is glass. The glass was made into fine threads and often woven into a sort of cloth and wool as to be used in the fabrication process of fiberglass. While the plastic matrix holds the glass fibers together and protects them from damage by sharing the applied force on them. Fiberglass has been widely used in many applications such as in building panel, roofing, pipes and automobiles (Kieronski *et al.*, 2004). With further development in the composite technology, the advanced composites are now made by using carbon fibers instead of fiberglass. This microscale carbon material is much lighter and stronger than fiberglass and is practically used in expensive sports equipment such as golf sport accessories and in the vehicle body parts in the automotive industry (Allhoff and Moore, 2009, Szeteiová, 2010). Since then, the carbon-fiber-reinforced polymer composites (CFRP) have remained as the major standard for polymer composite based materials in high performance applications.

Recently, carbon nanotubes (CNTs) are one of the desired carbon materials to be use in the composite since they have the ability to serve as multifunctional

nanofiller (Fiorito, 2008). The demands of having CNTs as the nanofiller have captured huge interest among the researchers to study the insertion of this carbon material in the composite. The prospect of carbon nanotubes in making advanced composite was blooming as they are even lighter and tougher compared to the carbon fibers (Ajayan *et al.*, 2000).

### 1.5 Carbon nanotubes as multifunctional filler

Carbon nanotubes are one-dimensional carbon allotropes which have outstanding characteristics based on its tensile strength, elastic modulus and flexibility. In general, carbon nanotubes can be visualized as a rolled nanoscale graphene layers in a form of cylinders of micrometer length (Bokobza, 2007). Figure 1.3 shows the illustration of the carbon nanotubes structure.



**Figure 1.3** (a) Illustration model of carbon nanotubes by rolling sheets of graphene into a cylinder of nanometer size diameter (b) The structure of CNTs explored by high-resolution transmission electron microscopy. This figure is adapted from Endo (2010)

The utilization of carbon nanotubes as multifunctional filler has opened a new dimension for the development of nanocomposite at present. A shift to nanoscale fillers offers the potential for lower filler content (as low as 2-5 wt %) compared to

the traditional microscale fillers. Based from the previous study, the percentage composition of the microscale filler in the composite was formulated in the range of 10-70 wt% (Ma et al., 2010). Besides of offering lower content of filler consumption, carbon nanotubes also has excellent flexibility and strength to control structural deformation of the composite. Therefore, the nanosized dimension of carbon nanotubes might improves the physical properties of the nanocomposite, by blocking the micro-cracking occurrence, even at the lower percentage loading of carbon nanotubes (Barraza *et al.*, 2002, Borowski *et al.*, 2015).

Apart from the above mentioned of carbon nanotubes characteristic, they are also have high aspect ratio properties, according to the proportional relationships between the width and the length of its tubular structures. As their aspect ratio is high, the van der Waals forces among the carbon-carbon atoms which build the hexagonal structure framework of carbon nanotubes become stronger, caused to the agglomeration of carbon nanotubes floss. Therefore, controlling the amount loading of carbon nanotubes is a critical aspect in the manufacturing of carbon nanotubes-polymer composite as they are not easily dispersed in any medium or solvent due to the van der Waals forces. Thus, the uniform dispersion of carbon nanotubes in a viscous polymer matrix is extremely difficult to be prepared. However, the best possible processing technique in assisting carbon nanotubes dispersion still remains a challenge.

## **1.6 Surfactant assisted dispersion of carbon nanotubes**

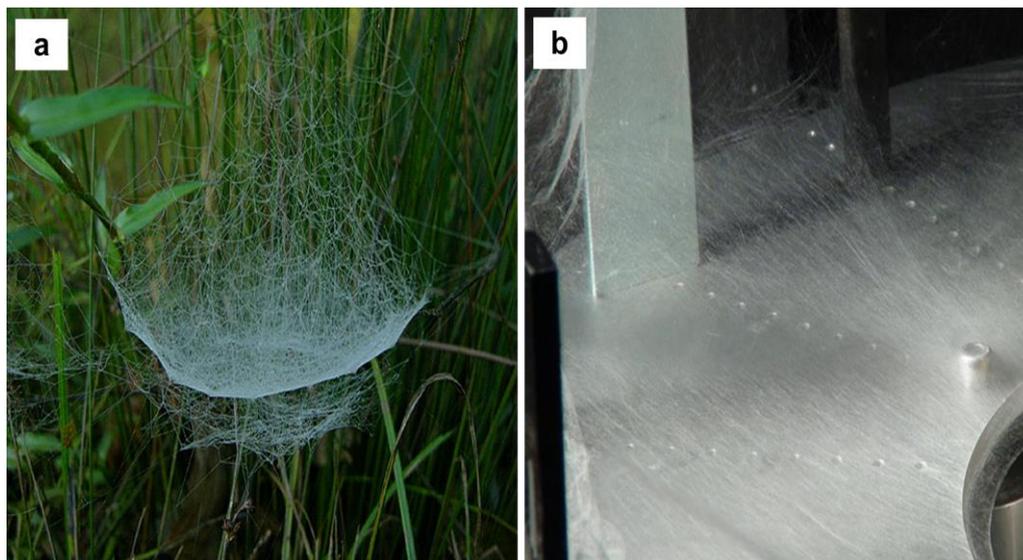
Shi *et al.*, (2013) and Moniruzzaman and Winey (2006) highlighted the significant challenges on the dispersion of carbon nanotubes that must be overcome for the effective use of carbon nanotubes. Carbon nanotubes dispersion can be improved over prior processing techniques known as surface activation. These are including the use of strong oxidant such as concentrated acid and strong oxidizing agent. The surface activation using strong oxidant is known as the most frequently used technique for dispersing carbon nanotubes (Martínez-Hernández *et al.*, 2010).

However, this oxidizing treatment normally caused severe damages to the structure of carbon nanotubes (Matarredona *et al.*, 2003).

Since carbon nanotubes lack in active groups and has high surface energy (Lau *et al.*, 2003), the use of wetting agent in the surface activation is probably the best method for dispersing carbon nanotubes. Surfactant is an excellent wetting agent which is able to preserve important properties of carbon nanotubes. Despite of scissoring the length of carbon nanotubes as the oxidizing treatment, the surfactant molecules, will be attached to the surface of carbon nanotubes by non-covalent interaction, making this technique as a better strategy for dispersion of carbon nanotubes in smaller aggregates (Angelikopoulos and Bock, 2012). The mechanism for the dispersion is expected to be primarily due to hydrophilic and hydrophobic interactions, where attraction between the surface of carbon nanotubes and the hydrophobic segment of surfactant facilitates adsorption, while the hydrophilic group of surfactant associates with water, forming a stable suspension of carbon nanotubes aggregates (Blanch *et al.*, 2010). The stabilization of carbon nanotubes floss in smaller aggregates is vital for controlling the rheological of the carbon nanotubes-polymer composite especially in controlling the structural formation of the electrospun polymer composite nanofibers by electrospinning.

