

LA 1934 30 2009

SYNTHESIS OF ALKYD RESIN BASED ON BLEND OF NAHAR SEED OIL AND KARAWILA SEED OIL

This thesis was submitted to the Department of Chemical & Process Engineering at University of Moratuwa in partial fulfillment of the requirement for the degree of MSc.

LIBRARY
UNIVERSITY OF MORATUWA, SRI LANKA
MORATUWA



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
M.D.Y. Milani
www.lib.mrt.ac.lk

University of Moratuwa



93379

No Commercial Value

Department of Chemical & Process Engineering,
University of Moratuwa,
Sri Lanka.
April 2009.

93379

66 "09"

676 (543)

93379

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for any degree or diploma in any university and to the best of my knowledge and belief it does not contain any material previously published, written or orally communicated by another person except where due reference list made the test.

UOM Verified Signature

.....
Signature of the candidate (M.D.Y. Milani)



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

To the best of my knowledge above particulars are correct.

UOM Verified Signature

.....
Supervisor (Dr. S. Amarasinghe)

Abstract

Blend of seed oil; Mesua ferrea and Momodica charantia (50:50 w/w %) as a potential source of fatty oil in manufacturing air drying long oil alkyd resin was investigated. Monoglyceride process at a temperature of 240 °C was used in the synthesis process due to relatively low acid values of the oils. Alkyd resins were prepared using various proportions of fatty oil, pentaerythritol and phthalic anhydride. Physicochemical properties of oils and prepared alkyd were determined. Film properties of alkyd resins were examined. All films of the resins were shown reasonably low drying time. Water resistance, acid resistance and hardness of the films of the resins were improved with increase of molar percentage of OH groups from 12% to 24% above stoichiometric amount.



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

Acknowledgement

First I wish to express my deepest and sincere gratitude to my supervisors Dr. Shantha Amarasinghe and Dr. Jagath Premachandra for their invaluable advices, guidance, and encouragements extended through out this research project. I very much appreciate their constructive comments, which have been received during the preparation of this manuscript.

I also take this opportunity to thanks MSc Course Coordinator Dr. Shantha Walpolage who was arranged this opportunity for me.

A special word of thanks also goes to Dr. P.A.B. Prashantha for his guidance to success this research project.

I take this opportunity to convey my sincere thanks to Dr. Weerasooriya and his laboratory staff at ICI paints, Ratmalana for their willing help given to me for carrying out testing using their laboratory facilities.

Special word of thanks is for Mr. Mohamed Dilshan and Mechanical Department at University of Moratuwa for their support to fabricate the set up used for the synthesis process.

I wish to extend my special thanks to laboratory staff at University of Moratuwa and library staff at ITI, University of Moratuwa and University of Colombo for their support to success this work.

I also give my grateful thanks to my colleagues Ms.Umanga De Silva, Mr.K.Vitharana and Mr.L.A.S.Kodikara for their kind cooperation given to me through out this research project.

At last, I extend my gratitude for my parents, sisters and especially Mr. S.G. Thilakarathna who help me in all the way at the beginning till end of this research work.



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

Content

Abstract	i
Acknowledgment	ii
Content	iii
List of tables	vi
List of figures	vii
Chapter1	
Introduction	
1.1 Introduction	1
1.2 Objective and justification	3
1.3 Outline of thesis	4
Chapter2	
Diversity of plant Mesua ferrea and Memodica charantia	
2.1 Plant Mesua ferrea	5
2.2 Bio-diversity and medicinal properties of Mesua ferrea	5
2.3 Plant Momodica charantia	7
2.4 Bio-diversity and medicinal properties of Momodica charantia	7
2.5 Oil extraction method	8
2.5.1 Solvent extraction method	8
Chapter 3	
Alkyd resins	
3.1 Historical development of alkyd resins	10
3.2 Classification of alkyd resins	12
3.3 General reaction mechanism of alkyd resins	12
3.4 Specific reactions applied for the synthesis of alkyd resins	13
3.4.1 Direct esterification	14
3.4.2 Transesterification	15
3.4.3 Polyesters from anhydrides	17
3.4.4 Polyester from acid chlorides	17
3.5 Raw material used for alkyd synthesis	18
3.5.1 Polyhydric Alcohol	18
3.5.2 Polybasic Acids	20
3.5.3 Fatty acids and oils	21
3.5.3.1 Fatty acid composition	22
3.6 Synthetic procedure for oil modified alkyd resins	26
3.6.1 Fatty acid process	27
3.6.2 Monoglyceride process	28
3.6.3 Acidolysis process	30
3.6.4 Fatty acid/oil process	31

3.7 Modifications of alkyd resins	31
3.7.1 Modification with Nitrocellulose	32
3.7.2 Amino resin modification	32
3.7.3 Chlorinated rubber modification	32
3.7.4 Modification with phenolic resins	32
3.7.5 Modification with vinyl resins	33
3.7.6 Modification with polyisocyanate and epoxy resins	33
3.7.7 Silicon modification	33
3.7.8 Modification of alkyd with polyamides	33
3.7.9 Other modifications	34
3.8 Air drying alkyd resins	34
3.9 Drying mechanism of air drying alkyds	35
3.9.1 Air drying mechanism in conjugated double bonds	37
3.9.2 Air drying mechanism in non conjugated double bonds	39
3.10 Driers	40
3.11 Alkyd constant	41
3.12 Gel formation during polyesterification reaction	41

Chapter 4



University of Moratuwa, Sri Lanka.

Electronic Theses & Dissertations

www.lib.mrt.ac.lk

Recipes & Methodology for the synthesis of alkyd resins based on Nahar & Karawila seed oils

4.1 Synthesis of alkyd resins from a blend of Nahar and karawila seed oil	42
4.2 Determination of Physicochemical properties of seed oils and resulted alkyd resins	44
4.2.1 Acid value	44
4.2.2 Saponification value	44
4.2.3 Viscosity	45
4.2.4 Clarity	45
4.2.5 Colour	45
4.2.6 Non Volatile Matter content	45
4.2.7 Specific gravity	45
4.3 Testing of film properties	45
4.3.1 Testing of drying properties	46
4.3.2 set-to-touch drying time	46

4.3.3 Dry-to-touch drying time	46
4.3.4 Testing of Hardness of dried film	46
4.3.5 Testing flexibility of dried film by conical mandrel	47
4.3.6 Testing of solvent resistance properties	47
4.4 Calculation procedure of recipes	47
Chapter 5	
Results and Discussion	51
Chapter 6	
Conclusion and future work	
6.1 Conclusion	65
6.2 Future work	66
6.3 References	67



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

List of Tables

Table number	Topic	Page
Chapter 1		
Table 1.1	usages of fats and oil in surface coating	2
Table 1.2	Custom statistics of alkyd resins imported to Sri Lanka	3
Chapter 3		
Table 3.1	Physicochemical data of some fatty oils	23
Table 3.2	Unsaturated fatty acids in fatty oil & some common sources	24
Table 3.3	Fatty acid composition of some fatty oils	25
Table 3.4	Order of catalytic activity of catalyst	29
Chapter 4		
Table 4.1	Calculation procedure of recipe	49
Table 4.2	Recipe of each alkyd resin	50
Chapter 5		
Table 5.1	Physicochemical properties of Nahar & Karawila seed oil	51
Table 5.2	Experimental data obtained for resulted alkyd resins	60
Table 5.3	Physicochemical properties of resulted alkyd resins	60
Table 5.4	Film properties of resulted alkyd resins	62
Table 5.5	Solvent resistance properties of resulted alkyd resins	63

List of figures

Figure number	Topic	Page
Chapter3		
Figure 3.1	Reaction between ethylene glycol and phthalic anhydride	10
Figure 3.2	Reaction between phthalic anhydride and glycerol	11
Figure3.3	Reaction between triglyceride in fatty oil and glycerol	11
Figure 3.4	Generalized reaction mechanism of alkyd resins	13
Figure 3.5	Direct esterification between same molecules	14
Figure 3.6	Direct esterification between different molecules	14
Figure 3.7	Reaction between diester and polyol	16
Figure3.8	Polycondensation reaction via removal of polyol	16
Figure 3.9	Reaction between carboxylic acid and acetate ester	16
Figure 3.10	Reaction between carboxylic ester and glycol ester	16
Figure 3.11	Reaction between acid anhydride and polyol	17
Figure 3.12	Reaction between acid chloride and polyol	17
Figure 3.13	Reaction between pentaerythritol and formaldehyde	18
Figure 3.14	Chemical structures of polyol	19
Figure 3.15	Chemical structures of polybasic acids	21
Figure 3.16	Glycerol molecule	27
Figure 3.17	Reaction between fatty oil and pentaerythritol	28
Figure 3.18	Etherification of polyols	30
Figure 3.19	Reaction between isophthalic acid and triglyceride	30
Figure3.20	Oxygen attack to the conjugated double bonds	38
Figure3.21	Oxygen attack to the non conjugated double bonds	39

Chapter4		
Figure 4.1	Reaction between free fatty acid and pentaerythritol	47
Figure 4.2	Reaction between triglyceride and pentaerythritol	48
Chapter5		
Figure 5.1	Acid value & temperature Vs Time during oil upgrade process for NK12	53
Figure 5.2	Acid value & temperature Vs Time during oilupgrade process for NK18	53
Figure 5.3	Acid value & temperature Vs Time during oil upgrade process for NK24	54
Figure 5.4	Acid value & temperature Vs Time during oil upgrade process for NK30	54
Figure 5.5	Temperature profile for NK12	55
Figure 5.6	Temperature profile for NK18	56
Figure 5.7	Temperature profile for NK24	56
Figure 5.8	Temperature profile for NK30	57
Figure 5.9	Acid value & temperature Vs Time during polyesterification reaction for NK12	58
Figure 5.10	Acid value & temperature Vs Time during polyesterification reaction for NK18	58
Figure 5.11	Acid value & temperature Vs Time during polyesterification reaction for NK24	59
Figure 5.12	Acid value & temperature Vs Time during polyesterification reaction for NK30	59

Chapter 1

Introduction

1.1 Introduction

Paint has become universal after few people realized that it has a remarkable commodity. Paint in the can remains liquid almost indefinitely, but when spread on a surface it is transformed within few hours in to a hard, durable coating which protects and beautiful for many years.

Although no thicker than a few sheet of paper , paint coating are more durable than some metal at equal thickness and paint protects billion of dollars in wood and steel structures and metal goods from decay and corrosion.

Paint is defined in the ASTM designation D16-47 as a pigmented liquid composition which is converted to an opaque solid film after application as thin layer ¹.

The products of the paint industry are essential for the protection and decoration of the majority of the manufactured goods and architectural and industrial structures which characterize our complex material civilization. Paint coating are much diversified, but despite this wide variety they may be classified in to two general groups called architectural coatings and industrial coating².

Architectural coatings include varnishes, paints and enamels for both interior and exterior of dwelling. Architectural coating is used for protective and decorative purpose.

Industrial coatings are applied on a very wide range of materials including metal, wood, paper, textile, leather, glass and plastics. Industrial coatings are essential to the efficient functioning of our many industrial operations. Motors, radios, and other electrical apparatus produced each year require millions of miles of wire, paper, and cloth covered with insulating coatings. Steel automobile bodies without paint would rust by marine organisms and salt water from converting them in to unsafe, corroded surface. Beer in tin can was not practical until a special coating was developed to protect the beer from the can and the can from the beer. Bakers pan no longer need greasing after developing a special coating marketed as nonstick. Each of these applications illustrate that the importance of industrial coatings.

During the past one hundred years, the coating industry has employed large quantities of fats and oils. The information in Table 1.1 demonstrates that the coating industry used larger quantities of fats and oil all over the world in each decade until the 1950's³. From 1950's usage of oil in coating industry began to decline. The decline in fats and oil has largely been a result of the substitution of petroleum products over the vegetable oil.

Table 1.1 usages of fats and oil in surface coating

Year	Million pounds
1931-34	474
1940	652
1950	873
1960	716
1972	525
1987	293
1992	302
1997	345
2002	390
2007	440



University of Moratuwa, Sri Lanka.
 Electronic Theses & Dissertations
www.lib.mrt.ac.lk

Petroleum based products usage increased dramatically over the past decade, due to its consumer convenience in clean-up, short dry time and low odors. As coatings based on these products further penetrate the existing market, the usage of oil-based coating will continue to decline until 1992.

Since the price of petroleum-derived solvents have and continue to increase drastically and unpredictably, the main raw material of paint industry depends on the foreign petroleum creates an optimistic picture of its future. This will again switch on the developing of renewable raw material for paint industry. This indicates an opportunity for expansion the utilization of oil from plant derivatives as a one of the conservation of imported petroleum expected in future. Thus the oil used in the coating industry was again increased gradually after 1992 as indicated in Table 1.1. Resin derived from plant oil are renewable-resource materials that are grown on farmlands in all agricultural

countries and can survive independently from the increasing foreign petroleum demands and price fluctuations.

In current paint industry in Sri Lanka is also diversified with different types of coatings such as architectural, industrial and other special types. Statistical data obtained from Sri Lanka custom department about the amount of imported alkyd resins are also represented the gradual increase of alkyd resin usage in local paint industry as shown in Table 1.2.

