SYNTHESIS AND CHARACTERIZATION OF POLYVINYL ALCOHOL/CERIUM (III) ACETATE NANOFIBER COMPOSITES OF VARIOUS RATIO OF [OH^-]: [Ce^{3+}]

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Thesis submitted in fulfillment of the requirements
for the award of the degree of
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SUPERVISORS' DECLARATION

I hereby declare that I have checked the thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Applied Science (Honor) Material Technology.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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DEDICATION

I want to dedicate my dissertation work to my parents. Thank you my lovely parents, Andrew Balasan Siang and Julia Ujut for the moral support and reprimandations during the course of this thesis. My forgetfulness and slacky attitude are always remedied by my parent advices.

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LIST OF SYMBOLS

~	-	approximately
%	-	percent
^{o}C	-	degree celcius
Å	-	angstrom (10^{-10})
g	-	gram
h	-	hour
t	-	time
ml	-	milliliter
cm	-	centimeter
nm	-	nanometer

LIST OF ABBREVIATIONS

MW	-	Molecular weight
TGA	-	Thermogravimetric analysis
PVA	-	Polyvinyl alcohol
FESEM	-	Field Emmision Scanning Electron Microscopy
DSC	-	Differential Scanning Calorimetry
TMO	-	Transition Metal Oxides
EDX	-	Energy Dispersive X-Ray
0D	-	Zero-dimensional
1D	-	One-dimensional
2D	-	Two-dimensional
3D	-	Three-dimensional
CVD	-	Chemical Vapor Deposition
FIST	-	Faculty of Industrial Science and Technology
Ce(III)Ac	-	Cerium (III) Acetate

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ABSTRACT

This research describes the synthesis and characterization of Polyvinyl Alcohol/Cerium (III) Acetate nanofibers by electrospinning using different molar ratios (PVA/Ce(III)Ac). The molecular weight of PVA used was MW 145,000 and Cerium (III) Acetate Hydrate at 99.9% purity. 11wt% of PVA solution with different molar ratio were prepared. The prepared solutions were molar ratios of PVA:Ce(III)Ac as 1:0, 1:1/3, 1:1/2, and 1:1. Viscosity results showed that increasing Ce(III)Ac ratio have decreased the viscosity of the prepared solutions. The pure solution was spun into nanofiber having good flexibility. Nanofiber having increasing ratio of Ce(III)Ac becomes less flexibility and more breakable. Observation under microscope reveals that the nanofibers of 1:0 were smooth, aligned, continuous and average diameter 550 ± 181 nm. Nanofibers with increasing ratio of Ce(III)Ac showed increasing beads, random allignment nanofibers, discontinuous and average diameter of 168 ± 54 nm, 216 ± 74 nm and 186 ± 47 nm. Thermal gravimetric analysis showed that nanofiber with increasing Ce(III)Ac at second stage experienced greater weight lost compared to the second stage of pure PVA. Pure PVA nanofiber has high thermal stability because onset temperature of second stage was 199°C whereas nanofibers of increasing rato of Ce(III)Ac were 160°C-181°C. Differential scanning calorimetry results of first heating cycle showed similar first melting point and cold crystallization at 32°C and 36°C respectively. For the second heating cycle showed that melting point had increased for recrystallization of all nanofiber compoites samples at around 223 ± 2°C but cold crystallization have changed for increasing Ce(III)Ac at 320 ± 24°C. The second melting point after cold crystallization occurs much later as for increasing Ce(III)Ac ratios.

ABSTRAK

Kajian ini menerangkan sintesis dan pencirian nanofibers Polyvinyl Alcohol / Cerium (III) Acetate oleh electrospinning menggunakan nisbah molar yang berbeza (PVA / Ce (III) Ac). Berat molekul PVA digunakan adalah MW 145,000 dan Cerium (III) Acetate Hydrate pada 99.9% ketulenan. 11wt% larutan PVA dengan nisbah molar yang berbeza telah disediakan. Larutan yang disediakan adalah dalam nisbah molar PVA: Ce (III) Ac sebagai 1: 0, 1: 1/3, 1: 1/2, dan 1: 1. Keputusan kelikatan menunjukkan bahawa peningkatan Ce (III) Ac telah mengurangkan kelikatan penyelesaian bersedia. Larutan tulen telah diputar ke dalam nanofiber mempunyai fleksibiliti yang baik. komposit Nanofiber mempunyai nisbah meningkat Ce (III) Ac menjadi kurang fleksibel dan lebih mudah pecah. Pemerhatian di bawah mikroskop mendedahkan bahawa nanofibers 1: 0 adalah licin, sejajar, berterusan dan diameter purata 550 ± 181 nm. Nanofibers dengan nisbah meningkat Ce (III) Ac menunjukkan pembentukan manik meningkat, susunan nanofibers rawak, diameter tidak berterusan dengan purata 168 ± 54 nm, 216 ± 74 nm dan 286 ± 47 nm. Analisa haba gravimetrik menunjukkan bahawa komposit nanofiber dengan peningkatan Ce (III) Ac pada peringkat kedua mengalami berat badan yang lebih besar hilang berbanding peringkat kedua PVA tulen. PVA tulen nanofiber mempunyai kestabilan haba yang tinggi kerana suhu peringkat kedua adalah 199°C manakala bagi nanofiber composite yang meningkat nisbah Ce (III) Ac adalah 160°C - 181°C. Keputusan imbasan calorimeter menunjukkan kitaran pemanasan pertama menunjukkan sama takat lebur pertama dan penghabluran sejuk pada 32°C dan 36°C masing-masing. Untuk kitaran pemanasan kedua menunjukkan bahawa titik lebur meningkat untuk penghabluran semula semua compoites nanofiber sampel pada kira-kira 223 ± 2°C tetapi penghabluran sejuk telah berubah untuk meningkatkan Ce (III) Ac pada 320 ± 24°C. Takat lebur kedua selepas penghabluran sejuk berlaku lebih kemudian sebagai untuk meningkatkan nisbah Ce (III) Ac.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF RESEARCH