## **1.7 Electrospinning in nanofibers technology**

Electrospinning is a technique use for the making of nanofibers by utilizing electrostatic interaction, which was discovered and patented by Formhals in 1934. Through the discovery, he pointed out that as when a polymer solution is subjected to an electric field, the consistent electrostatic forces will gradually cause the polymer solution to be drawn into a fibrous form (Formhals, 1934, Formhals, 1939). This technique has the ability to transform polymer solution into nanofibers structure in the form of interconnected web, which is in similar to the spider web-like structure as depicted in Figure 1.4.



**Figure 1.4** Photograph of (a) spider web (b) electrospun nanofiber web

Electrospun nanofibers are also considered as one-dimensional materials according to the high aspect ratios of this material, which related to the huge difference of the nanofibers width compared to its length. Since electrospun nanofibers are a small-scale filament with high surface area, they have great potential to be used in many applications such as chemical resistance materials, filtration materials, biomedical and surgical materials and also high-strength protective fabric materials. However, there are challenges in optimizing the production of electrospun nanofibers polymer composite using electrospinning technique especially with the presence of carbon nanotubes as the nanofiller.

## 1.8 Problem statement

Obtaining stable aqueous dispersions is one of the main challenges obstructing an effective use of carbon nanotubes. These are the result of hydrophobically driven van der Waals force interactions, which are an inherent consequence of their carbon  $sp^2$  hybridization network. This, combined with extremely high aspect ratios and strong surface energy, causes to strong adhere into tightly agglomerates form of carbon nanotubes floss. Thus, the major problem in dealing with carbon nanotubes as nanofiller is to overcome the poor dispersion of the carbon nanotubes.

The dispersion technique via non-covalent interaction between surfactant and carbon nanotubes surface has the advantage of preserving the conjugated  $\pi$  system of carbon nanotubes, upholding their electrical and mechanical properties. Affecting factor in the dispersion using surfactant is surfactant concentration, as there will always be an optimum surfactant concentration for a specific loading of carbon nanotubes. At very low surfactant concentration, the dispersion quality will be poor because carbon nanotubes are still in a form of entangled bundles. While, at very high surfactant concentration, dispersion quality becomes poor, as the surfactant are starting to form micelles. Besides, the other factors such as the influence of surfactant affinity towards the formation of surfactant-carbon nanotubes aggregates, the size of carbon nanotubes aggregation and the preferred orientation of accumulated surfactant molecules on the surface of carbon nanotubes also need to be investigate.

Another importance of having well dispersed form of carbon nanotubes is to avoid the problem of clogging during electrospinning. Clogging of the spinneret tip through gelation of the spinning solution can be very disruptive to the spinning process as it causes production losses. This issue is more apparent when higher concentration spinning solution with filler addition is used, which is likely due to higher viscosity, contributes to the clogging of the spinneret tip. The other problems arises in electrospinning process are including the formation of beads, the uncontrolled of nanofibers diameter size, the jet discontinuity and the instability of nanofibers structure retention. As a results, both of mechanical and physical properties of electrospun nanofibers composite would be poor. Besides, the effect of polymer concentration, solvent used and amount of carbon nanotubes filler loading towards the formation of the electrospun composite nanofibers has been few and inconclusive. Hence, appropriate sets of electrospinning process parameters are necessary to identify the significant factors in optimizing the fabrication of electrospun composite nanofibers with the infusion of carbon nanotubes as nanofiller.

## 1.9 Objectives of the research

The aim of this research is to determine the fundamental principle in the electrospinning technology for the fabrication of nanofibrous materials of electrospun nanofibers composite of poly ( $\epsilon$ -lactide)-co-  $\epsilon$ -caprolactone) (PLCL) infused with multiwalled carbon nanotubes (MWCNTs). The objectives that will fulfill the aim of this research are listed as follows:

1. To synthesize the surface activated-MWCNTs using surfactant with different affinity.
2. To investigate the surfactant behavior on the surface of the MWCNTs by various characterization instruments.
3. To customize a lab-scale electrospinning system and optimization of the operational parameters for the production of PLCL-MWCNTs nanofibers composite.
4. To investigate the effect of solvent and amount of surfactant surface activated-MWCNTs loading in the formation of PLCL-MWCNTs nanofibers composite.
5. To study the physical and mechanical properties of the electrospun PLCL-MWCNTs nanofibers composite using various characterization instruments.

## 1.10 Scope of the research

The first scope of this research is modification of the MWCNTs hydrophobic properties through MWCNTs surface activation process via non-covalent interaction using surfactants. The purpose of the modification process is to have smaller size of stabilized MWCNTs aggregates as nanofiller in the polymer composite. Three types of surfactants with different ionic character, which are anionic, cationic and non-ionic, were utilized for the surface modification of the MWCNTs. The conceptual arguments on the surfactant structure and behavior of the hydrophobic tails, head

charged and its polarity effect towards the dispersion of carbon nanotubes were studied in depth using various spectroscopic techniques and particle size analyzer.

The analysis studied was chemical characterization by Fourier Transform Infrared (FTIR) spectroscopy and Raman spectroscopy. The thermal stability of MWCNTs after surface activation was investigated using Thermal Gravimetric Analysis (TGA). While, the morphology of MWCNTs upon surface modification was analysed using X-ray Diffraction (XRD), and Field Emission Scanning Electron Microscope (FESEM). Atomic Force Microscope (AFM) was used to examine the MWCNTs aggregation size upon surface modification process, and then roughly determine the smallest size of MWCNTs colloidal among the different surfactant used in surface activation process.

Besides, this research is working on the customization of the lab-scale electrospinning reactor system by assembling the basic component for a low-cost electrospinning set-up. Since there are few arrangements in the electrospinning reactor, the customized electrospinning system in this study is arranged in vertical position especially to reduce the applied voltage by following the gravitational field.

The optimization of the operating parameters involves in the electrospinning process was part of the scope in this research study. In this research, the preparation of the spinning solution using various solvent mixtures was explored. The binary solvent system comprised of DCM, DMF and acetones were used to investigate the suitability of solvent for the electrospinning of PLCL. The control steps over the electrospinning operating parameter by stabilizing the jet formation is also part of this research study. The influence of the related operational parameters for the electrospinning processing including the spinneret-to-collector distance, applied current voltage and flow rate on the electrospun nanofiber structure are also investigated in this research study. The use of surface activated MWCNTs as the nanofiller in the electrospun nanofibers composite was investigated. The effect on the different loading of MWCNTs on the physico-chemical and mechanical properties of the MWCNTs-PLCL nanofibers composite was explored and for this

part, the smallest MWCNTs aggregates upon the surface activation is utilize in the electrospinning of the nanofibers composite.

Lastly, this research also is focused on the evaluation and characterization of the electrospun nanofibers composite produced. Morphological study of PLCL nanofibers and the infusion of MWCNTs within the MWCNTs-PLCL nanofibers composite were analysed using the Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM). The mechanical testing based on tensile measurement of the nanofibers sample was pursued to study the mechanical properties enhancement of the electrospun composite nanofibers reinforced with MWCNTs.