Table 1.2 Custom statistics of alkyd resins imported to Sri Lanka

Year	Expenditure in million rupees	Quantity of alkyd resins in metric tone
1999	172.28	2442.12
2000	182.26	2512.44
2001	179.50	2276.90
2002	206.45	2316.25
2003	287.18	3092.13
2004	375.45	3313.16
2005	374.65	3023.52
2006	460.96	3471.81
2007	481.25	2987.44

Since that it is an immense important to develop an alkyd resin from suitable fatty oil source available locally to save millions of rupees within the country.

1.2 Objective and justification

Main objective of this research is to produce long oil, air drying alkyd resin with desired properties from natural fatty oil source together with polyol and Phthalic anhydride in different proportions. Experiments are carried out to find best recipe which results superior air drying alkyd resin with best film properties.

Scarcity & rising cost of petroleum products lead the development of alternate sources of raw materials for domestic & industrial uses. Renewable resources are now greatly being favored in preference to the petroleum products due to their bio degradable characteristics. Vast varieties of plants & herbs which contain a large amount of oil in their seeds are available in Sri Lanka & as well as all over the world. This oil seems to be viable alternative for petroleum resource. Oil of the traditional seeds like linseed, Soybean, coconut and Castor have been commercially used for the synthesis of different kinds of polymeric resins like alkyd, epoxies and polyester amides⁵. In addition to those widely used fatty oils tobacco seed oil⁶, Karawila (*Momodica charantia*) seed oil⁴ and Nahar (*Mesua ferrea*)⁵ seed oil are also viable sources to synthesize alkyd resins.

Nahar is a plant that produces high oil content seeds (~75w/w %), possessing both unsaturated and saturated fatty acids. Relatively low iodine value (89.26) of the Nahar seed oil indicates that it is a non drying oil and resulting alkyd is a non-drying one⁵. Whereas Karawila seed oil is a good drying oil with iodine value 116 and greatly differs from most of the other seed oils because of the presence of high amount of Eleosteric acid (63.4-67.9w/w %) ⁴. Due to the presence of high amount of Eleosteric acid in Karawila seed oil provides better drying properties to the resultant alkyd. During the present research study combination of Nahar seed oil and Karawila seed oil are used as natural fatty oil source together with polyol and Phthalic anhydride for the synthesize of long oil air drying alkyd resin since Nahar seed oil alone is resulting non-drying alkyd resin. Excess hydroxyl content is varied to find best recipe and reaction conditions which results optimum properties.

1.3 Outline of the Thesis

This thesis consists of four major areas of literature review, experimental work, results and discussion. In first chapter introduction is given to the research project. Second chapter discuss the diversity of plant *Mesua ferrea* and *Momodica charantia*. Third chapter focus on literature review on alkyd resins, reaction mechanism and reaction kinetics of alkyd preparation, drying mechanism of alkyd resins and gelation. Methodology of the experimental work and details of the selected recipes are given in fourth chapter. Fifth chapter discuss the experimental results such as physicochemical properties and film properties obtained from the research work. Sixth chapter conclude the obtained results from the research project and recommendations for future work.

Chapter 2

Diversity of plant *Mesua ferrea* and *Momodica charantia*

2.1 Plant *Mesua ferrea*

The plant *Mesua ferrea* is belonging to family Guttiferae/Clusiaceae. Different names are used in different languages and in Sri Lanka it is called as Diyana. In English it is known as Ceylon Iron Wood, in Tamil it is known as "Irul" and in Hindu as Nagkesar⁷. Scientific Classification of *Mesua ferrea*⁸ is as follows.

Kingdom: Plantae

Division: Magnoliophyta

Class: Mangoliopsida

Order: Malpighiales

Family: Clusiaceae

Subfamily: Kielmeyeroideae

Tribe: Calophylleae

Genus: *Mesua*

Species: *ferrea*



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

2.2 Bio-diversity and medicinal properties of *Mesua ferrea*

The plant *Mesua ferrea*, the national tree of Sri Lanka is native to tropical Sri Lanka., India, Southern Nepal, and Andaman Island. The national Ironwood forest is a 96 ha forest in Sri Lanka where *Mesua ferrea* trees dominates the vegetation. It is said that during King Dappula iv's period of 8th century AD, this forest was created and the remaining trees are the shoots of them. Hence it is considered the oldest manmade forest in Sri Lanka. This is the only ironwood forest in the dry zone with wet zone vegetation.

Nahar is a small to medium sized evergreen tree up to 13 m tall, often at the base with a trunk up to 90 cm in diameter. It has simple, narrow, oblong, dark green leaves 7-15 cm long with a whitish underside. The emerging young leaves are red to yellowish pink and drooping. The flowers are sessile, 1-3 together on a short peduncle in the axils of apical

leaves. Flower is 4.5 cm diameter with four white petals and a centre of numerous yellow stamens. Flowers are from April to June of the year^{7, 9}.

Fruits are depressed globose capsules, surrounded by enlarged sepals and bracts contain 1-4 seeds. Seeds are angular, testa crustaceous, smooth and chestnut brown in colour⁹.

The wood is very heavy and is used for railroad ties and as a structural timber. Its resin is slightly poisonous but many parts have medicinal properties. Though all the plant is used in various medicinal preparations main part is flowers. The flowers are used for acute bronchitis, pneumonia and problems like digestive, constipating and stomachic. Also use for condition like asthma, cough, fever and vomiting. Dried flowers are used for bleeding hemorrhoids and dysentery with mucus. Fresh flowers are useful remedy for itching, nausea, erysipelas, bleeding piles, excessive thirst and sweating. Seed oil is considered to be very useful in condition like scabies, wounds, vata disorders, skin diseases and rheumatism. Leaves are used an aphrodisiac for reproductive system. The root is used as antidote for snake poisons^{10, 11}.

Clinical studies of *Mesua ferrea* is found to be very useful in female patients suffering from vaginal monaliasis. The essential oil from the stamen showed that antifungal activity against *C. tropicalis*¹². Essential oil from the seed exhibited antiasthmatic activity and antifungal activity against a number of pathogenic fungi^{13, 14}. The volatile oil from flowers shows antibacterial, antifungal and anthelmintic activities as well as significant anti-inflammatory and styptic activities¹⁵.

Chemical constituent of stamen is mesuferrone-A, mesuferrone-B, mesuaferrol, mesuanic acid, β -anyrin, β -sitosterol. The seed and heartwood contain a number of xanthenes and coumarins. 4-alkyl and 4-phenyl 5,7- dihydroxycoumarins from *Mesua ferrea* blossoms shows the weak antiprotozol and potent antibacterial activity on resistant gram-positive strains.^{11, 12}.

Nahar is a plant that produce high oil content seeds (~75w/w %), possessing both unsaturated fatty acids (74.6w/w %) comprising mainly of oleic acids (52.3w/w %) and linoleic acid (22.3w/w %). 25.4w/w % saturated fatty acids comprising mainly of palmatic acid (15.9w/w %) and stearic acid (9.5w/w %) ⁵. Hence it can be utilized for the synthesis of polyester resins and other types of polymers like polyurethanes, polyester amides, etc. From the relatively low iodine value (89.26) of the Nahar seed oil indicates that resulting alkyd is a non-drying one⁵.

2.3 Plant *Momodica charantia*

The plant *Momodica charantia* belongs to family cucurbitacea. Different names are used in different languages some common names are bitter melon, bitter gourd and Chinese melon. In Sri Lanka it is called Karawila. The plant is tropical and cultivated in Africa, South America, Asia and Caribbean for the use of food and medicine. Scientific Classification of *Momodica charantia*¹⁶ is as follows.

Kingdom: Plantae
Division: Magnoliophyta
Class: Magnoliopsida
Order: Violales
Family: Cucurbitaceae
Genus: *Momodica*
Species: *charantia*

2.4 Bio-diversity and medicinal properties of *Momodica charantia*

Karawila plant is a climbing vine. It has life time over two years. A leaf has five lobes with uneven edges. Stem and leaves are hairy. Normally colour of the leaves is green but gradually turns in to yellow when fruits are ripen. A flower has five petals and yellow in colour. The fruits are ovoid in shape, 10-30 cm long and surface is uneven.

This plant has traditionally identified medicinal properties over several health problems in indigenous medicine. Karawila is very famous for the diabetes in many countries. Water extract of unripe fruits is used as a potent stimulator of insulin release from β -cells rich pancreatic islets in obese-hyperglycaemic mice and for gastric ailments including peptic ulcers⁴. In addition to that Karawila is used for hepatitis, diarrhea, malaria, fever, cough, rheumatism.

Karawila seed oil is greatly differ from most of the other seed oil due to the presence of Eleosteric acid. It is mainly consist of 1.6-1.9w/w % of palmatic acid, 0.12-0.16w/w% palmitoleic acid, 2.6-4w/w% oleic acid, 3.1-4.6w/w% linoleic acid, 0.54-.63w/w% linolenic acid, 21.7-26.5w/w% stearic acid and 63.4-67.9w/w% eleosteric acid⁴. Karawila seed oil has high potential to form dried films when a thin layer of oil is exposed to the air due to the presence of high amount of eleosteric acid. Hence it is a good drying oil and it provides better drying properties to the resultant alkyd.

2.5 Oil extraction methods

Oils can be extracted using a variety of methods. Currently the most popular method for extraction is solvent extraction but more efficient technologically advanced methods are being used for this purpose such as expeller pressed method, supercritical fluid technique, enzymatic extraction and osmotic shock method.

Expeller pressing is the method of extracting oil with a mechanical press rather than utilizing a chemical extraction process. There are no solvent residues in oil that has been expeller pressed and resulting in cleaner more pure oil, higher in natural color and flavor. An expeller press is a screw type machine, which presses oil seeds through a caged barrel-like cavity. This machine uses friction and continuous presses from the screw drives to move and compress the seed materials. The oil sieves through small openings that do not allow seed fiber solids to pass through it. Afterward, the pressed seeds are formed in to a hardened cake, which is removed from the machine. Pressure involved in expeller pressing creates heat in the range of 60-99 °C¹⁷.

The supercritical fluid /CO₂ extraction method, CO₂ is liquefied under pressure in a semi batch-flow extractor and heated to the point that it has the properties of both liquid and gas. This liquefied fluid then act as the solvent in extracting oil. Once the liquid depressurizes, the CO₂ returns to a gaseous state and only remaining is pure oil. The extraction rates increased with pressure, but decreased with temperature because of the variation in solvent density and resultant differences in oil solubility¹⁸.

Enzymatic Extraction uses enzymes to degrade the cell wall with water. Water is acting as a solvent and it makes fractionation of the oil much easier. The cost of this extraction process is estimated to be much greater than solvent extraction¹⁷.

Osmotic shock is a sudden reduction in osmotic pressure and ruptures the cell wall to extract the oil inside the cell. This method is commonly used to extract oil from algae¹⁷.

2.5.1 Solvent extraction method

Solvent extraction is the most popular method for oil extraction. Solvent extraction is achieved through the grinding of seed. The ground seed is then in the soxhlet apparatus and washed with a petroleum distillate. Most common chemical used is hexane, which release oil in the seed. The oil solvent blend is next heated to separate the distilled

hexane from the oil-solvent blend. The resultant mixture is placed in a rotary evaporator to remove the solvent completely¹⁷.

Thermodynamics play an important role in the principal of distillation in order for a liquid to be vaporized. Latent heat must be applied to this liquid until its temperature attains the point where its vapor pressure becomes equal to the surrounding atmospheric pressure. At this point the temperature will rise no further. When heat continuous to be applied, the liquid will take up this latent heat and vaporize at the appropriate rate. This is the boiling point under the prevailing pressure. When a vapor is converted back to liquid actually happening is a reduction and release of the latent heat.

When mutually insoluble compounds such as hexane and seed oil are present, the total pressure exerted by the mixed vapor then becomes the sum of the partial pressure exerted by each constituents present. This liquid mixture will boil when its temperature is raise to the point where the combined vapor pressure of its components becomes equal to the surrounding pressure.

At this temperature the mixture will boil and the hexane will vaporize in to the vapour as fast as its requirements of latent heat can be applied by external source. When this vapor mixture enters to the condenser, it is exposed to cool surface which again results in a transfer of latent heat of vapor mixture and converts the vapor back to its liquid state hexane¹⁸.



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

This hexane-oil mixture can be further separated by rotary-evaporator.

In the present research study Nahar seed was collected form Gampaha district and Karawila seed was collected from Vegetable Seed Centre-Gannoruwa. Oil was extracted using solvent extraction technique in soxhlet apparatus. Hexane was used as a solvent for the extraction. Residual hexane from the oil-hexane mixture was further removed using rotary evaporator and resultant oil was centrifuged to remove solid particles. Oil was oven dried until it achieved constant weight at 80°C to remove residual solvents.

Chapter 3

Alkyd resins

3.1 Historical development alkyd resins

Alkyd resins are condensation polymers of dibasic acids and dihydric alcohols. Molecular weights of alkyd resins are of the order of 1000-5000¹⁹. Alkyd is a word coined by Kienle in early 1927²⁰ and the name alkyd comes from its ingredients alcohol and acid¹⁹. The word "al" comes from alcohol and the word "cid" from acid and by euphony change "cid" became "kyd" and the word "alcid" became to "alkyd"²⁰. Alkyd resins provide improving drying potential and film forming properties for drying oil. An oil free resin can be prepared from ethylene glycol and phthalic anhydride as shown in Figure 3.1. It is a saturated polyester resin because the polymer chain is held together by a series of ester linkages and it is not aliphatic double bonds.

