PREPARATION AND CHARACTERIZATION OF NANOCELLULOSE THIN FILM FROM BROWN SEAWEED (*SARGASSUM* Sp.) REINFORCED X-CARBON NANOTUBE/POLYVYNIL ALCOHOL COMPOSITES

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I hereby declare that the material in this thesis is my own except for quotations, excerpts, equations, summaries and references, which have been duly acknowledged.

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ABSTRACT

Nowadays, celluloses not only can regenerate from nature but also by synthesizing with aid of the recent technology advancement. In this study, nanocellulose was extracted from brown seaweed *Sargassum* sp. via organosolvent and sulphuric acid treatments at specific ratio. It was found, the nanocellulose obtained are mostly crystalline with crystal index 77.1 %. In advance, varied amount of nanocellulose was added into polyvinyl alcohol (PVA) matrix with present of functionalized carbon nanotubes (*x*-CNT) to form a thin layer film via casting method. The thin films had an average thickness of 0.1 cm and then undergo characterization assessments. The results reveal that the optimized nanocellulose/PVA/*x*-CNT thin film possessed electrical properties around 2.68 x 10^{-07} S/m and tensile strength of 13.7 MPa with 62 % of elongation. Hence, nanocellulose/PVA/*x*-CNT thin film could be potentially utilized as a conductive material in electrical application in the future.

ABSTRAK

PENYEDIAAN DAN PENCIRIAN TERHADAP NANOSELULOSA FILEM NIPIS DARIPADA SARGASSUM SP. RUMPAI COKLAT GABUNGAN KARBON NANOTIUB YANG TELAH DIGUBAHSUAI

Pada hari ini, selulosa bukan sahaja ditemui pada alam semulajadi tetapi boleh juga dibentuk semula dengan teknologi terkini. Dalam kajian ini, pelarut organo dan asid sulfurik digunakan sebagai rawatan untuk mendapatkan nanoselulosa pada nisbah tertentu daripada Sargassum sp. rumpai laut warna coklat. Hasil ekstrak nanoselulosa ditemui memiliki ciri-ciri crystal dengan index sebanyak 77.1 %. Terlebih dahulu, nanoselulosa yang didapati tadi digabungkan bersama karbon nanotiub yang telah digubah suai (x-CNT) ke dalam matrik polivinil alcohol (PVA) untuk membentuk satu filem nipis. Filem nipis tersebut dibentuk menggunakan teknik casting dan mempunyai purata ketebalan sebanyak 0.1 cm dan seterusnya akan dibuat penilaian perincian. Data yang telah dikumpul membuktikan filem nipis yang telah dioptimumkan daripada filem nipis nanoselulosa/PVA/x-CNT memiliki ciri-ciri pengalir elektrik dengan nilai 2.68 x 10^{-07} S/m dan ciri-ciri tegangan dengan nilai 13.7 MPa pada pemanjangan filem yang hampir 62 % daripada kepanjangan asal filem tersebut. Oleh itu, filem nipis nanoselulosa/PVA/x-CNT boleh diguna pakai sebagai bahan semikonduktur dalam bidang elektrik pada masa akan datang.

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LIST OF ABBREVIATIONS/SYMBOLS

ACC	- Aqueous Counter Collision
Bis-GMA	- 2,2-Bis-[4-(Methacryloxypropoxy)-Phenyl]-Propane
BNC	- Bacterial Nanocellulose
CdS	- Polyaniline/Cadmium Sulfide
CdSe	- Cadmium Selenide
CdTe	- Cadmium Telluride
CH_3COOH	- Acetic Acid
CNCs	- Cellulose Nanocrystals
CNTs	- Carbon Nanotubes
Cu	- Cupper
DMF	- Dimethylformamide
DTG	- Derivative Thermal
E	- Elongation At Break
EIA	- Electronic Impedance Analysis
FESEM	- Field Emission Scanning Electron Microscopy
FOLEDs	- Organic Light Emitting Diodes
FTIR	- Functional Group By Using Fourier Transform Infrared Spectroscopy
H_2O_2	- Peroxide Acid
H_2S	- Hydrogen Sulphide
H_2SO_4	- Sulphuric Acid
HCl	- Hydrochloric Acid
l	- Thickness
M	- Moisture Content
Me_2Cd	- Dimethyl Cadmium