### **1.11 Significance of the research**

The significance of this research is the contribution in the optimization of carbon nanotubes dispersion technique using various type of surfactants, as an alternative to replace the conventional surface activation technique using oxidants. The influence of surfactant affinity in altering the dispersibility of carbon nanotubes has contributed an added value to the limited discussion in articles for established publications. An in depth discussions on the chemistry of the surfactant-MWCNTs interaction, cluster formation of MWCNTs aggregation and surfactant orientation on MWCNTs surface were highlighted in this study. The knowledge from the fundamental point of view has provided better insight to a better understanding towards the surfactant assisted in the dispersion of carbon nanotubes.

Another significant finding of this research is the establishment in the fabrication of nanofibrous materials of electrospun nanofibers composite of poly (L-lactide)-co- $\epsilon$ -caprolactone) (PLCL) infused with multiwalled carbon nanotubes (MWCNTs) using electrospinning technology. By the end of this research, an optimized lab-scale electrospinning reactor system is fabricated for the production of electrospun nanofibers purposes. A different structural form of PLCL-MWCNTs

electrospun nanofibers also can be spun by manipulating the optimized operational parameters of the electrospinning technique, using the right formulation of the specific nanofibers features needed. The difference in the solvent properties and their dielectric constant values in the three different binary solvent mixtures have contributed to the evolution of the PLCL nanofibers morphologies.

## REFERENCES

- Ajayan, P. M., Schadler, L. S., Giannaris, C. and Rubio, A. (2000). Single-walled carbon nanotube–polymer composites: Strength and weakness. *Advanced materials*. 12: 750–753.
- Ajayan, P. M., Stephan, O., Colliex, C. and Trauth, D. (1994). Aligned carbon nanotube arrays formed by cutting a polymer resin-nanotube composite. *Science*. 265(5176): 1212-1214.
- Ajayan, P. M., Terrones, M., De la Guardia, A., Huc, V., Grobert, N., Wei, B. Q. and Ebbesen, T. W. (2002). Nanotubes in a flash-ignition and reconstruction. *Science*. 296(5568): 705-705.
- Allhoff, F., Lin, P. and Moore, D. (2009). What is nanotechnology and why does it matter? from science to ethics. United Kingdom: John Wiley & Sons. 1<sup>st</sup> Edition. 3-16.
- Angelikopoulos, P. and Bock, H. (2012). The science of dispersing carbon nanotubes with surfactants. *Physical chemistry chemical physics*. 14(27): 9546-9557.
- Antonucci, V., Giordano, M., Nicolais, L., Calabro, A., Cusano, A., Cutolo, A. and Insera, S. (2003). Resin flow monitoring in resin film infusion process. *Journal of materials processing technology*. 143: 687-692.
- Baimark, Y. and Molloy, R. (2004). Synthesis and characterization of poly (L-lactide-co-ε-caprolactone) copolymers: Effects of stannous octoate initiator and diethylene glycol co-initiator concentrations. *Science asia*. 30: 327-334.
- Banhart, F. (2015). Chains of carbon atoms: A vision or a new nanomaterial? *Beilstein journal of nanotechnology*. 6(1): 559-569.
- Barraza, H. J., Pompeo, F., O'Rea, E. A. and Resasco, D. E. (2002). SWNT-filled thermoplastic and elastomeric composites prepared by miniemulsion polymerization. *Nano letters*. 2(8): 797-802.
- Baumgarten, P. K. (1971). Electrostatic spinning of acrylic microfibers. *Journal of colloid and interface science*. 36(1): 71-79.

- Bhadeshia, H. K. D. H. (2005). Bulk nanocrystalline steel. *Ironmaking & steelmaking*. 32(5): 405-410.
- Bhardwaj, N. and Kundu, S. C. (2010). Electrospinning: a fascinating fiber fabrication technique. *Biotechnology advances*. 28(3): 325-347.
- Blanch, A. J., Lenehan, C. E., and Quinton, J. S. (2010). Optimizing surfactant concentrations for dispersion of single-walled carbon nanotubes in aqueous solution. *The journal of physical chemistry B*. 114(30): 9805-9811.
- Bokobza, L. (2007). Multiwall carbon nanotube elastomeric composites: A review. *Polymer*. 48(17): 4907-4920.
- Borowski, E., Soliman, E., Kandil, U. F. and Taha, M. R. (2015). Interlaminar Fracture Toughness of CFRP Laminates Incorporating Multi-Walled Carbon Nanotubes. *Polymers*, 7(6):1020-1045.
- Buchko, C. J., Chen, L. C., Shen, Y. and Martin, D. C. (1999). Processing and microstructural characterization of porous biocompatible protein polymer thin films. *Polymer*. 40(26): 7397-7407.
- Burlatsky, S. F., Atrazhev, V. V., Dmitriev, D. V., Sultanov, V. I., Timokhina, E. N., Ugolkova, E. A. and Vincitore, A. (2013). Surface tension model for surfactant solutions at the critical micelle concentration. *Journal of colloid and interface science*. 393: 151-160.
- Cameron, D. J. A. and Shaver, M. P. (2011). Aliphatic polyester polymer stars: synthesis, properties and applications in biomedicine and nanotechnology. *Chemical society reviews*. 40(3): 1761-1776.
- Celebioglu, A. and Uyar, T. (2012). Electrospinning of nanofibers from non-polymeric systems: polymer-free nanofibers from cyclodextrin derivatives. *Nanoscale*. 4(2): 621-631.
- Chakoli, A. N., Cai, W., Jiehe, S. and Feng, J. T. (2009). Efficient load transfer to functionalized carbon nanotubes as reinforcement in polymer nanocomposites. *International journal of modern physics B*. 23(06n07): 1401-1406.
- Chen, Q., Zhu, C. and Thouas, G. A. (2012). Progress and challenges in biomaterials used for bone tissue engineering: bioactive glasses and elastomeric composites. *Progress in biomaterials*. 1(1): 1-22.

- Chen, Z. G., Mo, X. M. and Qing, F. L. (2007). Electrospinning of collagen-chitosan complex. *Materials letter*. 61: 3490-3494.
- Cheng, X., Zhong, J., Meng, J., Yang, M., Jia, F., Xu, Z. and Xu, H. (2011). Characterization of multiwalled carbon nanotubes dispersing in water and association with biological effects. *Journal of nanomaterials*. 2011: 14-25.
- Choudhary, V. and Gupta, A. (2011). Polymer/carbon nanotube nanocomposites. In Yellampalli, S. (Ed) *Carbon Nanotubes-Polymer Nanocomposites*. (pp 65-90). Croatia: INTECH Open Access Publisher.
- Coleman, B. D. (1986). Necking and drawing in polymeric fibers under tension. In C. M. Dafermos, D. D. Joseph, and F. M. Leslie (Eds) *The Breadth and Depth of Continuum Mechanics*. (pp 19-41). New York: Springer Berlin Heidelberg.
- Cox, H. L. (1952). The elasticity and strength of paper and other fibrous materials. *British journal of applied physics*. 3(3): 72-79.
- Dao, A. T. and Jirsak, O. (2010). Roller Electrospinning in Various Ambient Parameters. *Nanocon2010 conference*. Czech Republic. EU2010.
- Darani, K. K. and Reza Mozafari, M. (2010). Supercritical fluids technology in bioprocess industries: a review. *Journal of biochemical technology*. 2(1): 144-152.
- Datsyuk, V., Landois, P., Fitremann, J., Peigney, A., Galibert, A. M., Soula, B. and Flahaut, E. (2009). Double-walled carbon nanotube dispersion via surfactant substitution. *Journal of materials chemistry*. 19(18): 2729-2736.
- Dayal, P., Liu, J., Kumar, S. and Kyu, T. (2007). Experimental and theoretical investigations of porous structure formation in electrospun fibers. *Macromolecules*. 40(21): 7689-7694.
- De Aguiar, H. B., Strader, M. L., de Beer, A. G. and Roke, S. (2011). Surface structure of sodium dodecyl sulfate surfactant and oil at the oil-in-water droplet liquid/liquid interface: a manifestation of a nonequilibrium surface state. *The journal of physical chemistry B*. 115(12): 2970-2978.
- Della Pia, E. A., Macdonald, J. E., Elliott, M. and Jones, D. D. (2012). Direct Binding of a Redox Protein for Single-Molecule Electron Transfer Measurements. *Small*. 8(15): 2341-2344.

