PREPARATION AND CHARACTERIZATION OF PALM OIL BASED POLYALKYD FILMS AND COMPOSITES WITH MULTI-WALLED CARBON NANOTUBES

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Thesis submitted in fulfilment of the requirements for the award of the degree of
Doctor of Philosophy in Chemical Engineering

Faculty of Chemical and Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

AUGUST 2015

ABSTRACT

In this research, polyalkyd resins were prepared from palm oil by using polycondensation reaction. A two-step method viz., alcoholysis and esterification was conducted to synthesize polyalkyd resins. Prior to alcoholysis, crude palm oil was subjected for dehydration process to increase its unsaturation. Different types of catalysts such as, sulphuric acid, para-toluene sulfonic acid, phosphoric acid, sodium hydrogen sulphate and potassium hydrogen sulphate were used for the dehydration. In alcoholysis process, the triglyceride-based dehydrated oil was reacted with glycerol to produce monoglyceride. The prepared monoglyceride was further brought into contact with acid anhydride to prepare polyalkyds. Response surface methodology was used to optimize the reaction parameters for esterification like reaction temperature, reaction time, catalyst concentration, acid anhydride to mono-glyceride ratio and agitation speed. The optimum condition was used to prepare various types of polyalkyds by using different types of acid anhydrides such as, maleic anhydride, succinic anhydride, phthalic anhydride, 3,4,5,6-tetrahydrophthalic anhydride and cis-1,2-cyclohexanedicarboxylic anhydride. A comparison was drawn among the resins prepared by using different types and percentages of acid anhydrides. The produced bioresins were characterized for physico-chemical properties such as, viscosity, density, iodine value, acid value, drying time, non-volatile materials content, specific gravity, colour, etc. The resins prepared with optimum reaction parameters were subjected for curing process by using methyl ethyl ketone peroxide and cobalt naphthanate. To enhance the resinous property, multi-walled carbon nanotubes (MWCNTs) were dispersed into the resin at different percentages of loading such as, 0.5, 1.0 and 1.5 wt.%. The loading was optimized based on the tensile strength of the film. Finally, in-situ polymerization with carbon nanotubes during esterification was performed by adding optimum percentage of loading. The films produced from different formulations were characterized by different testing such as, adhesion, chemical resistivity, thermogravimetric analysis, differential scanning calorimetry, field-emission scanning electron microscopy, x-ray diffraction analysis, contact-angle measurement, tensile testing, pencil hardness, gloss, etc. In addition, the curing kinetics of the resin was analysed to evaluate the kinetic parameters such as, reaction rate, activation energy and degree of conversion in terms of time and temperature. Result analyses through RSM revealed a desirability of 0.985 for the reaction time of 88.64 min. Moreover, 91.5% fractional conversion was achieved actually, which is close to the predicted value. Analysis revealed that 3,4,5,6-tetrahydophthalic anhydride-based resin showed improved resinous property than others due to high degree of crosslinking. It was also found that higher amount of aliphatic acid anhydrides are responsible for high degree of crosslinking density, whereas higher thermal stability was ensured by the inclusion of aromatic acid anhydride. Finally, incorporation of MWCNTs into the alkyd resin enhanced the overall film properties, which was further improved through in-situ reaction. The physical bonding and mechanical entanglement were the possible reason for showing improved properties, as revealed from the analysis.