MEK	-	Methyl Ethyl Ketone
MWCNTs	-	Multiwall Carbon Nanotubes
NC	-	Nanocellulose
PAA	-	Peracetic Acid/Peroxyacetic Acid
PAN	-	Polyacrylonitrile
PE	-	Polyethylene
PET	-	Polyethylene Terephthalate
PMM	-	Poly(Methyl Metharcrylate)
PNs	-	Polymer Nanocomposites
POSS	-	Polyhedral Oligomeric Silsesquioxane
PVA	-	Polyvinyl Alcohol
PVAc	-	Polyvinyl Acetate
PVC	-	Polyvinyl Chloride
R	-	Residue Weight
Rb	-	Bulk Resistant
SC/AA	-	Sodium Chloride And Acetic Acid
SWCNTs	-	Single Wall Carbon Nanotubes
TEM	-	Transmission Electron Microscopy
TGA	-	Thermo Gravimetric Analysis
THF	-	Tetrahydrofuran
T_{max}	-	Major Degradation Peak Temperature
T_{on}	-	Onset Temperature
UTM	-	Tensile Properties By Using Universal Mechanical Testing Machine
UV	-	Ultraviolet
x-CNT	-	Modified Carbon Nanotube
ZnSe	-	Zinc Selenide

cm	-	Cetimeter
GPa	-	Giga Pascal
Hz	-	Hertz
kV	-	Kilo Voltage
min	-	Minute
mm	-	Milimeter
nm	-	Nanometer
rpm	-	Revolutions per minute
wt	-	Weight

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Polymer composite had been introduced into the world since early 1960s. Polymer nanocomposites are produced by incorporating materials on the nanometer scale (<100 nm) into a polymer matrix. These nanomaterials can be referred as nanofibril, nanocrystal or nanoparticles which having ability to improve stiffness, strength, toughness, thermal stability, barrier properties and flame retardant compared to the pure polymer matrix (Kamel, 2007: 547). The incorporation between polymer matrix and nanomaterial whether will improve the properties of matrix or creating a new ability of the composite either one or both.

There were precise types of material for every polymer matrix. While the properties of composites can directly affected by the filler volume fraction, the aspect ratio, alignment in the composite, and other geometric considerations (Mittal, 2010: 1). For an example, multiwall carbon nanotubes can disperse easily in polyacrylonitrile (PAN) matrix. In order to compose PAN matrix, Pirlot *et al.* (2002: 2) had stated that PAN can only be dissolved in dimethylformamide, but it will coagulate faster when contact with water.

Besides that, the filler in the polymer composite can be organic or inorganic materials. Cellulose is an example of organic material which is renewable sources. Cellulose can be derived to be nanomaterials that had played a major role in research and development of biocomposite technology by determining the properties and characteristic of the cellulose at the nano scale. Furthermore, cellulose is composed of repeating units of β-1,4 glucose by glycosidic linkage while nanocellulose have a nano scale dimension. As a result, the production and utility of nano scale cellulose fibres in polymer show a high strength and stiffness combined with low weight, biodegradability and renewability.

nanocellulose have a nano scale dimension. As a result, the production and utility of nano scale cellulose fibres in polymer show a high strength and stiffness combined with low weight, biodegradability and renewability.

The interesting characteristics and performance of cellulose-fibre-reinforced polymer composite such as low density, non abrasive, combustible, nontoxic, low cost, and biodegradable properties make it received much attention in a research field to prepare a various type of composites (Kalia *et al.*, 2009). Based on previous research, Legnani *et al.* (2008) has reported their work on nanocomposite substrates based on bacterial cellulose which is produced by Gram-negative, acetic acid bacteria Gluconacetobacter xylinus and Boehmite-siloxane systems were used as substrates for fabrication of flexible Organic Light Emitting Diodes (FOLEDs). They have claimed that the FOLEDs have a great improvement on the optical transmittance in the visible range. This showed that the cellulose also can incorporate with other material to generate conductivity.

On the other hand, this study is emphasizing on the incorporation of functionalized carbon nanotubes and nanocellulose. Carbon nanotubes (CNT) are tubular structures that are typically in nanometre diameter and many micrometres in length. This unique structure endowed CNT with various superior properties, for example, low density, very high stability, an outstanding tensile strength and resilience, good current carrying capacity and heat transmission ability, and extraordinary electronic behaviour (Collins and Avouris, 2000; Chu *et al.*, 2010: 1118). This idea of incorporation of CNT into nanocellulose is to make a new biodegradable product film that can conduct electricity. There are various techniques on how to synthesize the nanocomposite polymer such as drawing, template synthesis, phase separation, electro spinning and self-assembly. In this study, casting method will be used to make thin film composite. Where, a combination of polyvinyl alcohol matrix and nanocellulose reinforced with functionalized CNT were used. Subsequently, introduce conductivity property into polymer matrix.

1.2 Problem Statements

The demands of new end product in daily life are extremely challenging where the sources can be limited up to some point. Most of the industries are based on petroleum based polymer. As we know that, the petroleum oil can be derived into several stage of end user. Today, our daily products are mainly based from polymer material, such as, brusher, clothing, chair, car and other. Day after day, the product is improving, which will make more new product come out. At the same time, the sources will also be affected. But somehow, the sources of polymer based are not only from non-renewable feed stocks but also from renewable feed stock. The majority of polymers based are from non-renewable feed stock such as polyvinyl chloride, it has been widely used in many industries for various purposes like plastics and bottles. However, the petroleum feed stock is getting low so a new replacement from renewable feed stock is important to be practised.