- Deng, W., Lobovsky, A., Iacono, S. T., Wu, T., Tomar, N., Budy, S. M. and Smith, D. W. (2011). Poly (acrylonitrile-co-1-vinylimidazole): A new melt processable carbon fiber precursor. *Polymer*. 52(3): 622-628.
- Díaz, A., Katsarava, R. and Puiggali, J. (2014). Synthesis, properties and applications of biodegradable polymers derived from diols and dicarboxylic acids: From polyesters to poly (ester amide)s. *International journal of molecular sciences*. 15(5): 7064-7123.
- Emmert, K. (2015). *Determining the Critical Micelle Concentration of Polymer Matrix for Drug Delivery Purposes*. Honors Research Projects. University of Akron.
- Endo, M. (2010). *Progress and perspectives in the carbon nanotube world*, AZoNano.com, Jun 23, 2010.
- Endoh, K. and Suga, H. (1999). Phase diagram of salt–water system determined by TG-DTA. *Thermochimica acta*. 327(1): 133-137.
- Fendler, J. H. (1996). *The colloidal domain: Where physics, chemistry, biology, and technology meet*. By D. Fennell Evans and Hakån Wennerström. New York: VCH Publishers.
- Fernández, J., Etxeberria, A. and Sarasua, J. R. (2012). Synthesis, structure and properties of poly (L-lactide-co-ε-caprolactone) statistical copolymers. *Journal of the mechanical behavior of biomedical materials*. 9: 100-112.
- Fiorito, S. (2008). *Carbon nanotubes: angels or demons?*. 1<sup>st</sup> Edition. Singapore: Pan Stanford Publishing. 1-13.
- Fong, H. (2007). Electrospun polymer, ceramic, carbon/graphite nanofibers and their application, in: H.S. Nalwa (Eds)., *Polymeric nanostructures and their applications*. California: American Scientific Publisher. Stevenson Ranch. 451-474.
- Fong, H., Chun, I. and Reneker, D. H. (1999). Beaded nanofibers formed during electrospinning. *Polymer*. 40(16): 4585-4592.
- Formhals, A. (1934). Process and apparatus for preparing artificial threads. U.S Patent No. 1975704
- Formhals, A. (1939). Method and apparatus for spinning. US patent 2160962.
- Frazer, L. (2004). New spin on an old fiber. *Environmental health perspectives*. 112(13): A754- 757.

- Friedrich, K., Fakirov, S. and Zhang, Z. (Eds). (2005) *Polymer Composites: From Nano- to Macro-Scale*, New York: Springer. 1-7
- Fujigaya, T. and Nakashima, N. (2015). Non-covalent polymer wrapping of carbon nanotubes and the role of wrapped polymers as functional dispersants. *Science and technology of advanced materials*. 16(2): 024802-024821.
- Gao, H., Kong, Y., Cui, D. and Ozkan, C. S. (2003). Spontaneous insertion of DNA oligonucleotides into carbon nanotubes. *Nano letters*. 3(4): 471-473.
- Garkhal, K., Verma, S., Jonnalagadda, S. and Kumar, N. (2007). Fast degradable poly (L-lactide-co- $\epsilon$ -caprolactone) microspheres for tissue engineering: Synthesis, characterization, and degradation behavior. *Journal of polymer science part A: Polymer chemistry*. 45(13): 2755-2764.
- Geng, Y., Liu, M. Y., Li, J., Shi, X. M. and Kim, J. K. (2008). Effects of surfactant treatment on mechanical and electrical properties of CNT/epoxy nanocomposites. *Composites part A: Applied science and manufacturing*. 39(12): 1876-1883.
- Gite, B. E. and Margaj, M. S. R. (2013). Carbon Fibre As A Recent Material Use In Construction. *Amrutvahini college of engineering, sangamner: 1-6*.
- Greenfeld, I. and Zussman, E. (2013). Polymer entanglement loss in extensional flow: Evidence from electrospun short nanofibers. *Journal of polymer science Part B: Polymer physics*. 51(18): 1377-1391.
- Gupta, P. and Wilkes, G. L. (2003). Some investigations on the fiber formation by utilizing a side-by-side bicomponent electrospinning approach. *Polymer*. 44(20): 6353-6359.
- Haggenmueller, R., Gommans, H. H., Rinzler, A. G., Fischer, J. E. and Winey, K. I. (2000). Aligned single-wall carbon nanotubes in composites by melt processing methods. *Chemical physics letters*. 330(3): 219-225.
- Haggenmueller, R., Zhou, W., Fischer, J. E. and Winey, K. I. (2003). Production and characterization of polymer nanocomposites with highly aligned single-walled carbon nanotubes. *Journal of nanoscience and nanotechnology*. 3(1-2): 105-110.
- Harris, P. J. F. (2001). Carbon nanotubes and related structures: new materials for the twenty-first century. United Kingdom: Cambridge university press.
- Heinrich, G., Klüppel, M. and Vilgis, T. A. (2002). Reinforcement of elastomers. *Current opinion in solid state and materials science*. 6(3): 195-203.