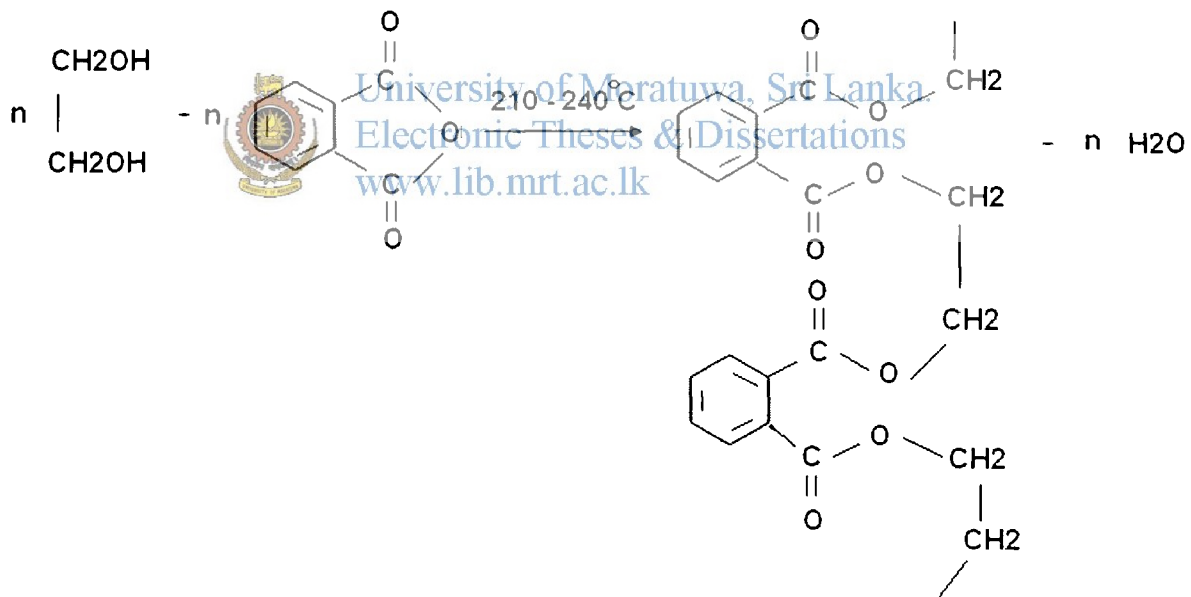


Figure 3.1: Reaction between ethylene glycol and phthalic anhydride

The first saturated polyester was synthesized at the beginning of this century in 1901 by Watson Smith²⁰. They were glyptal resin made from glycerol and phthalic anhydride as shown in figure 3.2. This resin had poor solubility and was hard and brittle.

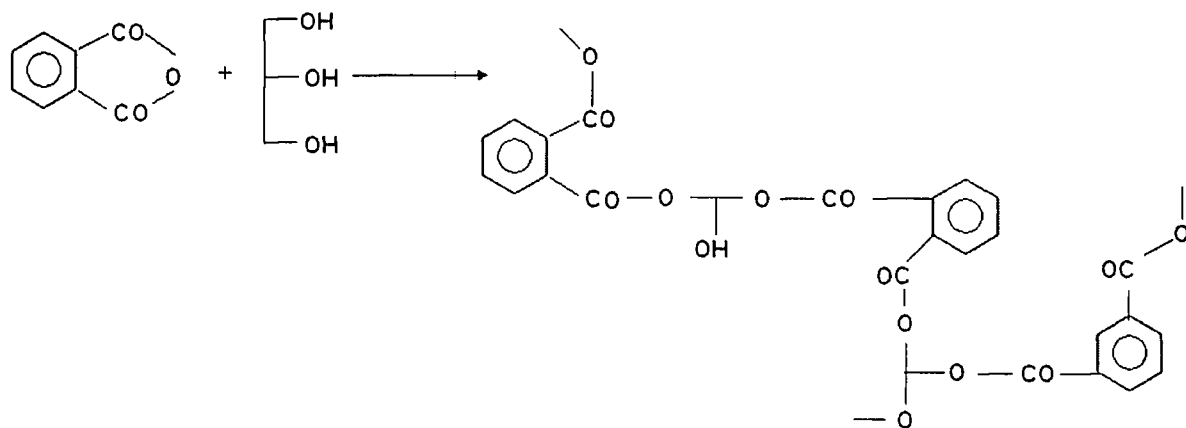


Figure 3.2: Reaction between phthalic anhydride and glycerol

Oil based alkyd resins can be prepared by reacting of monoglyceride prepared from oil with phthalic anhydride. The oil is converted to a monoglyceride by heating with glycerol before adding phthalic anhydride as shown in figure 3.3. During the monoglyceride process fatty acid moieties in the original oil are reacted with hydroxyl groups of glycerol and produced a mixture of monoglyceride, oil and glycerol.

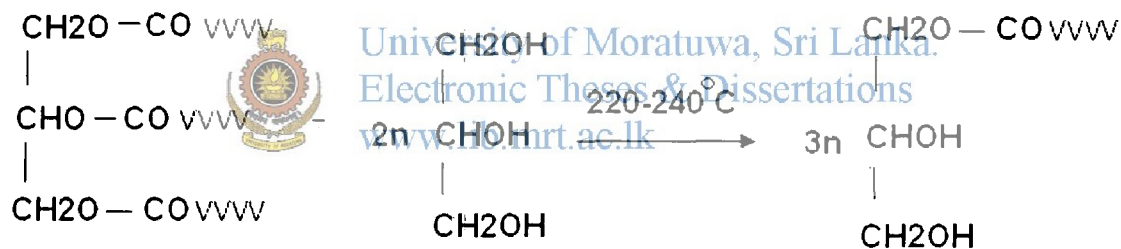


Figure 3.3: Reaction between triglyceride in fatty oil and glycerol

Possible geometry of polyester from the reaction between dibasic acid and dihydric alcohol are linear or ring structures²⁰. But when trihydric alcohol such as glycerol is used, same liner or ring structure is possible when two of the three hydroxyl groups are esterified only. Branch structure is produced during the esterification of third hydroxyl group. Branch structure can also be produced by using tetra functional polyol like pentaerythritol or hexafunctional polyol like sorbitol, manitol and dipentaerythritol.

Monobasic acid is used as a chain terminator to stop growth to achieve desired molecular weight of the resultant alkyd resin.

Drying oil or non drying oil can be used to prepare alkyd resins according to their end use. Non drying oils result plasticizing alkyds frequently used in stoving paints²⁰. Drying oils give drying alkyds which is drying faster than corresponding oil due to its high functionality. For example 58% oil length linseed oil glycerol phthalate alkyd contains about 2-10 fatty acid chains per average molecule, leads faster drying than linseed oil²⁰.

3.2 Classification of alkyd resins

Alkyds are classified into three groups according to its oil length which is expressed as a percentage. Oil length is the number of grams of oil used to prepare 100 grams of alkyd resin²⁰.

1. Short oil alkyds
2. Medium oil alkyds
3. Long oil alkyds

Below 45% oil is a short oil alkyd and 45-60% oil is a medium oil alkyd. Long oil alkyd contains above 60% oil. Long oil alkyds are soluble in aliphatic hydrocarbons where as short oil alkyds are soluble in aromatic hydrocarbons.

Properties of the alkyd resin depend on the polybasic acid and the polyhydric alcohol. Increasing the number of carbon atoms between the carboxyl groups in the acid or the hydroxyl groups in the alcohol leads to more flexible resins. Extent of the branching can be controlled by acid and alcohol functionality. Colour retention depends on the oil and oil length. Oil length of the alkyd resin controls solubility, cross linking potential during drying and compatibility with other resins.

3.3 General reaction mechanism of alkyd resins

Alkyds are classified as step-growth polymers²¹. Step-growth polymerization reactions of alkyd are proceeded via addition-elimination reaction at a carbonyl bond of carboxylic acid or carboxylic acid derivatives. Carbonyl carbon is electropositive due to the polarization of carbonyl carbon-oxygen double bond.

Nucleophile adds to this electropositive carbon atom at carbonyl group and form an intermediate structure. The intermediate structure is highly reactive since electron pair from the carbon-oxygen double bond has become localized on the oxygen atom. This intermediate structure can undergo either elimination of nucleophile to re-form the original reactant or elimination of constituent which binds to carbonyl carbon atom to form product or addition of a proton to form an ortho ester type of compounds.

Rate of the reaction and the product of the reaction depend on the monomer structure and the reaction medium. In the presence of electron-withdrawing groups at carbonyl group decrease the electron density at the carbonyl carbon atom. This can be facilitated the rate of attacking nucleophile. Also rate of the reaction can be facilitated by increasing the base strength or electron density of nucleophile. Catalyst and the steric effect of the reactant also affect the rate of the reaction.

In aromatic reactants, bulky, substitute in 2 and 6 position from the reactive site retards the rate of the reaction. In aliphatic reactants bulky substitute in alpha or beta carbon atom retards the reaction rate but bulky groups in 3 beta carbon atoms retards the rate of the reaction even more effectively than on alpha carbon atom²¹.

Generalized reaction mechanism can be represented as shown in figure 3.4.

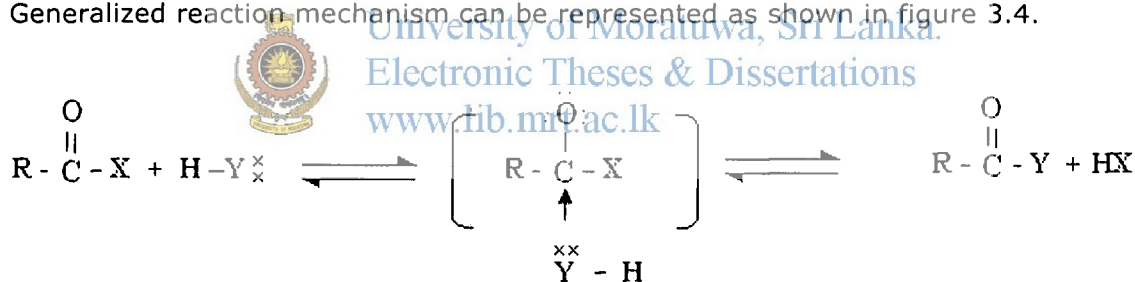


Figure 3.4: Generalized reaction mechanism of alkyd resins

In 1960 Bender suggest that substitute of X can be OH, OR¹, NH₂, NHR', CO, R or Cl. Y can be R'O⁻, R'OH, R'-NH₂ or R'COO⁻ and R or R' can be an alkyl or an aryl group²¹.

3.4 Specific reactions applied for the synthesis of alkyd resins

There are four main synthetic routes for the preparation of alkyd resins based on general reaction mechanism specified in the section 3.3²¹.

- 1) Direct esterification of carbonyl group with alcoholic hydroxyl group.
- 2) Transesterification such as alcoholysis, acidolysis and esterolysis.
- 3) Reaction of polyfunctional hydroxyl compounds with acid anhydrides.
- 4) Reaction of acid chloride with glycol or bisphenols.

3.4.1 Direct esterification

Direct esterification reaction is undergone between carboxyl and the hydroxyl groups contained either in same molecule or in two different molecules as shown in figure 3.5 and 3.6 respectively. This reaction is either self catalyzes by the second molecule of the carboxylic acid or by the independent acidic catalyst.

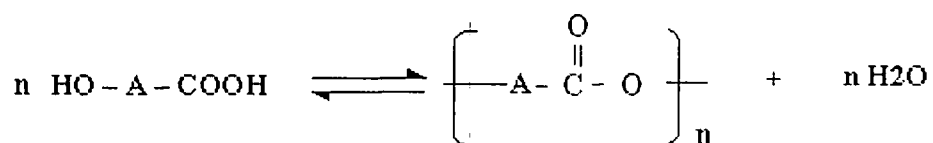


Figure 3.5: Direct esterification between same molecules



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

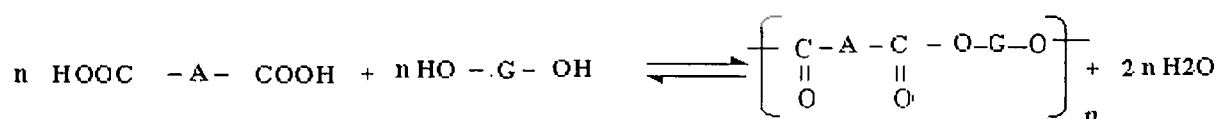


Figure 3.6: Direct esterification between different molecules

In 1967 Solomon followed by Ingold in 1953 proposed following mechanisms for the self-catalyzed polyesterification reaction²¹.

Oxonium ion is ionised from the autoprotolysis of the acid as follows.



Rate determine step of the reaction is as follows.



Above reactions are taken place simultaneously with the following reaction



Rate of the self-catalyzed direct esterification reaction can be expressed as second order reaction with respect to carboxylic acid²¹,

$$R \propto [\text{RCOOH}]^2 [\text{R}^1\text{OH}]$$

Second order kinetic has been proposed for the catalyzed esterification reaction. In 1846 Flurry observed that falling off of the reaction rate at higher conversion²¹. This is assigned the depletion of catalyst. At higher conversion the concentration of the end groups from carboxylic acid and hydroxyl becomes comparable with the catalyst concentration. Since that catalyst can be function as a chain - terminating agent.

3.4.2 Transesterification

Transesterification can be taken place in three different ways such as alcoholysis, acidolysis and esterolysis.