ABSTRAK

Dalam penyelidikan ini, resin *polialkid* telah disediakan daripada minyak sawit dengan menggunakan tindak balas polikondensasi. Satu kaedah yang merangkumi dua langkah, alkoholisis dan pengesteran telah dijalankan untuk mensintesis resin *polialkid*. Sebelum alkoholisis, minyak sawit mentah telah menjalani proses pendehidratan untuk meningkatkan ketidaktepuannya. Pemangkin yang berbeza seperti asid sulfurik, para-toluena asid sulfonic, asid fosforik, natrium hidrogen sulfat dan kalium hidrogen sulfat telah digunakan untuk proses pendehidratan minyak sawit. Dalam proses alkoholisis, minyak berasaskan trigliserida yang terhidrat telah ditindak balaskan dengan gliserol untuk menghasilkan monogliserid. Monogliserid yang terhasil terus ditindak balaskan dengan asid anhidrida untuk menyediakan polialkids. Kaedah gerak balas permukaan digunakan untuk mengoptimumkan parameter tindak balas pengesteran seperti suhu, masa tindak balas, kepekatan pemangkin, nisbah asid anhidrida kepada mono-glyceride dan kelajuan pengacauan. Keadaan optima telah digunakan untuk menyediakan pelbagai jenis alkyds dengan menggunakan asid anhidrida seperti anhidrida maleic, anhidrida phthalic, anhidrida succinic, anhidrida 3,4,5,6 - tetrahydrophthalic dan cis - 1,2- cyclohexanedicarboxylic anhidrida. Perbandingan antara resin juga dilakukan dengan menggunakan jenis dan peratusan asid anhidrida yang berbeza. Bioresin yang terhasil telah menjalani ujian ciri fiziko – kimia seperti kelikatan, ketumpatan, nilai iodin, nilai asid, masa pengeringan, kandungan bahan-bahan yang tidak meruwap, graviti tentu, warna, dan lain-lain. Resin disediakan daripada tindak balas parameter optimum akan menjalani proses pengawetan dengan menggunakan metil etil keton peroksida dan kobalt naphthanate. Untuk meningkatkan ciri resin, nanotiub karbon berbilang berdinding (MWCNTs) akan disebarkan ke dalam resin mengikut peratusan yang berbeza seperti 0.5, 1.0 dan 1.5 % berat. Kemasukan pengisi telah dioptimumkan bergantung pada kekuatan tegangan filem tersebut. Akhirnya, pempolimeran in-situ dengan karbon nanotiub melalui proses esterifikasi dilakukan dengan menambah bahan mengikut peratusan yang optimum. Filem-filem yang dihasilkan daripada formulasi yang berbeza telah dicirikan oleh ujian yang berbeza seperti lekatan, kerintangan kimia, analisis termogravimetri, pengkamiran pengimbasan kalorimeter, bidang - pelepasan imbasan elektron mikroskop, analisis x- ray pembelauan, pengukuran sentuhan sudut, ujian tegangan, kekerasan pensil, gloss dan lain-lain. Tambahan pula, kinetik pengawetan resin dianalisis untuk menilai parameter kinetik seperti kadar tindak balas, tenaga pengaktifan, tahap penukaran dari segi masa dan suhu. Keputusan analisis melalui RSM mendedahkan 0.985 didapati dengan tindak balas masa 88.64 min. Selain itu, 91.5 % penukaran yang dicapai menunjukkan data direkod berhampiran dengan nilai yang diramalkan. Analisis menunjukkan bahawa resin berasaskan anhidrida 3,4,5,6 - tetrahydophthalic menunjukkan peningkatan ciri resin daripada yang lain kerana darjah sambung-silang yang tinggi. Ia juga menunjukkan bahawa peningkatan kuantiti anhidrida alifatik bertanggungjawab bagi peningkatan darjah ketumpatan Sambung-silang, manakala kestabilan haba yang lebih tinggi dipastikan oleh kemasukan asid anhidrida aromatik. Akhir sekali, penggabungan MWCNTs ke dalam resin alkyd yang optimum dipertingkatkan ciri-ciri keseluruhan resin, dengan peningkatan ketara melalui tindak balas in-situ. Ikatan fizikal dan penyangkutan mekanikal adalah sebab yang mungkin untuk menunjukkan sifat-sifat baik, seperti yang dinyatakan daripada analisis.