- Hiemenz, P. C. and R. Rajagopalan. (1997). *Principles of colloid and surface chemistry*. New York: Marcel Dekker. 3<sup>rd</sup> Edition. 25-45.
- Hohman, M. M., Shin, M., Rutledge, G. and Brenner, M. P. (2001). Electrospinning and electrically forced jets. I. Stability theory. *Physics of fluids*. 13(8): 2201-2220.
- Holmberg, K., Joënsen, B., Kronberg, B. and Lindman, B. (2002). *Surfactant and Polymers In Aqueous Solution*. West Sussex: John Wiley and Sons. 108-109.
- Hou, H and Ge, J. J. (2005). Electrospun polyacrylonitrile nanofibers containing a high concentration of well-aligned multiwalled carbon nanotubes. *Chemistry of materials*. 17(5): 967-973.
- Hsu, C. M. and Shivkumar, S. (2004). N, N-Dimethylformamide Additions to the Solution for the Electrospinning of Poly ( $\epsilon$ -caprolactone) Nanofibers. *Macromolecular materials and engineering*. 289(4): 334-340.
- Hu, C. and Hu, S. (2009). Carbon nanotube-based electrochemical sensors: principles and applications in biomedical systems. *Journal of sensors*. 9: 1-40.
- Hu, C. Y., Xu, Y. J., Duo, S. W., Zhang, R. F. and Li, M. S. (2009). Non-Covalent Functionalization of Carbon Nanotubes with Surfactants and Polymers. *Journal of the chinese chemical society*. 56(2): 234-239.
- Huang, W., Zou, T., Li, S., Jing, J., Xia, X. and Liu, X. (2013). Drug-loaded zein nanofibers prepared using a modified coaxial electrospinning process. *Journal of the american association of pharmaceutical scientists*. 14(2): 675-681.
- Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature*, 354(6348): 56-58.
- Inai, R., Kotaki, M. and Ramakrishna, S. (2005). Deformation behavior of electrospun poly (L-lactide-co- $\epsilon$ -caprolactone) nonwoven membranes under uniaxial tensile loading. *Journal of polymer science part B: polymer physics*. 43(22): 3205-3212.
- Jarusuwannapoom, T., Hongrojjanawiwat, W., Jitjaicham, S., Wannatong, L., Nithitanakul, M., Pattamaprom, C. and Supaphol, P. (2005). Effect of solvents on electro-spinnability of polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibers. *European polymer journal*. 41(3): 409-421.

- Jeong, S. I., Kim, B. S., Kang, S. W., Kwon, J. H., Lee, Y. M., Kim, S. H. and Kim, Y. H. (2004). In vivo biocompatibility and degradation behavior of elastic poly(l-lactide-co- $\epsilon$ -caprolactone) scaffolds. *Biomaterials*. 25(28): 5939-5946.
- Jin, Y., Yang, D., Kang, D. and Jiang, X. (2009). Fabrication of necklace-like structures via electrospinning. *Langmuir*. 26(2): 1186-1190.
- Jung, W. R., Choi, J. H., Lee, N., Shin, K., Moon, J. H. and Seo, Y. S. (2012). Reduced damage to carbon nanotubes during ultrasound-assisted dispersion as a result of supercritical-fluid treatment. *Carbon*. 50: 633-636.
- Kelly, A. and Tyson, A. W. (1965). Tensile properties of fibre-reinforced metals: copper/tungsten and copper/molybdenum. *Journal of the mechanics and physics of solids*. 13(6): 329-350.
- Kerwin, B. A. (2008). Polysorbates 20 and 80 used in the formulation of protein biotherapeutics: structure and degradation pathways. *Journal of pharmaceutical sciences*. 97(8): 2924-2935.
- Kessick, R., Fenn, J. and Tepper, G. (2004). The use of AC potentials in electro spraying and electrospinning processes. *Polymer*. 45(9): 2981-2984.
- Keulder, L. (2013). The preparation of polyolefin nanofibres by solution electrospinning. Doctoral dissertation, Stellenbosch: Stellenbosch University.
- Khare, R. and Bose, S. (2005). Carbon nanotube based composites-a review. *Journal of minerals & materials characterization & engineering*. 4(1): 31-46.
- Kieronski, E. A., Knock, K. K., Fallon, W. P., Walker, G. M. (2004). Mechanism of adhesive bonding of fibreglass composites with peel ply surface preparation, ASTM STP 1455: 78-91.
- Kizildag, N., Beceren, Y., Kazanci, M. and Cukul, D. (2012). Effect of needle diameter on diameter of electrospun silk fibroin nanofibers. In *RMUTP. Proceedings of the International Conference: Textiles & Fashion*: 3-4.
- Konya, Z., Vesselenyi, I., Niesz, K., Kukovecz, A., Demortier, A., Fonseca, A. and Kiricsi, I. (2002). Large scale production of short functionalized carbon nanotubes. *Chemical physics letters*. 360(5): 429-435.
- Kulshrestha, A. S. and Mahapatro, A. (2008). Polymers for Biomedical Applications. *ACS symposium series*. 977: 1-7.

- Lau, K. K., Bico, J., Teo, K. B., Chhowalla, M., Amaratunga, G. A., Milne, W. I., and Gleason, K. K. (2003). Superhydrophobic carbon nanotube forests. *Nano letters*. 3(12): 1701-1705.
- Leach, M. K., Feng, Z. Q., Tuck, S. J., and Corey, J. M. (2011). Electrospinning fundamentals: optimizing solution and apparatus parameters. *J vis exp*. 47 (e2494): 1-4.
- Lee, K. H., Kim, H. Y., Khil, M. S., Ra, Y. M. and Lee, D. R. (2003). Characterization of nano-structured poly ( $\epsilon$ -caprolactone) nonwoven mats via electrospinning. *Polymer*. 44(4): 1287-1294.
- Li, X., Thompson, J. D., Zhang, Y., Brady, C. I., Zou, G., Mack, N. H., Williams, D., Duque, J. G., Jia, Q. and Doorn, S. K. (2011). Efficient synthesis of tailored magnetic carbon nanotubes via a noncovalent chemical route. *Nanoscale*. 2011(3): 668–673.
- Li, Y. and Ishida, H. (2002). A differential scanning calorimetry study of the assembly of hexadecylamine molecules in the nanoscale confined space of silicate galleries. *Chemistry of materials*. 14(3): 1398-1404.
- Li, Z. Q., Lu, C. J., Xia, Z. P., Zhou, Y. and Luo, Z. (2007). X-ray diffraction patterns of graphite and turbostratic carbon. *Carbon*. 45(8): 1686-1695.
- Lim, J. Y., Liu, X., Vogler, E. A. and Donahue, H. J. (2004). Systematic variation in osteoblast adhesion and phenotype with substratum surface characteristics. *Journal of biomedical materials research part A*. 68(3): 504-512.
- Liu, C. X. and Choi, J. W. (2012). Improved dispersion of carbon nanotubes in polymers at high concentrations. *Nanomaterials*. 2(4): 329-347.
- Liu, M., Yang, Y., Zhu, T. and Liu, Z. (2007). A general approach to chemical modification of single-walled carbon nanotubes with peroxy organic acids and its application in polymer grafting. *The journal of physical chemistry C*. 111(6): 2379-2385.
- Liu, W., Huang, C. and Jin, X. (2014). Tailoring the grooved texture of electrospun polystyrene nanofibers by controlling the solvent system and relative humidity. *Nanoscale research letters*. 9(1): 1-10.
- Louchev, O. A., Sato, Y. and Kanda, H. (2001). Multiwall carbon nanotubes: Self-organization and inhibition of step-flow growth kinetics. *Journal of applied physics*. 89(6): 3438-3446.