Transesterification by alcoholysis is taken place in two stages. One is reaction of a diester and a polyol using excess polyol to facilitate the forward reaction since this is a reversible reaction as shown in figure 3.7.

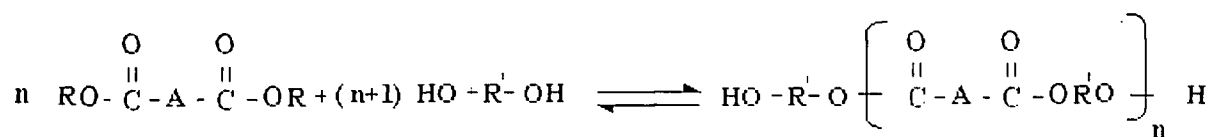


Figure 3.7: Reaction between diester and polyol

Second stage is polycondensation as shown in figure 3.8 at higher temperature and under vacuum condition by elimination of polyol.

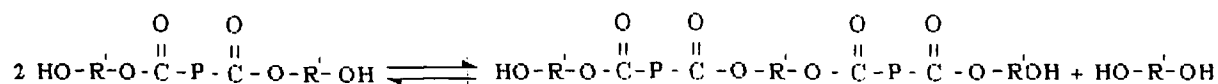


Figure 3.8: Polycondensation reaction via removal of polyol

Transesterification is possible without a catalyst. Also it can be catalyzed by salt of Ca, Mn, Zn, Cd, Pb, and Co. The second order reaction kinetic was proposed for both uncatalyzed and catalyzed transesterification reactions²¹. But order of the reaction can be varied due to various factors such as difficulty in suppressing reverse reaction, rate of loss of volatile components according to the change in string speed and vessel geometry and changes of reaction volume during the progress in reaction.

Polyester resins can be prepared by reacting carboxylic acid with acetate ester as shown in figure 3.9 called acidolysis.

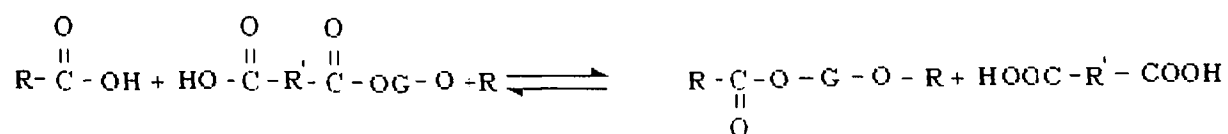


Figure 3.9: Reaction between carboxylic acid and acetate ester.

Polyester resins can be prepared by esterolysis of glycol esters and carboxylic esters as shown in figure 3.10.

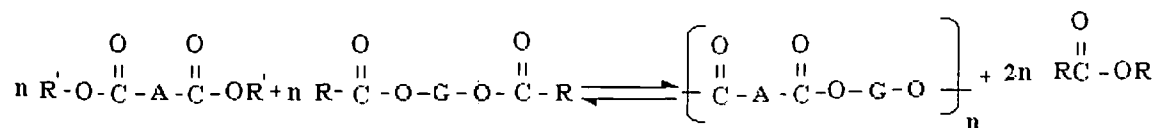


Figure 3.10: Reaction between carboxylic ester and glycol ester

3.4.3 Polyesters from anhydrides

This reaction is widely used for commercial production of polyesters in paint and plastic industry. Reaction undergoes in two steps as shown in figure 3.11. Esterification of the free carboxyl group is the slowest step, which determined the rate of the overall reaction.

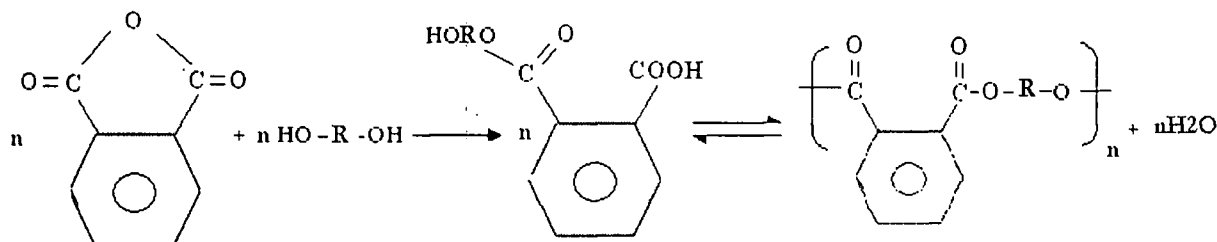


Figure 3.11: Reaction between acid anhydride and polyol

3.4.4 Polyester from acid chlorides

This reaction is mainly used for the preparation of polycarbonates which take place in two steps. This reaction has second order kinetic and slowest second step is the rate determining step. Equilibrium of the reaction can be shifted to forward direction by removing formed HCl from the system.

This reaction is limited for aromatic diols such as bisphenols since reaction between aliphatic diols and acid chlorides are very slow.

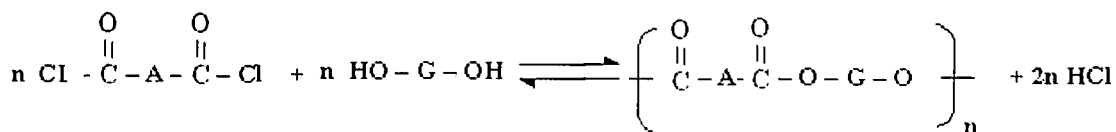


Figure 3.12: Reaction between acid chloride and polyol

3.5 Raw material used for alkyd synthesis

Synthesis of alkyd resin basically needs three different types of chemical constituents. They are polyol with hydroxyl functionality greater than two, polybasic acid or acid anhydrides and fatty oils or their fatty acids. Fatty oils can be drying, semi drying or non drying.

3.5.1 Polyhydric Alcohol

Glycerol and pentaerythritol are the most important widely used polyol in alkyd synthesis. Glycerol is having three hydroxyl functionality with two primary hydroxyl groups and one secondary hydroxyl group. Where as pentaerythritol is having four hydroxyl functionality. In pentaerythritol all four hydroxyl groups are primary. Pentaerythritol forms more complex resins with phthalic anhydride than with glycerol.

High functionality of pentaerythritol is especially used for long oil alkyd which contains more than 60% oil length. This results higher viscosity, faster drying, greater hardness, better gloss, better gloss retention and improved water resistance than alkyd having same oil length prepared with glycerol²¹.

Rate of viscosity increase is very high due to the presence of polypentaerythritol up to 15% which imparts high functionality to the resin²¹.

Reactivity of pentaerythritol can be reduced by several ways such as partially replace of pentaerythritol by using various types of glycols, large proportion of fatty acids and formaldehyde²¹.

During the reaction between pentaerythritol with formaldehyde cyclic-formals are produced as shown in figure 3.13.

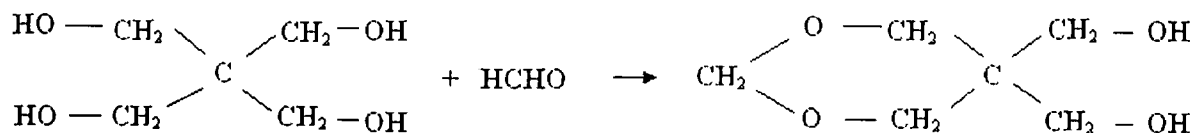


Figure 3.13: Reaction between pentaerythritol and formaldehyde

Using formaldehyde to reduce reactivity of pentaerythritol has another advantage which reduces the phthalic anhydride losses due to sublimation. But it renders the faster drying due to the presence of easily oxidizing $-\text{CH}_2$ groups and the presence of easily break down hydroperoxide instead of hydroxyl group which gives H bond²¹.

For the preparation of medium oil and short oil alkyds frequently used a mixture of pentaerythritol and ethylene glycol. These resins impart better compatibility, gloss retention and durability, than alkyd prepared from glycerol only²¹.

Some common polyols which are used to synthesize alkyd resins are shown in Figure 3.14.

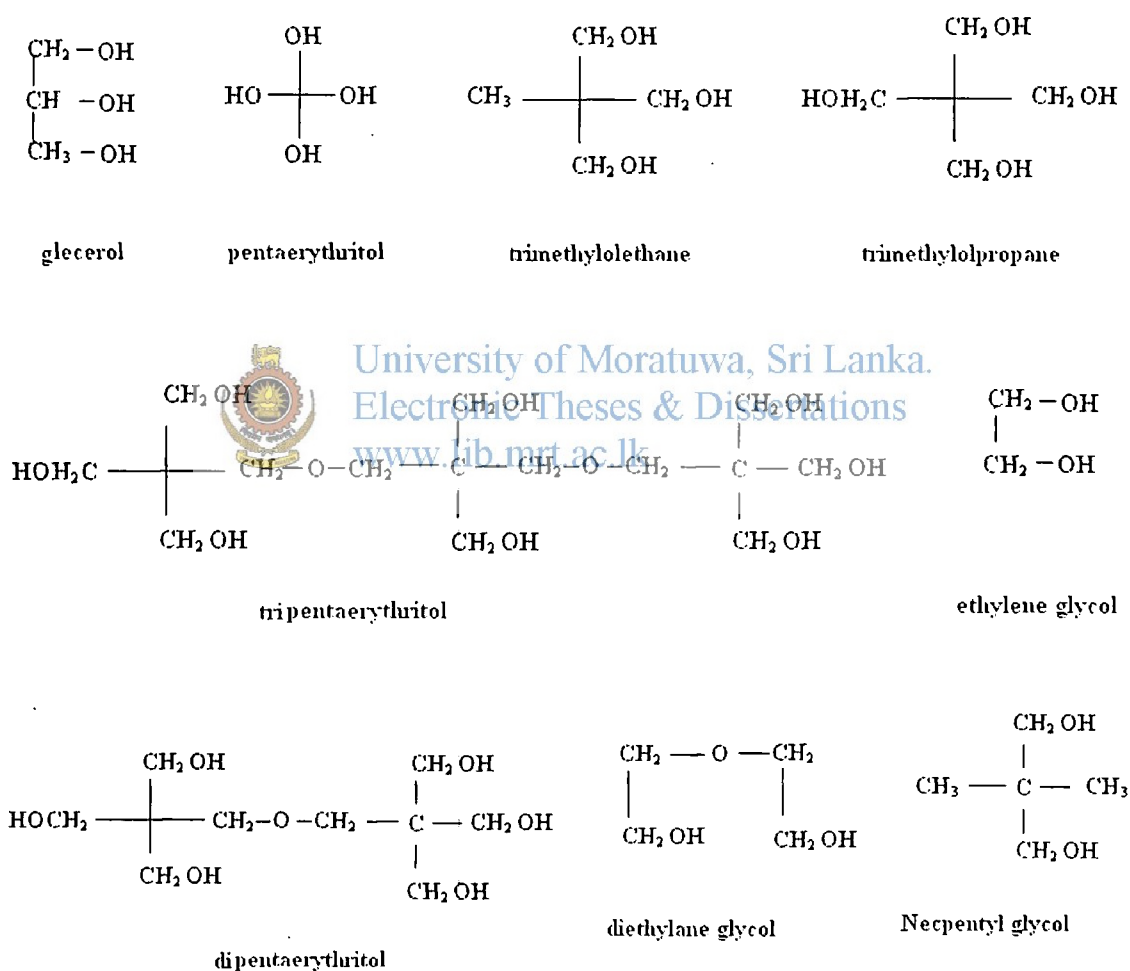


Figure 3.14: Chemical structures of polyol

Greater the distance between hydroxyl groups results softer flexible alkyds. This is due to the greater rotational freedom of the molecule. The non hydroxyl group of the polyol is

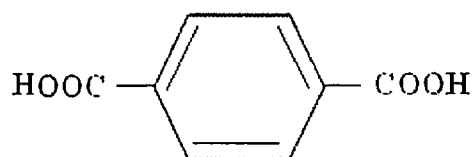
also affected the properties of the resins. For example trimethylolpropane based resins shows higher solubility in hydrocarbon solvents, better flexibility and more water and alkali resistance compared to the glycerol based resins due to the shielding effects of the hydrocarbon chains protect the ester group from foreign attacks²¹.

3.5.2 Polybasic Acids

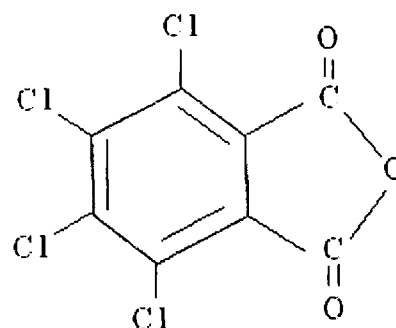
Phthalic anhydride is widely used polybasic acid in the synthesis of alkyd resins. In addition to that isophthalic acid, terephthalic acid, maleic anhydride, succinic acid, adipic acid, tetrachlorophthalic anhydrides are some of the polybasic acids used in the synthesis of alkyd resins.

Some common polybasic acids which are used to synthesize alkyd resins are shown in Figure 3.15.





Terephthalic acid



Tetrachlorophthalic anhydride

Figure 3.15: Chemical structures of polybasic acids

Main difference between Isothalic acid and terephthalic acid over phthalic anhydride is resulting a high molecular weight, high viscous alkyds. This is due to the absence of intramolecular ring formation which results decrease in the functionality of the polymer chain. Isophthalic alkyds show faster drying, more flexible tougher films²¹.