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A	Pre-exponential factor or Arrhenius factor
α	Degree of cure
σ_t	Tensile strength (MPa)
β	Heating rate (^{0}C/min)
β_o	Unknown coefficient in RSM analysis
B_i	Unknown coefficient in RSM analysis
B_{ij}	Unknown coefficient in RSM analysis
d	Interplaner spacing
$d\alpha/dt$	Reaction rate
δ_{ij}	Unknown coefficient in RSM analysis
ε	Random error of experimentation
η^*	Complex viscosity
θ	Bragg scattering angle
E_a	Activation energy (J mol^{-1})
ΔH	Heat of fusion of sample
ΔH_m	Heat of fusion of 100% crystalline reference material
H_R	Total heat of reaction
ΔH_R	Heat of reaction
dH/dt	Normalized heat generated per unit time
ΔH_t	Released heat per unit of mass up to the time, t
I_{DSC}	Degree of crystallinity (%)
k	Rate constant
K	Scherer's constant
m	The order of reaction
n	The order of reaction
M_n	Number average molecular weight
M_w	Weight average molecular weight
R	Gas constant
T_g	Glass transition temperature (^{0}C)
T_m	Melting temperature (^{0}C)
T_c	Crystallization temperature (^{0}C)

T_{max}	Temperature of maximum reaction rate (^{0}C)
x	Reaction order
x_i	Matrix of the un-coded process variables
x_j	Matrix of the un-coded process variables
Y	Fractional conversion
Y_n	Fractional conversion
λ	X-ray wavelength
Z	Frequency factor

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
ASTM	American standard testing method
AV	Acid value
BPH	N-benzyl pyrazinium hexafluoroantimonate
CN	Carbon number
CFA	Cottonseed oil fatty amide
CNT	Carbon nano tube
CPEA	Cotton seed oil based polyester amide
DA	Dimer acid
DB	Double bond
DCC	Dicyclohexylcarbodiimide
DDA	Dicyandiamide
DEA	Diethanolamine
DES	Design expert software
DGEBA	Diglycidyl ether of bisphenol A
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetry
DOE	Design-of-experiment
DVB	Divinyl benzene
EB	Elongation at break
EMI	2-ethyl-4-methylimidazole
ESO	Epoxidized soybean oil
FE-SEM	Field-emission scanning electron microscopy
FTIR	Fourier transforms infrared spectroscopy
GF	Gel fraction
GPC	Gel permeation chromatography
HBPEA	Hyper branched polyester amide
HBPU	Hyper branched polyurethane
HELA	N, N-bis (2-hydroxyethyl) linseed oil fatty acid amide
HPLC	High performance liquid chromatography
^{1}H NMR	Proton Nuclear Magnetic Resonance

IPN	Interpenetrating polymer network
LCP	Liquid crystal polymer
LOFA	Linseed oil fatty acid
LPU	Linear polyurethane
MDI	Methylene diphenyl isocyanate
MEKP	Methyl ethyl ketone peroxide
MG	Monoglyceride
MHHPA	Methylhexa hydrophthalic anhydride
MPOB	Malaysian Palm Oil Board
MTO	Methyltrioxorhenium (VII)
MWCNT	Multi-walled carbon nano tube
NIPU	Non-isocyanate based polyurethane
NPGA	N-phthaloylglutamic acid
NV	Non-volatile content
PDI	Polydispersity index
PEA	Polyester amide
PA	Phthalic anhydride
PAA	Pyromellitimide acetic acid
PHBA	p-hydroxybenzoic acid
PMMA	Poly (methyl methacrylate)
PTSA	Para-toluene sulphonic acid
PU	Polyurethane
PUD	Polyurethane dispersions
PVA	Poly vinyl acid
rpm	Revolution per minute
RSM	Response surface methodology
SA	Succinic anhydride
SR	Swelling ratio
SEM	Scanning electron microscopy
SIN	Simultaneous interpenetrating network
SIPN	Sequential interpenetrating polymer networks
SWCNT	Single-walled carbon nano tube
TDI	Toluene diisocyanate