- Luong-Van, E., Grøndahl, L., Chua, K. N., Leong, K. W., Nurcombe, V. and Cool, S. M. (2006). Controlled release of heparin from poly ( $\epsilon$ -caprolactone) electrospun fibers. *Biomaterials*. 27(9): 2042-2050.
- Ma, J. C. and Dougherty, D. A. (1997). The cation- $\pi$  interaction. *Chemical reviews*. 97(5): 1303-1324.
- Ma, P. C., Siddiqui, N. A., Marom, G. and Kim, J. K. (2010). Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review. *Composites part A: applied science and manufacturing*. 41(10): 1345-1367.
- MacDiarmid, A. G. (2001). Synthetic metals: a novel role for organic polymers. *Synthetic metals*. 125(1): 11-22.
- Makadia, H. K. and Siegel, S. J. (2011). Poly lactic-co-glycolic acid (PLGA) as biodegradable controlled drug delivery carrier. *Polymers*. 3(3): 1377-1397.
- Malhotra, S. K., Goda, K. and Sreekala, M. S. (2012). Part one Introduction to polymer composites. Polymer composite Volume 1, Macro and micro-nanocomposites. New Jersey: John Wileys & Sons Inc.
- Mamunya, Y. (2011). Carbon Nanotubes as Conductive Filler in Segregated Polymer Composites-Electrical Properties. INTECH Open Access Publisher. Croatia:Rijeka
- Marquis, D. M., Chivas-Joly, C. and Guillaume, É. (2011). Properties of nanofillers in polymer. In Dr. John Cuppoletti (Ed.) *Nanocomposites and Polymers with Analytical Methods* (pp 261-284). Croatia: INTECH Open Access Publisher.
- Martínez-Hernández, A. L., Velasco-Santos, C. and Castano, V. (2010). Carbon nanotubes composites: processing, grafting and mechanical and thermal properties. *Current nanoscience*. 6(1): 12-39.
- Matarredona, O., Rhoads, H., Li, Z., Harwell, J. H., Balzano, L. and Resasco, D. E. (2003). Dispersion of single-walled carbon nanotubes in aqueous solutions of the anionic surfactant NaDDBS. *The journal of physical chemistry B*. 107(48): 13357-13367.
- Matsumoto, H. and Tanioka, A. (2011). Functionality in electrospun nanofibrous membranes based on fiber's size, surface area, and molecular orientation. *Membranes*. 1(3): 249-264.

- Maurin, G., Stepanek, I., Bernier, P., Colomer, J. F., Nagy, J. B. and Henn, F. (2001). Segmented and opened multi-walled carbon nanotubes. *Carbon*. 39(8): 1273-1278.
- Megelski, S., Stephens, J. S., Chase, D. B. and Rabolt, J. F. (2002). Micro-and nanostructured surface morphology on electrospun polymer fibers. *Macromolecules*. 35(22): 8456-8466.
- Meng, Z. X., Zheng, W., Li, L. and Zheng, Y. F. (2010). Fabrication and characterization of three-dimensional nanofiber membrane of PCL-MWCNTs by electrospinning. *Materials science and engineering C*. 30: 1014-1021.
- Mirjalili, V., Ramachandramoorthy, R. and Hubert, P. (2014). Enhancement of fracture toughness of carbon fiber laminated composites using multi wall carbon nanotubes. *Carbon*. 79: 413-423.
- Moniruzzaman, M. and Winey, K. I. (2006). Polymer nanocomposites containing carbon nanotubes. *Macromolecules*. 39(16): 5194-5205.
- Moore, V. C., Strano, M. S., Haroz, E. H., Hauge, R. H., Smalley, R. E., Schmidt, J. and Talmon, Y. (2003). Individually suspended single-walled carbon nanotubes in various surfactants. *Nano letters*. 3(10): 1379-1382.
- Muherei, M. A. and Junin, R. (2007). Effect of electrolyte on synergism of anionic-nonionic surfactant mixture. *Journal of applied sciences*. 7: 1362-1371.
- Mylvaganam, K. and Zhang, L. C. (2007). Ballistic resistance capacity of carbon nanotubes. *Nanotechnology*. 18(47): 475701-475704.
- Nadler, M., Mahrholz, T., Riedel, U., Schilde, C. and Kwade, A. (2008). Preparation of colloidal carbon nanotube dispersions and their characterisation using a disc centrifuge. *Carbon*. 46(11): 1384-1392.
- Natarajan, L., New, J., Dasari, A., Yu, S. and Manan, M. A. (2014). Surface morphology of electrospun PLA fibers: mechanisms of pore formation. *RSC advances*. 4(83): 44082-44088.
- Njuguna, J., Vanli, O. A. and Liang, R. (2015). A Review of Spectral Methods for Dispersion Characterization of Carbon Nanotubes in Aqueous Suspensions. *Journal of spectroscopy*. 2015: 1-11
- Pawłowski, K. J., Belvin, H. L., Raney, D. L., Su, J., Harrison, J. S., and Siochi, E. J. (2003). Electrospinning of a micro-air vehicle wing skin. *Polymer*. 44: 1309-1314.

- Pichot, R., Watson, R. L. and Norton, I. T. (2013). Phospholipids at the interface: current trends and challenges. *International journal of molecular sciences*. 14(6): 11767-11794.
- Prabhakaran, M. P., Venugopal, J. R., Chyan, T. T., Hai, L. B., Chan, C. K., Lim, A. Y. and Ramakrishna, S. (2008). Electrospun biocomposite nanofibrous scaffolds for neural tissue engineering. *Tissue engineering Part A*. 14(11): 1787-1797.
- Qi, Y. Y., Tai, Z. X., Sun, D. F., Chen, J. T., Ma, H. B., Yan, X. B., Liu, B. and Xue, Q. J. (2013). Fabrication and characterization of poly (vinyl alcohol)/ graphene oxide nanofibrous biocomposite scaffolds. *Journal of applied polymer science*. 127: 1885-1894.
- Qian, D., Dickey, E. C., Andrews, R. and Rantell, T. (2000). Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites. *Applied physic letter*. 76: 2868-2870.
- Qin, X. H. and Wang, S. Y. (2008). Electrospun nanofibers from crosslinked poly (vinyl alcohol) and its filtration efficiency. *Journal of applied polymer science*. 109(2): 951-956.
- Ragab, T. and Basaran, C. (2009). Joule heating in single-walled carbon nanotubes. *Journal of applied physics*. 106(6): 063705-1 -063705-5.
- Ramakrishna, S. and Fujihara, K (2005). An introduction to electrospinning and nanofibers. Singapore: World Scientific Publishing. 135-137
- Rana, M. and Chandra, A. (2007). Filled and empty states of carbon nanotubes in water: Dependence on nanotube diameter, wall thickness and dispersion interactions. *Journal of chemical sciences*. 119(5): 367-376.
- Rastogi, R., Kaushal, R., Tripathi, S. K., Sharma, A. L., Kaur, I. and Bharadwaj, L. M. (2008). Comparative study of carbon nanotube dispersion using surfactants. *Journal of colloid and interface science*. 328(2): 421-428.
- Reichardt, C. (1990) Solvents and Solvent Effects in Organic Chemistry. In Thomas Welton (Ed). (pp 534).VCH: Weinheim (D) John Wiley & Sons.
- Reneker, D. H., Kataphinan, W., Theron, A., Zussman, E. and Yarin, A. L. (2002). Nanofiber garlands of polycaprolactone by electrospinning. *Polymer*. 43(25): 6785-6794.
- Rentsch, B., Bernhardt, R., Scharnweber, D., Schneiders, W., Rammelt, S. and Rentsch, C. (2012). Embroidered and surface coated polycaprolactone-co-