Chlorinated polybasic acids such as tetrachlorophthalic anhydride are used to synthesis alkyds need fire retardant properties. Meleic anhydride produces more complex alkyd resins with high viscosity. Since that risk of gelation is very high²¹.

3.5.3 Fatty acids and oils

Alkyd resins can be prepared from fatty oils or their fatty acids. Fatty oils belong to group of biological compound called lipids. In 1954 Jamieson classified fatty oils in to three categories as drying oil, semi drying oil and non drying oil according to the iodine number. Iodine number corresponding the degree of unsaturation in oil. For drying oils iodine number is >140. For semi drying oils iodine number is 125-140 whereas non drying oils have iodine number <125²¹.

Selections of the fatty oil or fatty acid for the synthesis of alkyd resin depend on the final use of the resin. For example if the resins are to be used as a film-forming materials drying or semi drying fatty oil or fatty acids are used to synthesis the resins. Since that

alkyd can undergo auto-oxidation at ambient temperatures through the attack of atmospheric oxygen at the unsaturated groups present in the fatty oil or fatty acid²². Fatty oils or fatty acids which are fully saturated or contain only one double bond are used for the synthesis process if the resin is used as a plasticizer. Film properties of the alkyd resin such as drying time, hardness, yellowing can be controlled choosing suitable oil or fatty acid for the synthesis process.

Physicochemical data of some commonly used fatty oils for the synthesis of alkyd resins are shown in Table 3.1^{4, 21}.

3.5.3.1 Fatty acid composition

Even though the iodine value imparts the unsaturation of oil it does not express the nature and the arrangement of fatty acids in oil. Fatty acid composition of each oil is important for that. Unsaturated fatty acid with $-\text{CH}=\text{CH}-$ group is called ethylenic fatty acids, those with $-\text{C}\equiv\text{C}-$ group is called acetylenic fatty acids.

Ethylenic fatty acids are the most abundant fatty acid type in vegetable oils. They are further categorized into monoenoic fatty acids and polyenoic fatty acids according to number of double bonds present in the fatty acids. Most available monoenoic fatty acid in vegetable oil is oleic acid. Polyenoic double bonds are further classified into two groups as conjugated and non conjugated fatty acids. Drying properties of the resultant alkyd depend on the type of unsaturation as well. Table 3.2 and 3.3 indicate the type of fatty acids in fatty oil and fatty acid composition in some common fatty oils^{4, 21}.

Table 3.1: Physicochemical data of some fatty oils

Fatty oil	Iodine value	Acid value	Saponification value	Refractive index
Linseed oil	170-190	2-6	188	1.4795
Perilla oil	193-208	Below 5	187-197	1.4780
Stillingia oil	169	3.7	206	1.4817
Hempseed oil	150	4	192	1.4670
Chi oil	196	0.6	192.2	1.4855
Alfalfa seed oil	154.2	-	172	1.4783
Tung oil	144-171	0.9-1.69	197-199	1.4761
Lumbang oil	151	1.2	190.8	1.4749
Perilla oil	193	1.7	191.3	1.4816
Figseed oil	169	0.9	190	1.4775
Cacahuananche seed oil	153	0.8	187	1.5163
Oiticica seed oil	144-155	4.0	186-193	1.505
Safflower oil	142-120	0.2-0.5	188-194	1.4742
Belladonna seed oil	145	-	191	1.4726
Passion seed oil	140	-	190	1.4737
Dehydrated castor oil	134	4.3	190.5	1.4835
Walnut oil	135	-	193	1.4730
Poppy seed oil	134	1.5	192	1.4751
Sunflower oil	135	2.0	190	1.473
Soyabean oil	135	2.5	190	1.473
Grape seed oil	125	-	186	-
Papaw seed oil	111	6.4	194	-
Lemon seed oil	106	-	192.7	1.4664

Table 3.2: Unsaturated fatty acids in fatty oil & some common sources

Structural formula & IUPAC name	Common name & unsaturation	Source
$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ Cis-9,cis-12-octadecadienoic acid	Linoleic acid (Non conjugated)	Sunflower oil, soybean oil, corn oil, Nahar seed oil
$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOHCOOH}$ Cis-9, cis-12, cis-15-octadecatrienoic acid	Lenolenic acid (conjugated)	soybean oil, linseed oil, sea food oil, Nahar seed oil
$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ Cis-9,trans-11,trans-13-octadecatrienoic acid	Eleosteric acid (conjugated)	Tung oil, karawila seed oil
$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ Cis-9,trans-11,cis-13-octadecatrienoic acid	Punicic acid (conjugated)	Pomegranate family
$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ trans-9,trans-11,cis-13-octadecatrienoic acid	Catalpic acid (conjugated)	Catalpa ovate seed oil
$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_6\text{COOH}$ trans-8,trans-10,cis-12-octadecatrienoic acid	Catalpic acid (conjugated)	Marigold seed oil
$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ Cis-9-tetradecenoic acid	Myristoleic acid (Monoenoic)	Seed oil of Myristicaceae Dolphin head oil, Whale head
$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ Cis-9-hexadecenoic acid	Palmitoleic acid (Monoenoic)	Seed oil of Asclepiaceae Connaraceae and proteaceae
$\text{CH}_3(\text{CH}_2)_{10}\text{CH}=\text{CH}(\text{CH}_2)_4\text{COOH}$ Cis-6-octadecenoic acid	Petroselinic acid (Monoenoic)	Seed oil of Umbelliferae and Araliaceae
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ Cis-9-octadecenoic acid	Oleic acid (Monoenoic)	Most of vegetable oil
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOH}$ Cis-13-docosenoic acid	Oleic acid (Monoenoic)	Most of vegetable oil

Table 3.3: Fatty acid composition of some fatty oils

Fatty oil	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Other fatty acids
Linseed oil		6	22	17	51		
Perilla oil		7		8	38	47	
Stillingia oil				10.4	49.9	25.4	8.6
Hempseed oil				12.6	53	24.3	10.1
Chi oil				0.8	48.6-30.3	39.3-56.2	8.1-10.6
Alfalfa seed oil				3.3	23.5	73.2	
Tung oil		4	2	4	8		Eleosreic 82
Lumbang oil		4.7	4.1	32	35	24	
Figseed oil		5.2	2.2	19	33.7	32.9	1.0
Oiticica seed oil		5	5	6	10		74
Safflower oil							
Belladonna seed oil		5.9					
Passion seed oil		6.8					
Walnut oil	0.4	3.3					
Poppy seed oil				30.1	62.2		7.7
Sunflower oil				34.1-42	52.0-58.5		6-9.6
Soyabean oil		8	4	28	55	5	
Grape seed oil				32.1-44.3	46-55.3	0.1-2.3	5.3-9.2

Fatty acid compositions of fatty oil express the percentage of each fatty acid to the total amount of fatty acid in the oil. Iodine value expresses the relative distribution of fatty

acid in unit mass of fatty oil. It is more convenient to use both fatty acid composition as well as iodine value to identify the drying properties of fatty oil.

Drying efficiency of fatty oil can be expressed using fatty acid composition. Hilditch and Graeves formulated a quick drying indices⁴. Hilditch method has two indices.

1. Polyenoic content "p" is expressed as follows.

$$P_2 \text{ Lin} + \text{Len}$$

Where "Lin" is Linoleic acid and "Len" is Linolenic acid content

2. Quick drying index = $P \times \text{Len} \times 10^{-2}$

Graeves index is defined as $\text{Lin} + 2 \text{ Len}$

To be a good drying oil P value should be at least 60 and Hilditch drying index should be 25. By using above indices can express drying efficiency of fatty oil²³.

Drying rate of the fatty oil increases hyperbolically with increasing of polyenoic acid content and maximum rate is achieved when polyenoic content is at 50%²¹. Also drying rate depends on the configuration of the polyenoic acid. Cis-configuration has faster drying than trans-configuration. However oil having polyenoic acid with trans-configuration is further drying after drying the surface of the oil film²¹.

Hardness of the film is proportional to the polyenoic acid content but hardness does not depend on the Linoleic: Linolenic acid ratio, dienoic: trienoic acid ratio or conjugated: non conjugate ratio if the total polyenoic acid content is unchanged²¹.

Highly unsaturated fatty acids are used to produce high viscosity alkyds.

Initial gloss, gloss retention or storage stability does not depend on the fatty acid composition. Yellowing of alkyds depends on the polyenoic acid content of the fatty acid²¹.

3.6 Synthetic procedure for oil modified alkyd resins

Preparation methods of the alkyd resins mainly depend on the chemical properties of raw materials. Incompatibility of non polar fatty oil with polar polyol and polybasic acid or acid

anhydride form two phases results unwanted gel products. To overcome this problem four different synthetic paths of alkyd resins have been developed ²¹.

1. Fatty acid process
2. Monoglyceride process
3. Acidolysis process
4. Fatty acid oil process

3.6.1 Fatty acid process

In the fatty acid process polyol, dibasic acid & the monobasic acid are reacted simultaneously at temperature 220-260 °C, until the required degree of polymerization is achieved. Any polyhydric alcohol or polyhydric alcohol blend can be used in this process. This process is also called "High Polymer Technique" which is modified by Kraff in 1957²¹. This involves the incremental addition of a portion of the monobasic acid to the polymer. In the presence of monobasic acid reduce the chain terminating reactions in the early stages of polymerization resulting in high molecular weight backbone polymers which the added monobasic acid is attached as a side chains. Resulting alkyd resins imparts the faster drying & better chemical resistance properties. Primary hydroxyl group present in the glycerol as shown in figure 3.16 react more rapidly with carboxylic groups present on the phthalic anhydride and the phthalate half esters than carboxylic groups present on the fatty acid. Secondary hydroxyl group react more rapidly with fatty acids carboxyl groups than carboxylic groups on phthalic anhydrite or half phthalate ester²¹.

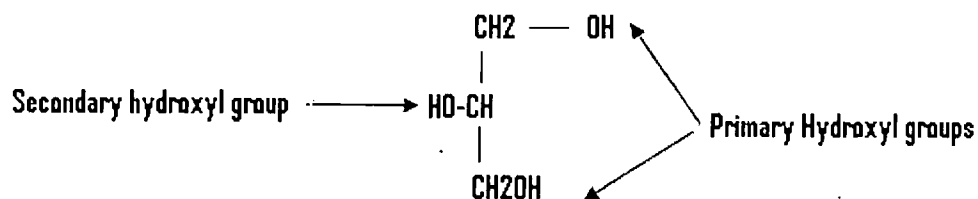


Figure 3.16: Glycerol molecule

3.6.2 Monoglyceride process

Oils are normally available as triglyceride of fatty acids. When these oils are reacted together with polyol and dibasic acids to produce alkyd resins, resulting a heterogeneous mixture due to the preferential condensation of dibasic acids with polyol to produce polyester. These polyesters are insoluble in oil phase and gel at low degree of reaction. To overcome this incompatibility problem, Bernard and Frick obtained a patent in 1936 for monoglyceride process in synthesis of oil modified alkyd resins²⁴. This process includes two stages called alcoholysis followed by polyesterification. In monoglyceride process triglyceride of oils are initially reacted with polyol at 225-250 °C in the presence of catalyst to form monoglyceride before condensation. At the beginning of monoglyceride process less polar oil and relatively more polar polyols are in two phases. As the reaction progress fatty oil and polyol become single phase homogeneous mixture of monoglyceride. After a certain extent of the reaction, a resultant single phase reaction with sufficient amount of monoglyceride become compatible with dibasic acids and acid anhydride. Figure 3.17 is shown the reaction between fatty oil and pentaerythritol.

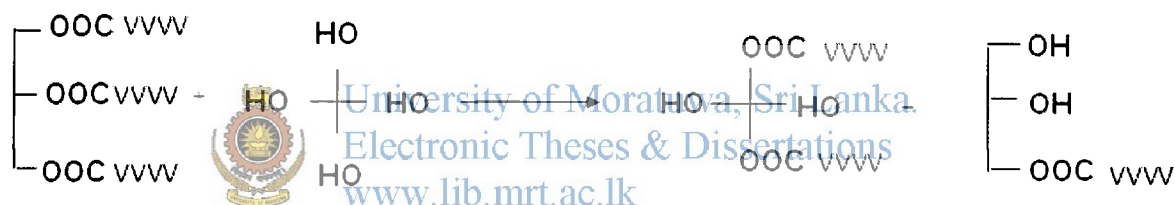


Figure 3.17: Reaction between fatty oil and pentaerythritol

Among the catalyst, PbO, Ca (OH)₂, CaO, Na₂CO₃, LiCO₃, sodium methoxide (MeONa) and calcium soaps are commonly used. Catalytic activity of calcium octate, MeONa, Dibutyltin oxide (DBTO), LiOH, lead oxide on alcoholysis reaction of soyabean oil, linseed oil and dehydrated castor oil with glycerol, pentaerythritol and neopentyl glycol are summarized in Table 3.4⁴.

Table 3.4 Order of catalytic activity of catalyst

Oil	Polyol	Order of catalytic activity
Soya bean oil	Neopentyl glycol	DBTO < PbO < LiOH, CaOct < MeONa
	Glycerol	DBTO < PbO < LiOH, CaOct < MeONa
	Pentaerytritol	MeONa, CaOct < DBTO < LiOH, < PbO
Linseed oil	Neopentyl glycol	LiOH, CaOct < PbO < DBTO < MeONa
	Glycerol	CaOct < MeONa < DBTO < LiOH < PbO
	Pentaerytritol	CaOct < MeONa < DBTO < LiOH < PbO
Dehydrated castor oil	Neopentyl glycol	DBTO < MeONa < LiOH, CaOct, PbO
	Glycerol	DBTO < PbO < CaOct, LiOH < MeONa
	Pentaerytritol	CaOct, MeONa < DBTO < LiOH < PbO



University of Moratuwa, Sri Lanka.