TGA	Thermogravimetric analysis
THF	Tetra hydro furan
TS	Tensile strength
TTS	Time–temperature superposition
VOC	Volatile organic compound
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Polymers as versatile materials are being used in various technical purposes and applications depending on their varieties of properties. A large range of functional differences and behaviours has made them to be used in a wide range of applications. They possess properties like, tough, flexible, brittle, elastomeric, plastic, fibrous, chemically-inert, non-degradable, biodegradable, crystalline, amorphous, linear, cross-linked, branched, hyper-branched, non-conductive, conductive, low-density, high-density, hard, soft, rigid, light-weight, low-molecular weight, high-molecular weight, thermally-stable, non-flammable, gas-permeable, thermoplastic, thermosetting, *etc.*

Generally, the monomer and its source of origin (aromatic or aliphatic, organic or inorganic, natural or synthetic) can decide the dominating properties of polymers. For example, aromatic originated polymers are found to be high temperature resistant due to the presence of structurally stable benzene ring (Guner et al., 2006). On the contrary, aliphatic polymers show relatively lower thermal stability. Except the origin or source of the polymers, some additives or fillers like, initiator, plasticizer, stabilizer, anti-oxidant, cross-linker (hardener), curing agent, co-monomer, compatibilizer, coupling agent, etc. also contribute and support specific roles, which are reflected on the properties showed by the individuals. The major portions of these polymers are made from organic sources and mainly consist of carbon, hydrogen and oxygen atoms, although some other inorganic atoms may be present. The endless numbers of options to create or modify the polymers have made these materials attractive to the researchers to investigate with.

Innovation of new materials from renewable resources, instead of using fossil feed stocks, is rising up day by day due to the concerns of low-cost materials, industrial pressures for new materials and environmental sustainability. Currently, polymers are being consumed so widely that their production has been reached 365 million tonnes in the year 2015, and hence petroleum-based polymer industries are growing up everywhere in the world. Petroleum resources are fixed and limited; there should be some other alternative resources to meet the uprising demand. Nowadays, polymers from renewable resources are attracting the researchers to work on those for advance level of researches. In addition, high price of synthetic polymers, their non-biodegradable nature, involvedness of significant amount of greenhouse gas emission, huge heat consumption during processing, scarcity of the raw materials, environmental legislations or restrictions, *etc.* are also important reasons for searching bio-based alternatives. The bio-based alternatives should be inherently biodegradable and annually renewable. Among the renewable bio-based resources, the triglyceride based vegetable oils (Luo et al., 2013; Tan et al., 2013; Das et al., 2009a; Altuna et al., 2010; Das et al., 2010), lignin-based plant biomasses (Domínguez et al., 2013; Xu et al., 2010) and proteins (Blomfeldt et al., 2011) are mentionable resources from which polymers can be produced.

The current focusing area includes only vegetable oil based biopolymers and their derivatives with major characteristics features. Vegetable oils and modified oils are being used as main raw materials for resin preparation. For example, linseed oil and tung oil were used for coating ingredients in oil paints and varnishes for several decades due to their fast-drying nature (Samadzadeh et al., 2011; Xiaoyin et al., 1997). Sometimes, modifications of non-drying oils by drying oils are found to be effective for the preparation of bio resin. For example, modified palm oil (non-drying oil) was produced by interesterification process with tung oil (drying oil) for the preparation of water-reducible acrylic-alkyd resin (Saravari et al., 2005). In other applications, vegetable oil was used with commercial resin for improved flexibility and solubility (Hintze-Bruning, 1992). Various polymerization reactions such as, cationic (Lu et al., 2010), condensation (Sharma et al., 2008), radical copolymerization (Saravari et al., 2005) etc. have been used to produce various types of polymers. Among the polymers, polyesters or polyalkyds (Blaise et al., 2012), polyester amides (Pramanik et al., 2013), epoxies (Kim et al., 2012; Sinadinović-Fišer et al., 2012) and polyurethanes (Das et al., 2013) are mentionable. Various types of oils such as, soybean oil (Tan et al., 2013), sunflower oil (Das et al., 2013), linseed oil (Pfister et al., 2010), castor oil (Sinadinović-Fišer et al., 2012), nahar seed oil (Dutta et al., 2005), rapeseed oil and jatropha oil (Patel et al., 2008) have been used for these purposes.