- lactide scaffolds: a potential graft for bone tissue engineering. *Biomatter*. 2(3): 158-165.
- Rentsch, C., Rentsch, B., Breier, A., Spekl, K., Jung, R., Manthey, S. and Biewener, A. (2010). Long-bone critical-size defects treated with tissue-engineered polycaprolactone-co-lactide scaffolds: A pilot study on rats. *Journal of biomedical materials research Part A*. 95(3): 964-972.
- Reznik, D., Olk, C. H., Neumann, D. A. and Copley, J. R. D. (1995). X-ray powder diffraction from carbon nanotubes and nanoparticles. *Physical review B*. 52(1): 116-124.
- Robertson, J. (2007). Growth of nanotubes for electronics. *Materials today*. 10(1): 36-43.
- Ryan, K. P., Cadek, M., Nicolosi, V., Blond, D., Ruether, M., and Armstrong, G. (2007). Carbon nanotubes for reinforcements of plastic? A case study with PVA. *Composite science technology*. 67: 1640-1649.
- S. Goyanes, G. R. Rubiolo, A. Salazar, A. Jimeno, M. A. Corcuera and I. Mondragon. (2007). Carboxylation treatment of multiwalled carbon nanotubes monitored by infrared and ultraviolet spectroscopies and scanning probe microscopy. *Diamond related materials*. 16(2): 412-417.
- Saba, N., Tahir, P. M. and Jawaid, M. (2014). A review on potentiality of nano filler/natural fiber filled polymer hybrid composites. *Polymers*. 6(8): 2247-2273.
- Saeed, K. and Park, S Y. (2007). Preparation and properties of multiwalled carbon nanotubes/polycaprolactone nanocomposites. *Journal of applied polymer science*. 104: 1957-1963.
- Sahay, R., Thavasi, V. and Ramakrishna, S. (2011). Design modifications in electrospinning setup for advanced applications. *Journal of Nanomaterials*, 2011: 1-17.
- Sanna, V., Roggio, A. M., Posadino, A. M., Cossu, A., Marceddu, S., Mariani, A. and Sechi, M. (2011). Novel docetaxel-loaded nanoparticles based on poly (lactide-co-caprolactone) and poly (lactide-co-glycolide-co-caprolactone) for prostate cancer treatment: formulation, characterization, and cytotoxicity studies. *Nanoscale research letters*. 6(1): 1-9.
- Saville, D. A. (1997). Electrohydrodynamics: the Taylor-Melcher leaky dielectric model. *Annual review of fluid mechanics*. 29(1): 27-64.

- Scarlet, R., Manea, L. R., Sandu, I., Martinova, L., Cramariuc, O. and Sandu, I. G. (2012). Study on the solubility of polyetherimide for nanostructural electrospinning. *Revista de chimie (Bucharest)*. 63: 688-692.
- Sengupta, J., Jana, A., Singh, N. P., Mitra, C. and Jacob, C. (2010). Site-selective synthesis of in situ Ni-filled multi-walled carbon nanotubes using Ni (salen) as a catalyst source. *Nanotechnology*. 21(41): 415605-415610.
- Shi, Y., Ren, L., Li, D., Gao, H. and Yang, B. (2013). Optimization conditions for single-walled carbon nanotubes dispersion. *Journal of surface engineered materials and advanced technology*. 3(1): 6-12.
- Shrivastava, N. K., Kar, P., Maiti, S. and Khatua, B. B. (2012). A facile route to develop electrical conductivity with minimum possible multi-wall carbon nanotube (MWCNT) loading in poly (methyl methacrylate)/MWCNTnanocomposites. *Polymer international*. 61(11): 1683-1692.
- Son, W. K., Youk, J. H., Lee, T. S and Park, W. H. (2004). Electrospinning of ultrafine cellulose acetate fibers: studies of a new solvent system and deacetylation of ultrafine cellulose acetate fibers. *Journal of polymer science; part B: Polymer physic*. 42(1): 5-11.
- Spitalsky, Z., Tasis, D., Papagelis, K. and Galiotis, C. (2010). Carbon nanotube-polymer composite: chemistry, processing, mechanical and electrical properties. *Progress in polymer science*. 35: 357-401.
- Strano, M. S., Moore, V. C., Miller, M. K., Allen, M. J., Haroz, E. H., Kittrell, C. and Smalley, R. E. (2003). The role of surfactant adsorption during ultrasonication in the dispersion of single-walled carbon nanotubes. *Journal of Nanoscience and Nanotechnology*. 3(1-2): 81-86.
- Sultana, N. (2012). Biodegradable Polymer-Based Scaffolds for Bone Tissue Engineering. Springer Science & Business Media. *Surfactant science and technology*, 3rd ed. Myers, Drew. Wiley-Interscience
- Szeteiová, K. (2010). Automotive materials: plastics in automotive markets today. Institute of Production Technologies, Machine Technologies and Materials, Faculty of Material Science and Technology in Trnava, Slovak University of Technology Bratislava.

- Szleifer, I. and Yerushalmi-Rozen, R. (2005). Polymers and carbon nanotubes-dimensionality, interactions and nanotechnology. *Polymer*. 46(19): 7803-7818.
- Tanvir, S. and Qiao, L. (2012). Surface tension of nanofluid-type fuels containing suspended nanomaterials. *Nanoscale research letters*. 7(1): 1-10.
- Taylor, G. (1964). Disintegration of water drops in an electric field. In Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences. The Royal Society. 280 (1382): 383-397.
- Tedeschi, A. M., D'Errico, G., Busi, E., Basosi, R. and Barone, V. (2002). Micellar aggregation of sulfonate surfactants studied by electron paramagnetic resonance of a cationic nitroxide: an experimental and computational approach. *Physical chemistry chemical physics*. 4(11): 2180-2188.
- Tetteh, G., Khan, A. S., Delaine-Smith, R. M., Reilly, G. C. and Rehman, I. U. (2014). Electrospun polyurethane/hydroxyapatite bioactive Scaffolds for bone tissue engineering: The role of solvent and hydroxyapatite particles. *Journal of the mechanical behavior of biomedical materials*. 39: 95-110.
- Thostenson, E. T., Ren, Z. and Chou, T. W. (2001). Advances in the science and technology of carbon nanotubes and their composites: a review. *Composites science and technology*. 61(13): 1899-1912.
- Troy, B. D. and Beringer, P. (2006). Remington: The science and practice of pharmacy. Philadelphia: Lippincott Williams &Wilkins Publisher, 21<sup>st</sup> Edition. 220-225
- Tummala, N. R. (2009). SDS surfactants on carbon nanotubes: aggregate morphology. *Acs nano*. 3(3): 595-602.
- Ulery, B. D., Nair, L. S. and Laurencin, C. T. (2011). Biomedical applications of biodegradable polymers. *Journal of polymer science part B: polymer physics*. 49(12): 832-864.
- Uyar, T. and Besenbacher, F. (2008). Electrospinning of uniform polystyrene fibers: The effect of solvent conductivity. *Polymer*. 49(24): 5336-5343.
- Vaisman, L., Marom, G. and Wagner, H. D. (2006). Dispersions of Surface-Modified Carbon Nanotubes in Water-Soluble and Water-Insoluble Polymers. *Advanced functional materials*. 16(3): 357-363.