Furthermore, non-renewable feed stock is often high cost compares to renewable feed stock as there are costs for processing a product. Since the economy is depending on petroleum oil and gas stock, there is no confirmation of fixed price for the raw materials. As a result, the availability of non-renewable feed stock will not last longer. As we know that, our petroleum oil prices are increasing from time to time. Emphasizing on renewable feed stock can be another solution to the matter above in order to produce a renewable new product.

Besides that, there is plenty of renewable feed stock sources such as plant and algal which can used to produce bio fuel or cellulose derivatives. But then, there only a few researches been conducted on brown seaweed field that specifying on cellulose composition. Since brown seaweed, especially *Sargassum* species was abundantly distributed on our beach coast area; with its rapid population that may cause a lot of problem. It is known that the *Sargassum* sp. is a non consumable product, which can be the choice to be highlighted to diversify its uses. The recent studies are also only revolving and focusing on the function of brown seaweed as a filtration unit; the research to utilize *Sargassum* sp. in this unprecedented field will venture into a new class of study to improve its usability.

1.3 Significance of Study

Cellulose from renewable feed stock could be a replacement for petroleum feed stock. There are plenty of researchers on the application of cellulose in our daily life product. Some of the research is still ongoing and some of it had already produced variety of products. Most of the researcher focused on cellulose from high level plant sources such big tree. There is limited study on acquiring cellulose from low level plants; while these vegetations are also proved to have cellulose content despite of its small amount, for example seaweed. Seaweed may contain low cellulose composition compared to high plant but they are in abundant population, and grow rapidly. Hence the amount of the cellulose to be extracted is adjustable.

In general, *Sargassum* sp. is one of brown seaweed family that has the ability of growing fast which make it abundantly available. Since the *Sargassum* sp. are non primary food sources for human being, making it a primary reason to be selected in this study. Furthermore, *Sargassum* sp. is abundantly found in Sabah area especially at Semporna district. Cellulose from *Sargassum* sp. can be used as a replacement material in many applications. In addition, using seaweed as raw material will contribute in significant cost savings of product.

Furthermore, the research on cellulose from *Sargassum* sp. can contribute to enhance knowledge on cellulose composition from brown seaweed family. A suitable method can be created in order to get cellulose from *Sargassum* sp., in which other method of extracting will be tested in this study. Moreover, cellulose can also be used in electric field with the help from reinforcement with metal. Thus, this study can be conducted to determine the ability of nanocellulose to act as a filler to gain mechanical properties and with the present of the x-CNT to possess the ability to conduct electricity in the film. So, alternative biodegradable film that is electric conductive can be presented in our electronic field which can be more preferable later on. Based on the literature, the research on the distribution of cellulose in electronic field was actually been initiated, but the source of the cellulose are from different green vegetation. Therefore the study of utilizing cellulose from brown seaweed *Sargassum* sp. was conducted with reinforcement of x-CNT to further enhance the nanocomposite polymer film with several physical and chemical attributes.

1.4 Objectives of Study

This study embarks on the following objectives:

i. To extract nanocellulose from brown seaweed *Sargassum* sp.

ii. To prepare and optimize fine thin film from the combination of nanocellulose and polyvinyl alcohol (PVA) matrix.

iii. To demonstrate the suitable ratio of combination of nanocellulose/PVA and functionalized CNT (*x*-CNT), will give a composite with good mechanical strength and conductive.

1.5 Scope of Study

The scope consists of three steps of preparation of thin film composite. Namely, the preparation of nanocellulose, optimizing the best thin film of nanocellulose/polyvinyl alcohol and synthesizing of nanocellulose film reinforced with x-CNT. The sample of this study is the brown seaweed *Sargassum* sp. which supplied from Semporna, Sabah. In the previous research on cellulose, it was stated that the best way to get cellulose is via organosolvent method. Therefore, in this study, the method was focused on using organosolvent which is the combination of two chemicals; acetic acid and hydrogen peroxide; also known as peroxyacetic acid. Peroxyacetic acid is a well-known delignification and bleaching agent. Cellulose will undergo acid hydrolysis as a final step to get nanocellulose.

The x-CNT will be added into nanocellulose/PVA polymer via casting method. Finally, the nanocellulose/PVA/*x*-CNT film will be characterized in term of morphology using Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM); thermal properties by using Thermo gravimetric analysis (TGA); crystallinity size via X-Ray diffraction (XRD); tensile properties by using Universal Mechanical Testing Machine (UTM); functional group by using Fourier Transform Infrared Spectroscopy (FTIR); conductivity test via electronic impedance analysis (EIA). The information will be used to redesign and optimized the nanocellulose composite film.