Vegetable oils are triglycerides, consisting of glycerol molecule connected with three similar or different types of saturated or unsaturated fatty acids. Depending on the unsaturated conditions or unsaturated fatty acids' percentages in the oil, the route of their modification on functional groups can be decided to produce a potential monomeric molecule (Bailey, 1996). The produced monomer can be subjected for suitable polymerisation process to formulate bio-polymers. The estimated amount of vegetable oils that are being utilized to prepare different kinds of coating materials is one million tonnes (Gunstone et al., 2007). Among the biopolymers, polyalkyds are being used efficiently in coating industries due to their short drying time, sufficient mechanical strength and acceptable chemical resistivity. There are several advantages of preparing polyalkyds from vegetable oils over traditional monomer based raw materials. Especially, the cost involved to produce plant based polyalkyds is lesser compared to the conventional polyalkyds. Moreover, it is environmental-friendly and associated with low-energy requirement during manufacturing. Furthermore, the polymerisation process is easy to control.

The current study deals with the reaction parameters involved in esterification process and their optimization through response surface methodology (RSM). The utilization of RSM was used earlier for different process optimization and found motivational for analysing process parameters (Islam et al., 2013; Uzoh et al., 2013). The design-of-experiment (DOE) was used for the characterization of the factors of esterification to obtain a targeted value of response. RSM was used for polyesterification process of palm oil in previous study (Uzoh et al., 2013). Reported results from the factor analyses were found to be significant for the optimization process. However, in the current study, five different types of catalysts were used prior to esterification to improve the unsaturation in the oil through dehydration process. After that, the best catalyst was chosen based on the highest unsaturation in the dehydrated oil and considered further for the esterification process.

Polyalkyds have been manufactured from different types of vegetable oils such as, palm oil, nahar seed oil, rapeseed oil, jatropha oil, *etc.* (Uzoh et al., 2013; Issam et al., 2009; Patel et al., 2008; Dutta et al., 2004). The properties of these polymers vary due to the constitutional composition of the fatty acids. Palm oil is non-drying oil and its unsaturation is lower compared to other drying oils like, tung oil, soybean oil and sunflower oil. Therefore, the drying time of palm oil based polyalkyds were found to be longer compared to drying oils-based one. Other properties like adhesion, hardness and chemical resistivity were also found to be moderate. Earlier, efforts were given to produce palm oil based polyalkyds, but the documented properties were not standard due to the presence of higher amount of saturated fatty acids in palm oil, nearly 50% (Issam et al., 2009). Especially, the drying time was found to be longer compared to that of drying oil-based polyalkyds. Thus due to non-drying property, palm oil was not explored extensively, and found discouraging for polymer synthesis. To solve this problem, palm oil based modified polyalkyds were prepared with drying oil (Ali et al., 2001). In a different study, due to poor mechanical property, modification or blending of palm oil based polyalkyds with commercial or petroleum based polyalkyds were studied by previous researchers (Saravari et al., 2005).

Except the constitutional variations during manufacturing, the curing parameters are also important to get reflected the desired properties in the formulated resins. For that, the curing kinetics is an important measure to reveal the nature of the curing process and other parameters involved. The widely used technique for the curing parameters determination is differential scanning calorimetry (DSC), established since long time before (Barton et al., 1985; Mijovic et al., 1984). Earlier, the curing process of different materials prepared form ester functional groups were analysed by DSC (Mazali et al., 2009; Jankovi et al., 2010; He et al., 2013; Sultania et al., 2010). In general, the dynamic and isothermal heating methods are found to be applied for curing kinetics analysis. The overall curing process can be depicted though single temperatures scan by analysing the reaction parameters with the help of curing isotherms (Kay et al., 1975). Earlier, the semi-drying oils such as, castor oil and soybean oil were used for curing kinetics analysis (Jovicic et al., 2008). A successful transformation of the dynamic DSC data through Ozawa kinetic model was found to be well-fitted, and the apparent degree of curing had a significant effect on the hardness of the polymeric films produced (Ozawa, 1970).