- Vaisman, L., Wagner, H. D. and Marom, G. (2006). The role of surfactants in dispersion of carbon nanotubes. *Advances in colloid and interface science*. 128: 37-46.
- Vassalli, J. T. (2008). Development of electrospun synthetic bioabsorbable fibers for a novel bionanocomposite hernia repair material (Doctoral dissertation, University of Missouri--Columbia).
- Vigolo, B., Coulon, C., Maugey, M., Zakri, C. and Poulin, P. (2005). An experimental approach to the percolation of sticky nanotubes. *Science*. 309(5736): 920-923.
- Viguet-Carrin, S., Roux, J. P., Arlot, M. E., Merabet, Z., Leeming, D. J., Byrjalsen, I. and Bouxsein, M. L. (2006). Contribution of the advanced glycation end product pentosidine and of maturation of type I collagen to compressive biomechanical properties of human lumbar vertebrae. *Bone*. 39(5): 1073-1079.
- Vroman, I. and Tighzert, L. (2009). Biodegradable polymers. *Materials*. 2(2): 307-344.
- Wachsmuth, J. P. (2008). Multiple Independent Extrusion Heads for Fused Deposition Modeling (Doctoral dissertation, Virginia Polytechnic Institute and State University).
- Wang, S., Tang, L. A. L., Bao, Q., Lin, M., Deng, S., Goh, B. M. and Loh, K. P. (2009). Room-temperature synthesis of soluble carbon nanotubes by the sonication of graphene oxide nanosheets. *Journal of the american chemical society*. 131(46): 16832-16837.
- Wang, X., Ding, B., Sun, G., Wang, M. and Yu, J. (2013). Electro-spinning/netting: a strategy for the fabrication of three-dimensional polymer nano-fiber/nets. *Progress in materials science*. 58(8): 1173-1243.
- Wang, X., Zhuang, J., Peng, Q. and Li, Y. D. (2005) A general strategy for nanocrystal synthesis. *Nature*. 437: 121–124.
- Wang, Y., Wu, J. and Wei, F. (2003). A treatment method to give separated multi-walled carbon nanotubes with high purity, high crystallization and a large aspect ratio. *Carbon*. 41(15): 2939-2948.
- Wannatong, L., Sirivat, A. and Supaphol, P. (2004). Effects of solvents on electrospun polymeric fibers: preliminary study on polystyrene. *Polymer international*. 53(11): 1851-1859.

- Wei, Z., Zhang, Q., Wang, L., Peng, M., Wang, X. and Yang, J. (2012). The preparation and adsorption properties of electrospun aramid nanofibers. *Journal of polymer science part B: Polymer physics*. 50(20): 1414-1420.
- Weldon, C. B., Tsui, J. H., Shankarappa, S. A., Nguyen, V. T., Ma, M., Anderson, D. G. and Kohane, D. S. (2012). Electrospun drug-eluting sutures for local anesthesia. *Journal of controlled release*. 161(3): 903-909.
- Xie, W., Gao, Z., Pan, W-P., Hunter, D., Singh, A. and Vaia, R. (2001). Thermal degradation chemistry of alkyl quaternary ammonium montmorillonite. *Chemistry of material*. 13: 2979–2990.
- Xu, Y., Pehrsson, P. E., Chen, L., Zhang, R. and Zhao, W. (2007). Double-stranded DNA single-walled carbon nanotube hybrids for optical hydrogen peroxide and glucose sensing. *The journal of physical chemistry C*. 111(24): 8638-8643.
- Xu, Y., Wu, J., Wang, H., Li, H., Di, N., Song, L., Li, S., Li, D., Xiang, Y., Liu, W., Mo, X. M and Q. Zhou. (2013). Fabrication of electrospun poly (L-lactide-co- $\epsilon$ -caprolactone)/ collagen nanoyarn network as a novel, three-dimensional, macroporous, aligned scaffold for tendon tissue engineering, *Tissue engineering: Part C*. 19(12): 925-936.
- Yakobson, B. I. and Avouris, P. (2001). Mechanical properties of carbon nanotubes. In *Carbon nanotubes*. Springer Berlin Heidelberg. 287-327.
- Yakobson, B. I., Brabec, C. J. and Bernholc, J. (1996). Nanomechanics of carbon tubes: instabilities beyond linear response. *Physical review letters*, 76(14): 2511.
- Yarin, A. L., Kataphinan, W. and Reneker, D. H. (2005). Branching in electrospinning of nanofibers. *Journal of applied physics*. 98(6): 064501-1-064501-14.
- Yu, J., Grossiord, N., Koning, C. E. and Loos, J. (2007). Controlling the dispersion of multi-wall carbon nanotubes in aqueous surfactant solution. *Carbon*. 45(3): 618-623.
- Yuan, X., Zhang, Y., Dong, C. and Sheng, J. (2004). Morphology of ultrafine polysulfone fibers prepared by electrospinning. *Polymer international*. 53(11):1704–1710.

- Zeleny, J. (1914). The electrical; discharge from liquid points and a hydrostatic method of measuring the electric intensity at their surface. *Physical Review*. 3(2): 69-91.
- Zeleny, J. (1917). Instability of electrified liquid surfaces. *Physical Review*. 10 (1): 1-6.
- Zhang, C. and Liu, T. (2012). A review on hybridization modification of graphene and its polymer nanocomposites. *Chinese science bulletin*. 57(23): 3010-3021.
- Zhang, Z. and Li, T. (2010). Carbon nanotube initiated formation of carbon nanoscrolls. *Applied physics letters*. 97(8): 081909-081912.
- Zhao, D., Lei, Q., Qin, C. and Bai, X. (2006). Melt process and performance of multi-walled carbon nanotubes reinforced LDPE composites. *Pigment & resin technology*. 35(6): 341-345.
- Zong, X., Kim, K., Fang, D., Ran, S., Hsiao, B. S. and Chu, B. (2002). Structure and process relationship of electrospun bioabsorbable nanofiber membranes. *Polymer*. 43(16): 4403–4412.
- Zuo, Y. Y., Veldhuizen, R. A., Neumann, A. W., Petersen, N. O. and Possmayer, F. (2008). Current perspectives in pulmonary surfactant-inhibition, enhancement and evaluation. *Biochimica et Biophysica Acta (BBA)-Biomembranes*, 1778(10): 1947-1977.
- Zussman, E., Rittel, D. and Yarin, A. L. (2003). Failure modes of electrospun nanofibers. *Applied physics letters*. 82(22): 3958-3960.