Electronic Theses & Dissertations

www.lib.mrt.ac.lk

Extent of alcoholysis is determined by checking the solubility of the reaction mixture in anhydrous methanol. When one volume of reaction mixture gives a clear solution in 2-3 volume of anhydrous methanol indicates that the formation of homogeneous monoglyceride mixture²¹. At this time dibasic acid is added and polyesterification reaction is conducted 200-260 °C to the desired alkyd specifications.

The extent of alcoholysis can be quantitatively checked by measuring electrical conductivity of the solution mixture²¹. Most undesirable reaction in the alcoholysis process is interetherification reaction between polyol molecules as shown in figure 3.18. This will rapidly form higher functional polyol which result unwanted gel product before achieving desired alkyd properties like low acid value during polyesterification reaction^{4, 21}. Rate of interetherification reaction is increased at high temperature in the presence of catalyst. Etherification rate is negligible at 200-220° C temperature range but reaction mixture required considerable period of time to complete the alcoholysis process. At temperature above 260°C, etherification is significant but alcoholysis is completed within short period of time. At temperature 240oC is resulted maximum monoglyceride within relatively short period of time with reasonably low amount of ether products of polyol⁴.

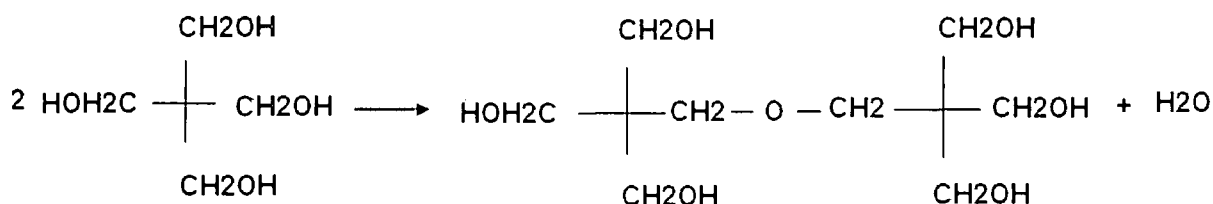
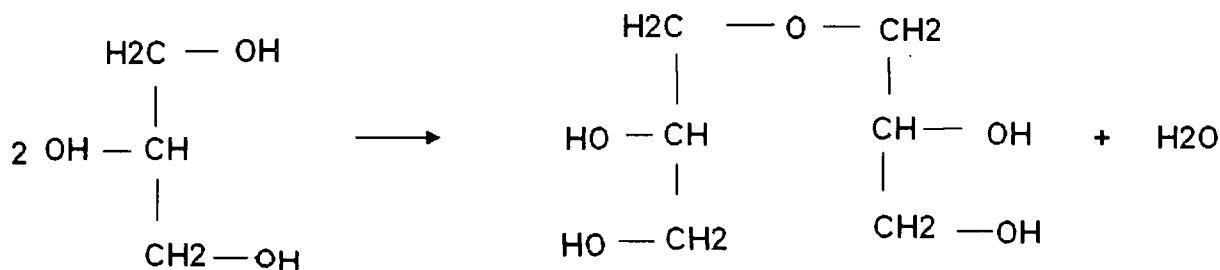


Figure 3.18: Etherification of polyols

3.6.3 Acidolysis process

Oils are subjected to acidolysis in the presence of acids prior to condensation reaction. Reaction between isophthalic acid and triglyceride in acidolysis can be shown as figure 3.19. In compatibility problem can be overcome using acidolysis process. This reaction is occurred at high temperature without a catalyst. Use of acidolysis process is limited to polybasic acids such as isophthalic acid and terephthalic acids. This process has been first described by Carston in 1959²¹. The resultant ester derivative of triglyceride can be polymerized in a polyol at later stage.

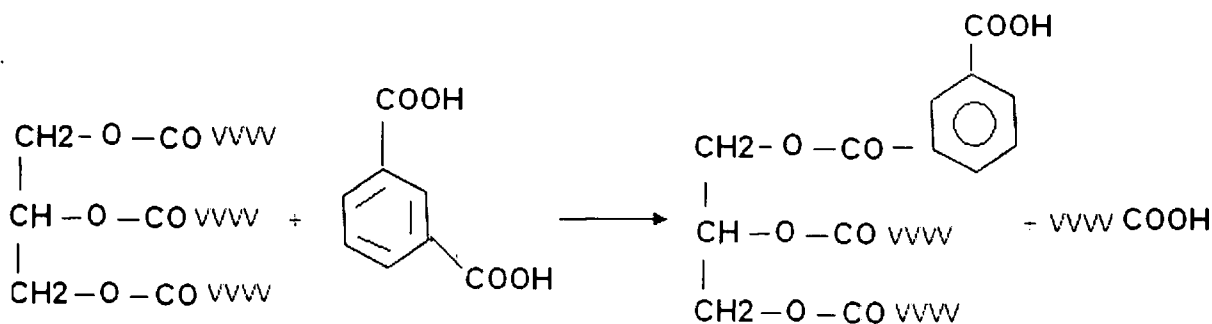


Figure 3.19: Reaction between isophthalic acid and triglyceride

3.6.4 Fatty acid/oil process

This process involves the direct reaction of fatty acid, vegetable oil, polyol and dibasic acid mixture. Homogeneity of the reaction mixture is depending on the ratio of the fatty acid to oil content in the mixture. This process can be used to produce high viscosity alkyds²¹.

Among the above mentioned four processes, fatty acid process is the most commonly used in the commercial scale of alkyd preparation. Fatty acid process has some advantages and disadvantages over the monoglyceride process. Fatty acid process has better formulation flexibility. Problem of oxidation and colour development can be eliminated since this process does not use alcoholysis catalyst. Molecular weight distribution can be controlled using high polymer technique. Main disadvantages of this process are storage problem due to the corrosiveness and discoloration, requirement of pre heating equipment due to high melting point of fatty acids and the relatively high cost of fatty acids.

The above processes can be carried out either in an absence or presence of a solvent²¹. Alkyd preparation without solvent is called fusion process and with solvent is called solution process. The fusion process is cheap and does not require complicated equipments. This process is often use to prepare alkyd contain oil length 60% or above²¹. Solvent process is also called azeotropic process which employed for alkyd recipes having high amount of volatile matters. This process involves condensation of volatile vapours, separating the water and returning the organic distillate to the reaction mixture continuously. Hot vapours of organic distillate are cleaned inside the reaction apparatus and improve the mixing by reducing the viscosity of reaction mixture. This will also help to remove the water from the reaction mixture and thereby equilibrium of the reaction can be shifted to forward direction to facilitate the polyesterification reaction. This method helps to better control of components and temperature of reaction mixture. The solvent used in this process should be inert and water immiscible.

3.7 Modifications of alkyd resins

Alkyd resins are modified with different types of chemical groups to achieve desired properties according to their final applications.

3.7.1 Modification with Nitrocellulose

Alkyds can be upgraded with respect to gloss, adhesion durability and cold resistance by introducing nitrocellulose. Nitrocelluloses are more compatible with short oil alkyds but it can be extended up to 55% oil length. Since short oil alkyds contain high degree of polarity arising from ester linkages and excess hydroxyl groups they are more compatible with nitrocellulose. Good drying and durability characteristics of the resin render with introducing nitrocellulose^{4, 16}.

3.7.2 Amino resin modification

Amino resin modified alkyds are generally used in industrial baking enamels. Short oil alkyds contain 38-45% phthalic anhydride and a high proportion of hydroxyl groups are the most suitable alkyds to modify with amino resins. High hydroxyl values in resins are compatible with urea formaldehyde and melamine formaldehyde resins. This results large number of reactive sites to the resin which can react with amino resin to give three dimensional network. These resins have good mechanical and solvent resistance properties⁴.



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

3.7.3 Chlorinated rubber modification

Combination of chlorinated rubber with alkyd results improved toughness, adhesion, solvent resistance, durability, drying rate, excellent alkali, acid and water resistance properties for the resultant alkyd. Chlorinated rubber is compatible with alkyd contain more than 54% fatty acid with similar linearity and low polarity. Chlorine modified alkyd resins are generally used for concrete-floor paints and swimming pool paints⁴.

3.7.4 Modification with phenolic resins

Phenolic resins are reacted with drying oil alkyds and results chroman-type structure. Phenolic modified alkyd resins are rendered excellent gloss retention, durability, and water and alkali resistance properties⁴.

3.7.5 Modification with vinyl resins

Alkyd resins can be modified with hydroxyl modified vinyl acetate resins. Generally these types of resins are used in coating for military and marine uses. Isophthalic acid based alkyds are modified with poly- α -methylstyrene and these resins are resulted improved drying and durability. Dried film of vinyl modified alkyds show light-colour and posses high gloss, excellent hardness and excellent chemical resistance properties^{21, 25}.

3.7.6 Modification with polyisocyanate and epoxy resins

Free hydroxyl groups present in the alkyd can be modified with polyisocyanate and resulting alkyd shows improved drying rate, chemical resistance and abrasion resistance. Alkyd contains less than 45% fatty acid can be combined with low molecular weight epoxy resins and melamine formaldehyde resins to obtain improved gloss, excellent adhesion to metals, improved colour retention and excellent water and chemical resistance²⁶. Since epoxy resins have high functionality, epoxy modified alkyd resins are prepared by defunctionalization techniques to avoid premature gelation²¹. In defunctionalization technique, epoxy resin first partially esterifies with fatty acid to obtain functionality between 1 to 4 and this resulting product using as a polyol in the preparation of alkyd resins²⁷.

3.7.7 Silicon modification

Hydroxyl group of air drying long oil alkyds react with silicon intermediates to form silicon modified alkyd with greatly improved durability, gloss retention and better heat resistance properties. Silicon modified paints are mainly used in marine and maintenance paints²¹.

3.7.8 Modification of alkyd with polyamides

Alkyd resins modified with polyamide results thixotropic resins. Thixotropic paints remain semisolid or jelly like state when at rest but upon shearing action immediately become thinner and spread. The paint again recovers its gelly-like state as soon as shearing

action is stopped. Since this behavior these are non Newtonian in viscosity behavior. Thixotropic behavior is important in architectural and maintenance paints to avoid sagging. Thixotropic paints can be applied without the prior priming necessary for ordinary paints. Alkyd and polyamide are heated at elevated temperatures occur amide and ester interchange reaction to split polyamide chains to affix to the alkyd molecules. Hydrogen bonding between the carbonyl and the amide groups throughout the alkyd-polyamide complex results the thixotropic behavior of the resin^{4, 21}.

3.7.9 Other modifications

Short oil alkyds can be modified with polycarbonates (4-10%) to obtain superior chemical resistance and electrical insulation properties²¹.

Alkyd resins can be modified with vinyl and acrylic resins through unsaturation and functional groups. These modifications can be carried out in either by mechanical blending, by copolymerization or by condensation reaction. In the process of mechanical blending compatibility is obtained either by polar interaction or by using low molecular weight entities. Copolymerization of vinyl or acrylic monomers can be carried out either through the double bonds or the active methylene groups present in the oil modified alkyds. Alkyd can also be modified with vinyl or acrylic polymers by reacting the functional groups in the alkyd molecule. Since modification is carried out through functional groups, this method can be used for alkyd derived from fully saturated fatty oils. Resulting alkyds are highly durable and shows better discoloration properties²¹.

3.8 Air drying alkyd resins

Normally air drying long oil alkyds are synthesized from drying oils. Non drying oils are used to synthesis short oil backing alkyds^{21, 19}.

Phthalic anhydride using as a poly basic acid for the synthesis of air drying alkyd resins has several advantages such as low cost, higher reactivity and superior film properties like colour retention, toughness, adhesion, gloss retention and exterior durability due to good resistance for degradation from UV light^{19,30}. In addition to that in 1957 Case has been shown the degree of polymerization necessary for gelation is significantly increased using asymmetric reactants like phthalic anhydride²¹. This assumed to be due to the

second group of carboxylic in anhydride is not available for the reaction until the other group of carboxylic is reacted. Thus phthalic anhydride is more suitable as a poly basic acid to increase the extent of polymerization with minimizing risk of gelation.

Synthesis of low viscous alkyd resin is also important in paint industry for ease of brushability. Traditional ways of reduction in alkyd resin viscosity are by lowering molecular weight, use of reactive diluents and narrowing molecular weight distribution^{31, 32}. Molecular weight can be reduced by increasing oil length but this can lead to unsatisfactory properties like slow drying, sagging and inferior pigment stabilization³³. In addition to that increasing oil length caused loose packing of molecules, less intermolecular interactions, decreasing number of H bond forming groups. These are further reduced the film compactness. Even though reactive diluents decrease the viscosity of coating it can be caused instability called can polymerization during storage. This can lead to early embrittlement of the film on ageing³². Incompatibility of reactive diluents and alkyd resin prevent the formation of homogeneous film. This can badly effect on overall coating performance. Because of above mentioned negative impacts, reduction in alkyd resin viscosity using these methods are not a practical approach.