Recent studies on the incorporation of nano materials into thermosetting polymers are found to be effective to improve the thermo-mechanical properties of the matrix.

Earlier, various nano materials such as, silica, silver and carbon black were used for different purposes. For example, they were used to enhance the corrosion resistivity, anti-microbial activity, thermal and mechanical properties (Zhang et al., 2007a; Dolatzadeh et al., 2011; Dinha et al., 2014). Among them, carbon nano tubes (CNTs) are potential materials which can be used to improve the film properties of the polyalkyds. The mechanical behaviour of CNTs and their fabrication process with suitable applications were discussed elaborately in previous articles (Thostenson et al., 2001; Liu et al., 2004; Choi et al., 2004). The processing of nanotubes or nanoparticles incorporation into liquid resin or polymers was found to be a tedious job for a uniform and evenly dispersion, which was considering a major shortcoming of this material (Gibson et al., 2007). The agglomeration or cluster formation of nanotubes is the reason for uneven or poor dispersion of them into the polymer matrix. Thus the aim of this research work is to disperse CNTs by physical stirring with the help of magnetic rotor in the presence of minimum frequency of ultrasound and following in-situ reaction technique during esterification process.

1.2 PROBLEM STATEMENT

Commercially available polymers are derived from non-renewable resources, mostly from fossil fuels, whose reservations are reducing day by day due to high demand. These polymers are not environmental-friendly, associated with higher manufacturing cost, non-biodegradable, and hence encounter disposable problems. During their manufacturing process, huge amount of heat energy along with greenhouse gas emissions are involved, which are harmful for the world’s sustainability. All this issues derive the researchers to find new, renewable, environmental-friendly and bio-based resources for polymer synthesis.

Recently, polyalkyds from drying oils have drawn interests among the researchers for their excellent drying property, which is absent in non-drying based polyalkyds. Palm oil is non-drying oil and the reported drying properties are not up to the level of drying oil based products, but the production of palm oil is highest compared to other vegetable oils worldwide. This huge amount can be used for the polymer production for the economic benefit and sustainability. Moreover, the price of this oil is very less compared to others. Therefore, improvement of drying property is essential for palm oil based polyalkyds.

CHAPTER 1

INTRODUCTION

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CHAPTER 3

MATERIALS AND METHODS

3.1 INTRODUCTION

The raw materials, chemical reagents and various types of apparatus used in this research have been mentioned in this chapter. In addition, the experimental design and methods for process analysis have been summarized. The response surface methodology for the optimization of process parameters has been mentioned. The characterization techniques for oil, bioresins and nanocomposite films have also been briefed in this chapter according to various ASTM methods. The cure kinetics and related parameters has been analysed by following established methods and theory. The followed standard methods for various testing have been mentioned accordingly. A general overview of process flow diagram is presented in Figure 3.1, whereas experimental design is illustrated in Figure 3.2.

