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

FATIRAH BINTI FADIL

UNIVERSITI TEKNOLOGI MALAYSIA

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FATIRAH BINTI FADIL

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بِسْمِ ٱللهِ ٱلرَّحْمٰنِ ٱلرَّحِيمِ

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 greatful of having both of you in my life. There is no better friend than a sister. Love you guys.

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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 (L-lactide-co-ε-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 (L-lactid-co-ε-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 polisorbat 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 penyerakan bagi setiap molekul surfaktan yang dikaji menunjukkan bahawa molekul surfaktan bukan ionik Tween-80 mempunyai liputan penjerapan 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, kebolehgunaan 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.

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LIST OF ABBREVIATIONS

PLCL	-	Poly ε-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_2SO_4	-	Sulphuric acid
HNO_3	-	Nitric acid
H_2O_2	-	Hydrogen peroxide
$SOCl_2$	-	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

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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.

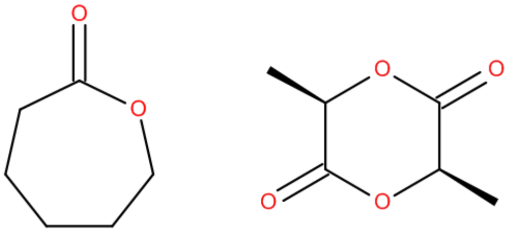
Electrospun polymer nanofibers were commonly produced from variety of polymers including, natural or synthetic polymer source, with or without filler, in melt or with solvent, on condition that the polymer solution was conductive enough to be drawn as fibrous form. Polymer based liquid precursor from 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

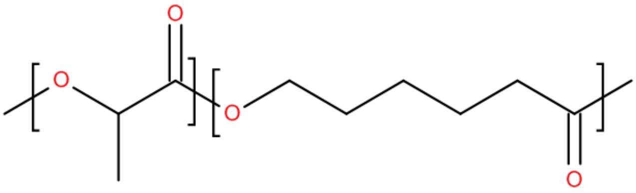
The synthetic biodegradable polymers offer an alternative over the non-degradable polymer materials which mostly used in the biomedical applications. The solution of biodegradable polymers can be processed into different solid forms through electrospinning technique. For instance, they can either be 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 biodegrable 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 (-ε-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- ε-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 ε-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 ε-caprolactone monomer unit, L-lactide monomer unit and PLCL copolymers.



ε- caprolactone monomer   L-lactide monomer



Poly ε- caprolactone co-lactide copolymer

Figure 1.1 Molecular structures of ε-caprolactone monomer, L-lactide monomer and PLCL copolymer

The advantage of PLCL properties over both poly carprolactone (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. ε-caprolactone-rich fragments on the other hand were hydrolyzed to produce ε-hydroxycaproic acid as shown in Figure 1.2. Both L-lactic acid and ε-hydroxycaproic acid will then metabolized and excreted from human body without any adverse toxicological effects (Baimark and Molly, 2004).

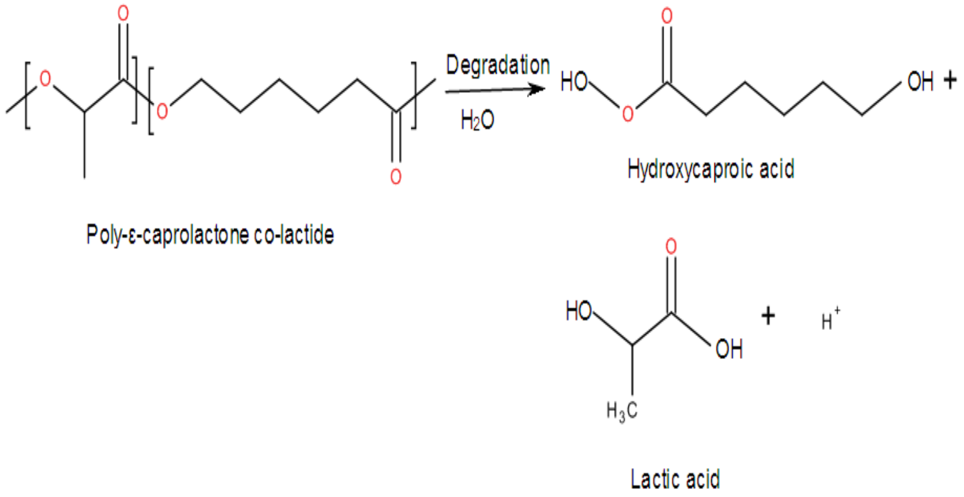


Figure 1.2 The degradation mechanism of PLCL by hydrolysis process

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 ε-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.