More recent way to achieve low viscous alkyd is creation of highly branched structure in the polymer back bone by using multifunctional monomers. Highly branched architecture helps to achieve resins with lower viscosity than its linear counterpart at a comparable molecular weight^{32, 33}. Recently hyper branched macromolecules as well as dendrimers are explored as monomers to make low viscous alkyds³².

3.9 Drying mechanism of air drying alkyds

Drying oil which consists of poly-unsaturation fatty acids undergoes film formation by oxidative drying. The most important reaction during drying is reaction with atmospheric oxygen and result isomerization, polymerization, degradation of C-C bonds and the formation of oxidation products. Oxidation depends on the unsaturation portion of the fatty acids such as number of carbon-carbon double bonds, whether it is conjugated or non conjugated and geometric arrangements of substitute groups.

Air drying process initially has an induction period. During this period antioxidant present in the film are destroyed²¹. Since that length of the induction period depends on the total amount of antioxidant present in the film.

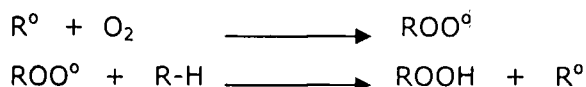
General mechanism of the air drying process can be sub divided into four steps such as initiation, propagation, hydroperoxide decomposition and termination. In more specific way conjugated and non conjugated double bonds undergo different drying mechanisms.

Initiation

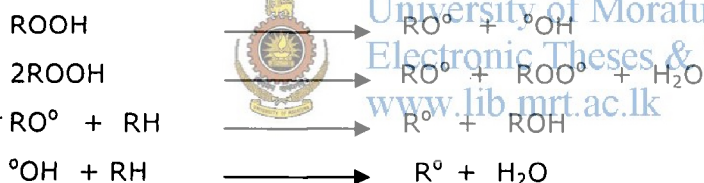


In initiation stage, allylic radicals are formed by hydrogen abstraction at the methylene group.

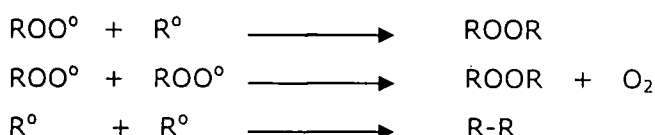
Propagation



Hydroperoxide decomposition



Termination



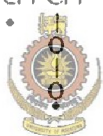
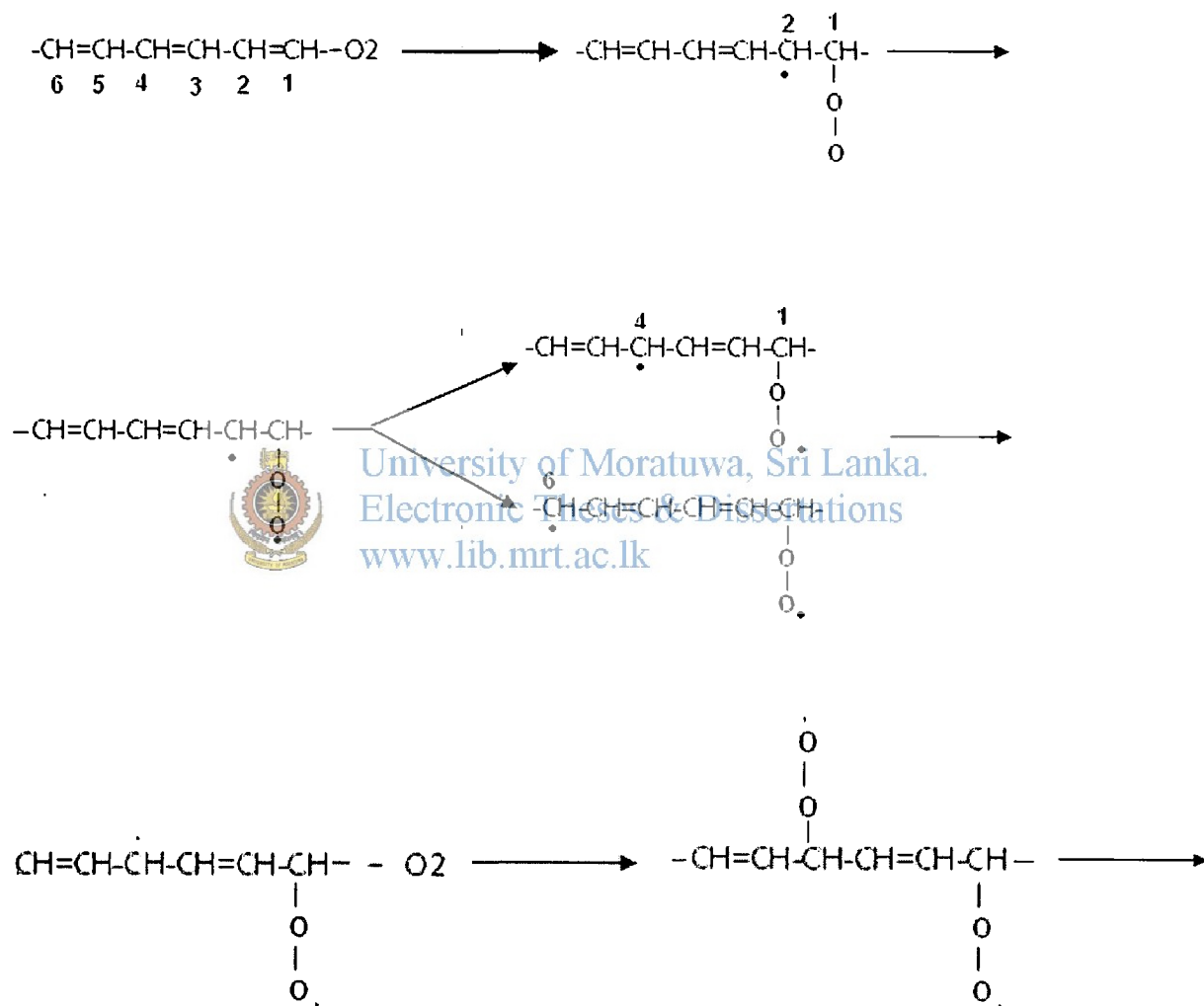
Terminations of free radicals form cross links between polymer chains and fatty acids moieties. Cross linked are formed between C-C bonds, C-O-C bonds, and C-O-O-C bonds. Direct addition of free radicals to $\text{C}=\text{C}$ is also possible reaction to form cross links.

Side reactions can be occurred by β -scission and Russell termination²¹. These side reactions do not form cross links. Aldehydes, carboxylic acids and CO_2 are the product of β -scission. Sharp smells during drying period of alkyd resins are due to these volatile

aldehydes by β -scission. Peroxi radicals form ketones and alcohols from Russell side reaction²¹.

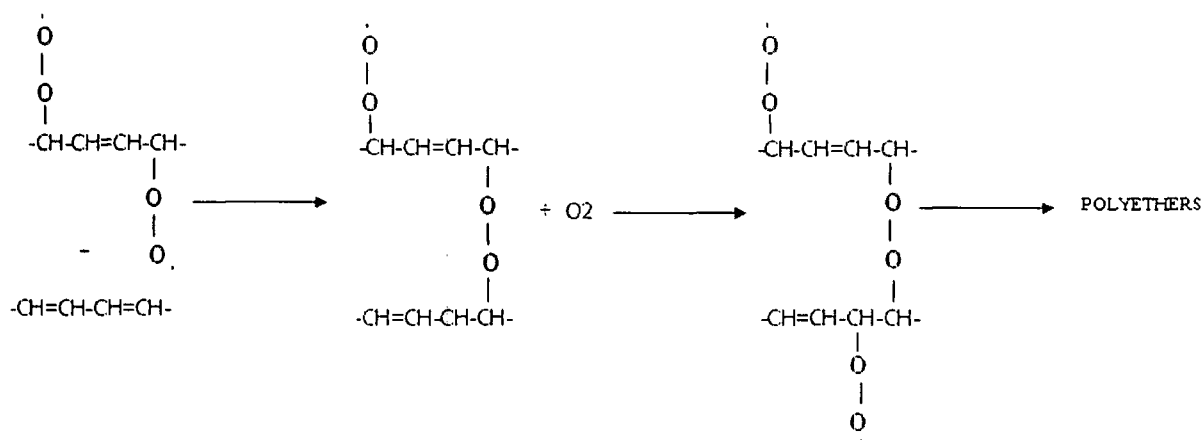
Conjugated diens and non conjugated diens are undergoing different reaction mechanisms during drying as shown in figure 3.20 and 3.21 respectively¹⁹.

3.9.1 Air drying mechanism in conjugated double bonds

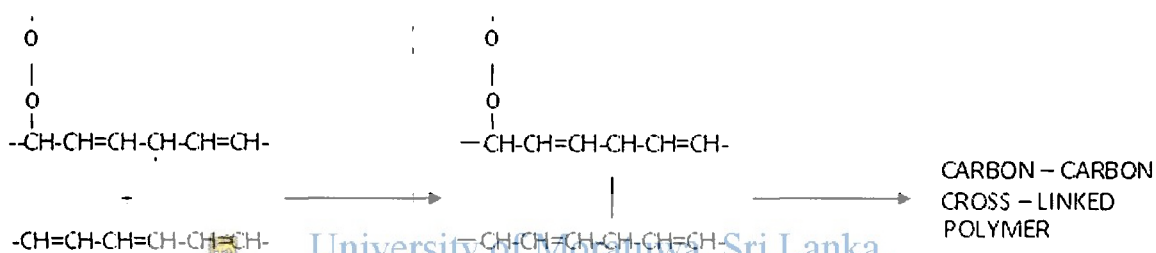



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

1)



2)




 University of Moratuwa, Sri Lanka.
 Electronic Theses & Dissertations
 www.10.mrt.ac.lk
 Figure 3.20: Oxygen attack to the conjugated double bonds

Oxygen attacks conjugated double bonds by direct addition to form diradicals. Double bonds are rearranged to form radical sites in 1, 4 and 1, 6 positions. Oxygen is further react with radical sites to form peroxy radicals. Polyperoxides are exceptionally stable but decomposed by heat and light to form alkoxy radicals. Cross linking can be occurred when alkoxy radicals and diradicals react with double bonds through the formation of ether linkages and c-c bonds respectively.

3.9.2 Air drying mechanism in non conjugated double bonds

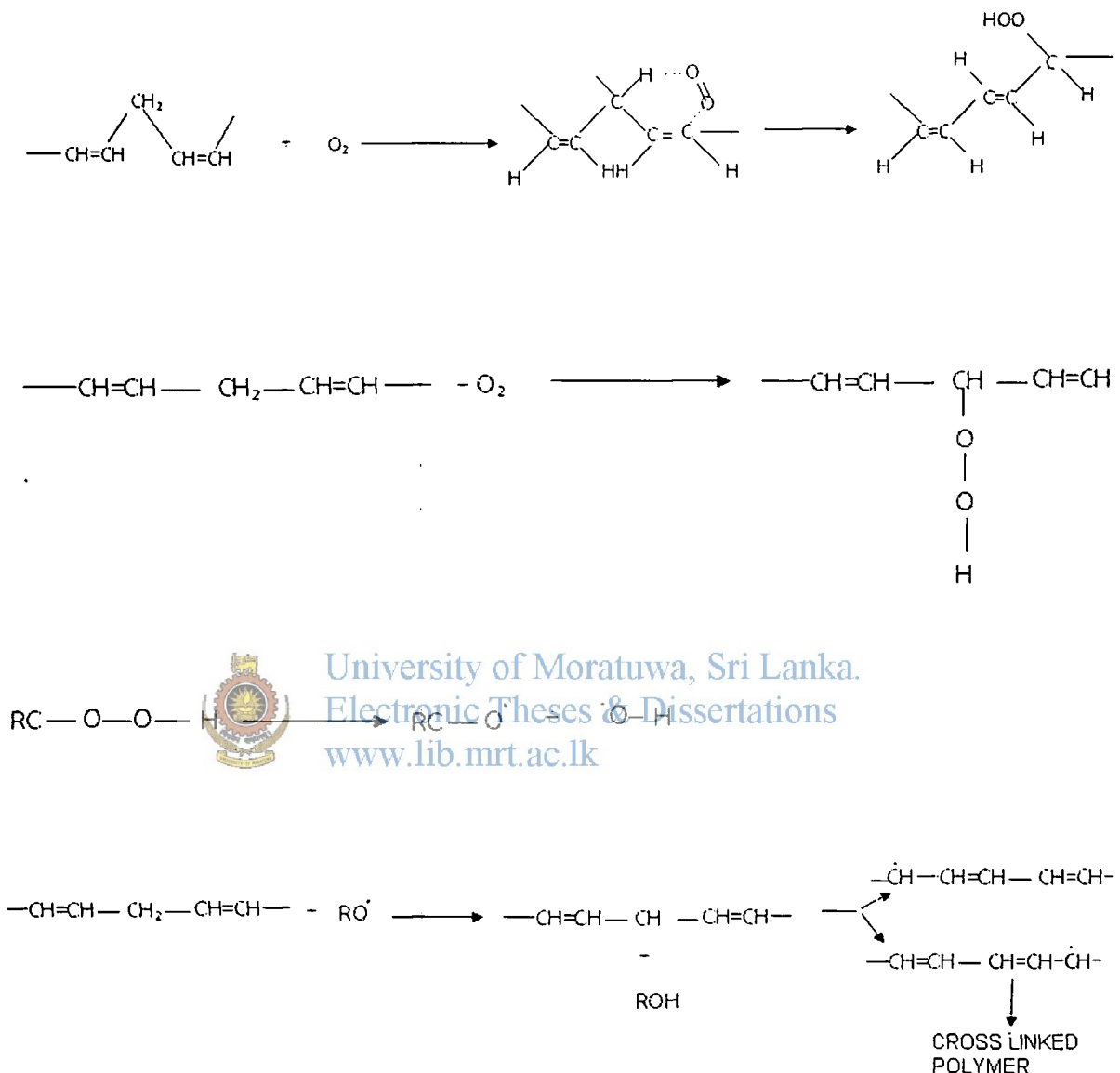


Figure 3.21: Oxygen attack to the non conjugated double bonds

Non conjugated double bonds are reacted with oxygen without loss of unsaturation. In non conjugated double bond system oxygen attack, hydroperoxide formation and double bond rearrangement are taken place simultaneously¹⁹. Oxygen can be attacked to the allylic hydrogen directly and resulting radical can be rearranged to form conjugated double bond. These free radicals further react with oxygen to form peroxy radicals. These peroxy radicals abstract hydrogen atom from methylene group and form hydroperoxides.