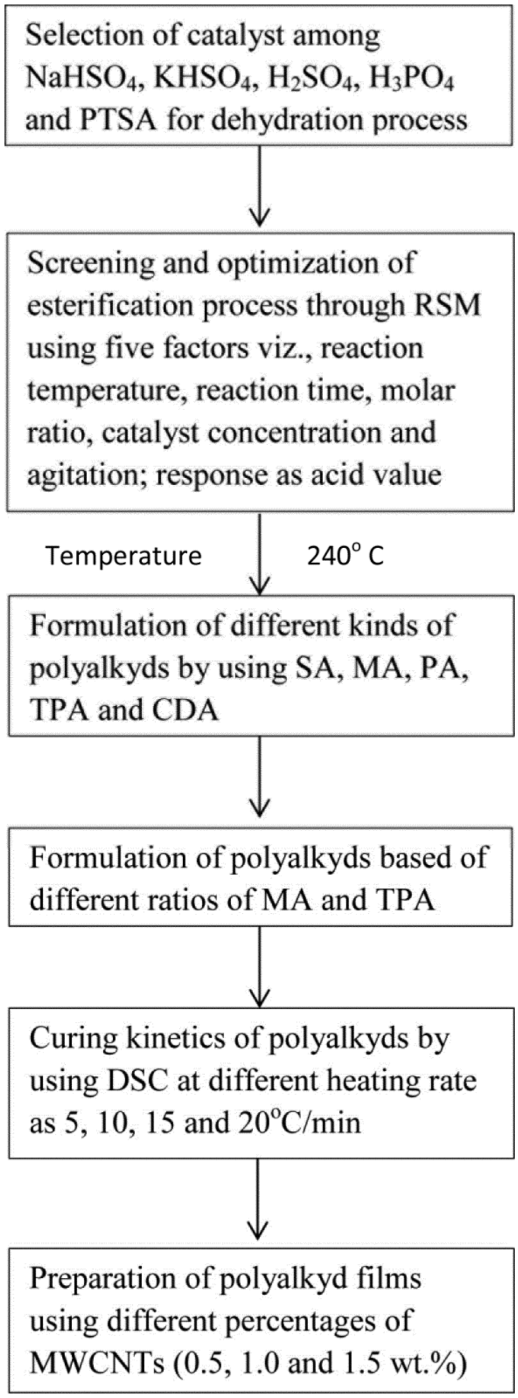

Figure 3.1: Process flow diagram.

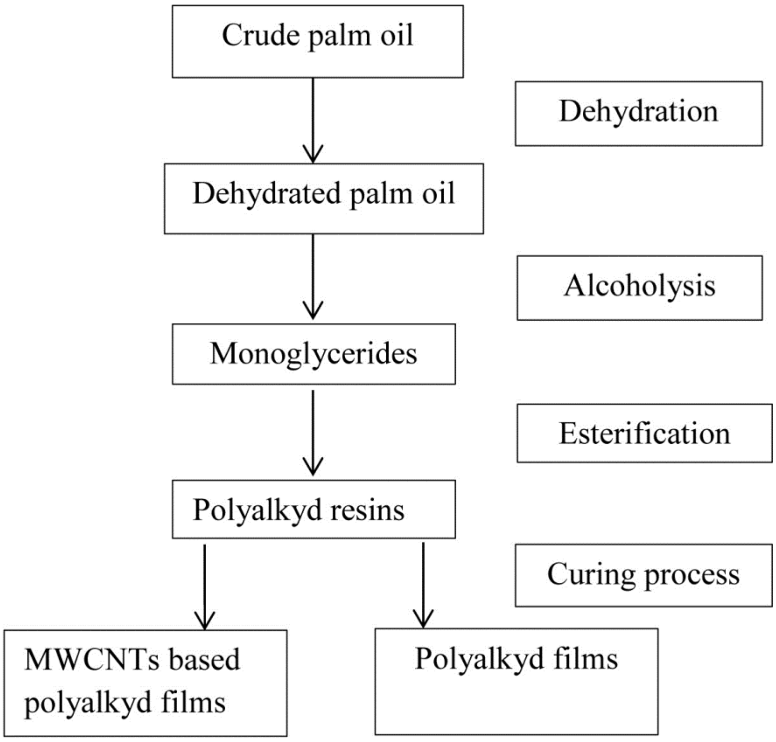

Figure 3.2: Experimental design of the research.

3.2 MATERIALS

The raw materials and chemicals used in this research are listed in the Table 3.1. The highly pure chemicals and analytical grade reagents were used in this research without any modification. Except the chemicals and reagents, various types of glass ware and lab apparatus have been used in this research. For example, four-necked round-bottom flask, ultrasound bath, pipette, burette, burette stand, water bath, magnetic heater with stirrer, soxhlet extractor, thermometer, condenser, dean-stark apparatus, iodination flask, beaker, Erlenmeyer flask, glass rod, Petri dish, etc. The type, molecular weight, density, chemical structure and formula with boiling points of different acid anhydrides are listed in Table 3.2.