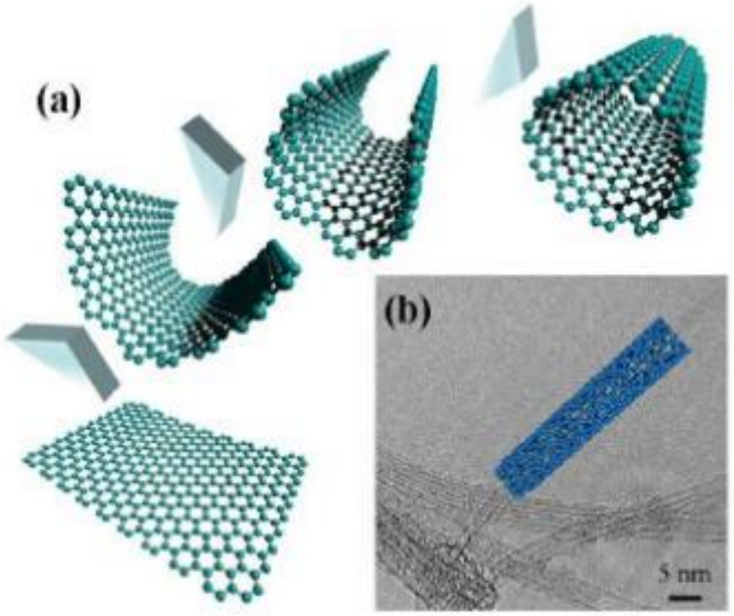


Figure 1.3 (a) Illustration model of cabon nanotubes by rolling sheets of graphene into a cylinder of nanometer size diameter (b) The structure of CNTs explored by high-resolution transmission electron microscopy. This figure is adapted from Endo (2010)

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 occurence, 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 (Angelikopoulus 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.

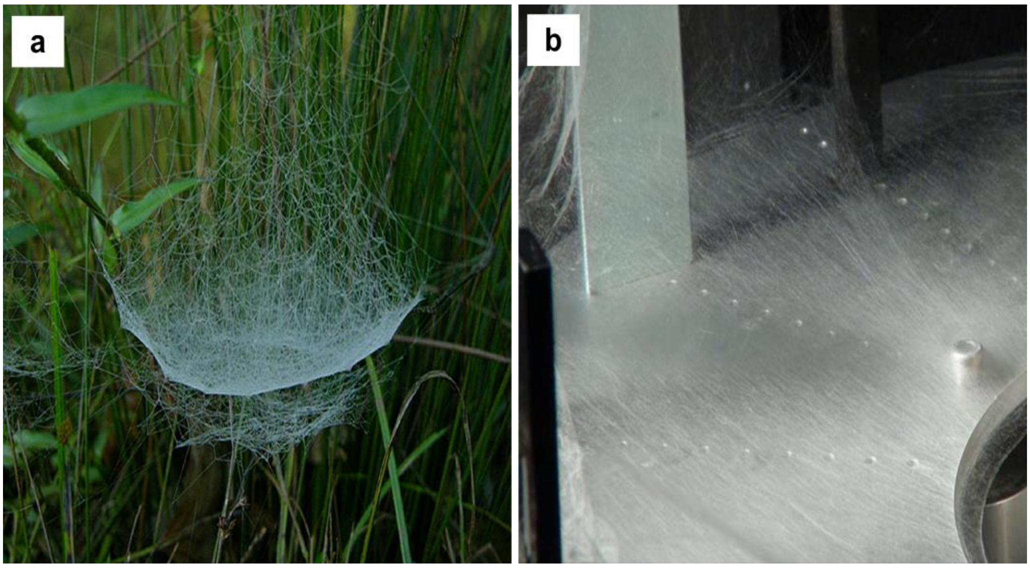


Figure 1.4 Photograph of (a) spider web (b) electrospun nanofiber web

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 π 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 cabon 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 identifiey 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 (L-lactide)-co- ε-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 alsoinvestigated 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 electospinning 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-ε-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.

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