Nanofibers and nanowires are synonymous with electrospinning. Electrospinning is a widely used technique to produce nanofibers for variety of applications including scaffold in tissue culture (Zulkifli, Shahitha, Yusuff, Hamidon, & Chahal, 2013), membranes in filtration separation (Desai et al., 2009), and nanowires of metal oxides (Vidyadharan, 2015) as materials for electrode in energy storage devices. It has the advantages of being the technique that offers simplicity and practicality of operation and handling of the equipment (Bhardwaj & Kundu, 2010).

A typical electrospinning involves ejection of a polymer solution, often containing other dissolved ingredients from a nozzle in an electric field. The trajectory travels across a set distance during which the solvent vaporises forming fibres that are collected on a rotating drum.

The main challenge facing the researchers has always been to obtain continuous nanofibres with uniform diameters and good reproducibility. Generally this can be achieved by controlling the electric field and the distance of trajectory and that the solution systems being spun having the optimum rheological properties that will allow continuous string formation instead of forming droplets (Haider, Haider, & Kang, 2015). It is apparent that the rheology of solutions is crucial where the knowledge and understanding of the solution properties is important in order to control reproducibility and quality.

The ability to sustain string formation depends on the viscoelasticity of the solution. Viscoelasticity of a polymer solution is dependent on the molecular weight and

concentration of the polymer solution. Since ensuring the process is environmental friendly, any new developments require that the solvent used is water which means a polymer has to be water soluble. Among the polymers that are commonly used in electrospinning include poly(vinyl acetate) (Khalf, Singarapu, & Madihally, 2015), poly(vinyl alcohol) (Paipitak, Pornpra, Mongkontalang, Techitdheer, & Pecharapa, 2011), polyamides (Tsou et al., 2013).

1.2 PROBLEM STATEMENT

Researchers particularly from FIST have been very active studying nanofibres spun by electrospinning for variety of purposes and applications. However practically all the studies reported characterization and properties of the nanofibres obtained either based on values reported by earlier researchers or by by trial and error. Specific studies focusing on the effect of molecular weight and concentration of polymers have rarely been reported. In previous studies, there have been not many manipulation on the parameter of number of moles for the polymer and salts. Particularly for effect of adding metal salts such as cerium.

Viscosity testing should be done to test these solution's viscosity. The obtained values of viscosity would help to correlate the role of cerium salts concentrations in these solution to their viscosity, and their viscosity to their continuous fiber formation morphologies in terms of density. The motivation to undertake this mini research project arises from the need to acquire further understanding on standard operating procedures of electrospinning technique and producing nanofibers conformed to the important varying parameters.

In particular, this research is to learn and better understand on the roles and influences of molecular weight and concentration of PVA that would allow control of reproducibility and quality in the production of nanofibers composites and eventual nanowires. Therefore, I have great interest in finding and determining whether the ratio of these component would affect the electrospinning process.

1.3 OBJECTIVES OF RESEARCH

This research focuses on synthesis and characterization of nanofibers using PVA and Ce(III)Ac

1. To study viscosity of solutions containing varying molar ratios of [OH^-] and [Ce^{3+}].
2. To study the electro-spinnability of the solutions and the effect of molar ratios.
3. To charecterize the thermal properties of PVA/Cerium(III) Acetate composite nanofibers
4. To obtain nanowires formed by calcination of the composite nanofibers

1.4 SCOPE OF STUDY

Below are the activities required to fulfil the objectives:

1) Preparation of the solutions of different molar ratios and measure viscosity properties using Brookfield DV-I Prime.
2) Electro spinning of the prepared solutions to produce continuous nanofiber.
4) Analyze using microscopy techniques of pure PVA and prepared molar ratios nanofibers using Optical Microscope, SEM, and FESEM
5) Thermal characterization of the nanofibers from ambient to 550°C using DSC and TGA.
6) Study calcination of nanofibers based on TGA profiles of pure PVA and Cerium(III) Acetate to optimize nanowires formation.
7) Analyze calcined nanowires using FESEM.

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