Hydroperoxides are decomposed by light and heat. Cross linking can be occurred through c-c bond formation.

3.10 Driers

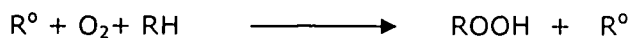
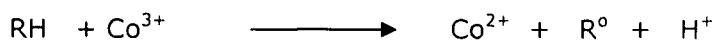
Oxidative drying can be catalyzed by metallic salt with an acid portion which can soluble in oil. These catalysts called as dryers. Driers bring the drying time of air drying alkyds into commercially feasible limits. Driers mainly consist of hydrocarbon soluble salt of octates, naphthenates, linoleates of selected metals such as Co, Mn, Pb, Ca, zn, Al complexes. In the presence of driers amount of O₂ required to dry the film is less.

Primary driers and the promoter driers are the two types of driers present for the catalytic activity of air drying alkyds. Primary driers are true catalyst which needs small amount for their catalytic activity. Normally 0.005%-0.2% based on oil²⁸. Co and Mn are example for primary dryers. These driers contain variable valency and more stable low valance can be oxidized to higher valence during the drying process. During the drying process primary driers catalyze the oxygen uptake as well as the decomposition of peroxides to free radicals. Promoter driers are salt of Ca, Zn and Ba. They are not capable to catalyze auto-oxidation alone. It is functioned as an activator for primary driers. Promoter driers can be used up to 0.6% based on oil. They are increased the drier stability, reduced blooming tendencies and given "through" drying to the alkyd film²⁸.

During the function of driers metal atom undergoes oxidation from lower valency to higher valency state by fatty acid hydroperoxyde present in the system as follows.



Mechanism of the oxygen uptake from the driers can be represented as follows.



Cobalt ion can be directly attacked to the double bond present in the oil.

Cobalt leads to more rapid drying at the surface of the film than lower layers. When the surface of the film dried first, film can be shrinking. Promoter driers can be used to

overcome this problem. Primary driers used with balanced amount of promoter driers can be overcome the shrinkage problem due to its "through" drying property¹⁹.

Aluminum alkoxide derivatives are recently developed promoter driers. Substituent groups in the alkoxide ion can be reacted with the hydrogen atom present on the carboxylic and the hydroxyl groups of alkyds. By this method several alkyd molecules can be bonded to one aluminium atom by eliminating volatile by-products from the drying film. In this type of system carboxyl:aluminium ratio should be formulated to one or less to ensure stability in the can during storage. These films show improved water resistance, gloss retention and yellowing resistance¹⁹.

3.11 Alkyd constant

In 1962 Patton has derived an alkyd constant using Carothers functionality equation to calculate suitable resin formulation to minimize the risk of gelation²¹. Alkyd constant (K) can be derived as follows.

$$\text{Alkyd constant (K)} = \frac{\text{Total number of acid \& hydroxyl bearing molecules at the beginning of a condensation reaction}}{\text{Total number of acid equivalents}}$$

Patton proposed that the value of alkyd constant should be 1.005 ± 0.014 for phthalic anhydride based resins and 1.05 ± 0.008 for isophthalic acid based resins²¹.



University of Moratuwa, Sri Lanka
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

3.12 Gel formation during polyesterification reaction

Formation of highly branched cross linked structure can lead to the formation of gel product before achieving the required extent of polymerization. Branching is occurred when one or more monomer molecules having more than two functional groups per molecule²⁹. Cross linking can be occurred branch or branches from one polymer molecule become attached to the other polymer molecule. Controlling of monomer concentration in the polyesterification reaction is essential to control the gelation before achieving the required degree of polymerization. The criteria for gelation in a system containing a reactant of functionality f is that at least one of the $(f-1)$ chain segments radiating from a branch unit will in turn to be connected to another branch unit²⁹.

According to the Carothers equation number average degree of polymerization becomes infinite at the gel point. Gel point is experimentally determined at the point where the reaction mixture losses its fluidity as indicated by the failure of bubble to rise in it²⁹.

Chapter 4

Experimental for the synthesis of alkyd resins based on Nahar & Karawila seed oils

Experimental was carried out to synthesis long oil air drying alkyd resin with 65w/w % oil length using Nahar seed oil, karawila seed oil, pentaerythritol and phthalic anhydride.

In the present study Nahar seed oil was used together with Karawila seed oil as a 50:50 w/w % blends with phthalic anhydride and pentaerythritol to synthesis long oil air drying alkyd resins. Branching was incorporated through pentaerythritol as a multifunctional polyol.

Four recipes were formulated with varying amount of pentaerythritol content were synthesized and studied their physicochemical properties as well as film performance properties.

4.1 Synthesis of alkyd resins from a blend of Nahar and karawila seed oil

Synthesis of alkyd resins with 65w/w % oil length using the blend of 50:50 w/w % Nahar and Karawila seed oil and evaluation of film properties were the two major part of the experimental work in the present study. Due to the reasonably low acid value of the Nahar and Karawila seed oil, monoglyceride process was selected as a synthetic path. Solvent process was used to minimize phthalic anhydride losses from sublimation during polyesterification reaction. Five-necked flask of 500ml equipped with mechanical stirrer, thermometer, N₂ gas inlet, Dean and stark apparatus was used for whole synthesis process. Middle neck of the flask was used to insert mechanical stirrer and three side necks were used to connect thermometer, N₂ gas inlet and Dean and stark apparatus. Remaining neck was used to withdraw sample as required and to introduce phthalic anhydride after conversion of all triglycerides of oil into monoglycerides. Dean and stark apparatus was used to remove the water produced during polyesterification reaction azeotropically. During the condensation of solvent and water in dean and stark apparatus sublimed phthalic anhydride bringing back to the reaction mixture.

Physicochemical properties of the oils were determined at the beginning of the process.

Synthesis process of alkyd resin in present study was carried out under three steps. They were oil upgrading process, monoglyceride process and polyesterification process.

In oil upgrade process, 50:50w/w % Nahar and Karawila seed oil and required amount of polyol to neutralize free fatty acids in oil mixture were stirred for 15 min for better mixing with N₂ stream to repel the air above the oil mixture. Reaction mixture was heated at the rate of 5 °C/min up to 240 °C with continuous stirring at 1650±10 rpm. Acid value was continuously measured until it reduced to 6mgKOH/g.

In monoglyceride process 0.2% sodium methoxide (w/w% to the oil) and required amount of polyol were added to the reaction mixture at 240 °C with continuous stirring at 1650±10 rpm. In the presence of catalyst, reaction mixture achieved homogeneous clear solution to methanol tolerance test (1 volume of reaction mixture: 2-3 volume of methanol)²¹ within 90 min at 240 °C under continuous stirring at 1650±10 rpm.

In polyesterification step, reaction mixture was cooled to 160 °C and required amount of phthalic anhydride was added to the reaction mixture under continuous stirring. 5% of xylene (w/w %) to the initial weight of polyesterification mixture was used as an azeotropic solvent. Reaction mixture was heated up to 200 °C under continuous stirring at 1650±10 rpm. N₂ gas was bubbled through out the polyesterification reaction to remove produced water from the reaction mixture to facilitate the polyesterification reaction equilibrium to forward direction. Temperature of the reaction mixture maintained at 200 °C while measuring the acid value at frequent intervals until it reached to gel point.

Non volatile content of the resultant alkyd was adjusted to 60w/w % by adding suitable amount of commercial turpentine. Cobalt octate (0.04w/w%), calcium octate (0.12w/w%) and zirconium octate (0.2w/w %) were used as drying agents and required amount of 60w/w % alkyd resin solution and drying agents were properly mixed to prepare varnish. Physicochemical properties of the varnish were determined. Prepared varnishes were applied on glass plate, metal plate and thin tin plate using 25 micron applicator bar to evaluate set-to-touch drying time, dry-to-touch drying time, pencil hardness, flexibility, and solvent resistance properties. An alkyd resin sample from commercial scale paint manufacturer in Sri Lanka was used as a reference and film properties were evaluated against the reference sample.

4.2 Determination of Physicochemical properties of seed oil and resulted alkyd resins

4.2.1 Acid value

Acid value of extracted seed oil sample and prepared alkyd samples were determined according to the ASTM D 1639-70. Acid value is expressed as the milligrams of KOH required to neutralize free fatty acid in one gram of oil. However for the practical purposes, NaOH is interchange with KOH but the result is always expressed in KOH equivalents²³.

Acid value = (Volume of NaOH × [NaOH] × 56.1) / sample weight

Seed oil mainly contains triglyceride of fatty acids with some amount of free fatty acids. Amount of free fatty acid content vary from type of source of the seed oil, seed condition and extent of refining. It is not useful for the identification of the type of oil.

Acid value of the alkyd resin depends on the amount of unreacted polybasic acid in the alkyd mixture. Extent of the polymerization depends on the final acid value of the alkyd resin.



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations

4.2.2 Saponification value mrt.ac.lk

Saponification value of the extracted seed oil sample was determined according to the ASTM D 1962. Saponification number is defined as the number of milligrams of potassium hydroxide that react with one gram of oil. It is not only for the neutralization of free fatty acid but also for the saponification of ester bonds in triglycerides of oil. This value is important to determine the molar mass of oil contains low amount of free fatty acids. Basically oil sample is refluxed with excess KOH for a sufficient period of time to break the ester linkages in monoglyceride, diglyceride and triglyceride as well as to neutralize the free fatty acids. Remaining amount of KOH is titrated with standard HCl solution. Same KOH solution was refluxed according to the same procedure and titrated with same HCl solution as a blank. Saponification value is calculated as follows.

Saponification value =
$$\frac{(\text{Volume of HCl for sample} - \text{Volume of HCl for blank}) \times [\text{HCl}] \times 56.1}{\text{sample weight}}$$

4.2.3 Viscosity

Viscosity of seed oil sample was determined using Brookfield viscometer with spindle No2, 60 rpm.

Viscosity of the alkyd resin sample was determined according to the ASTM D 1545. This method describes the time (bubble seconds) required to travel of an air bubble in cylindrical body tube called bubble viscosity tube at temperature 25 °C³⁴.

4.2.4 Clarity

Clarity was determined according to ASTM D 2090. Resin and oil samples were placed in a bubble viscosity tube and subjectively rated with respect to the water clarity.

4.2.5 Colour

Colour of the oil and resins were determined visually and using Lovibond 2000 colour compactor as per ASTM D 1544-80.



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

4.2.6 Non Volatile Matter content

Non volatile matter content was determined according to ASTM D 1259. Known amount of oil and resin samples were heated in an air oven at 105±2 °C for 90 min.

4.2.7 Specific gravity

Specific gravity was determined in seed oil according to the ASTM D 268. Standard gravity bottle was used for both oil sample and water at 25 °C.

4.3 Testing of film properties

60w/w % varnish was prepared using each alkyd resin sample prepared based on blend of Nahar & Karawila seed oil with commercial turpentine as a solvent and Co, Zr & Ca as

dryers. Varnish from reference alkyd sample was also prepared using same procedure. Those varnishes were used to evaluate film properties.

4.3.1 Testing of drying properties

Set-to-touch & dry-to-touch drying times of the film prepared from varnish solution were evaluated according to ASTM D640-69. A standard applicator rod (25 microns) was used to spread the varnish solution on Tin plates. Test specimens were exposed to diffuse day light at temperature 30 °C and relative humidity 50%.

4.3.2 Set -to-touch drying time

Set -to-touch drying time is very simple method to evaluate drying time of wet film. Wet film clings to the finger and degree of clinging depend on drying rate. Film is set-to-touch when the film does not transfer to the finger. At the end point of the test, film material should not be transferred from finger tip to clean glass plate.

4.3.3 Dry-to-touch drying time



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

After completion of set-to-touch, film surface is still sticky even though film material does not transfer to the finger tip. Film is dry-to-touch when it no longer adheres to the finger tip and does not rub up appreciably when the finger is lightly rubbed across the surface.

4.3.4 Testing of Hardness of dried film

Pencil method is used to evaluate hardness of the dried film after 48 hours from the application. Pencils are available in seventeen different grade of hardness. 9H is the one end represent harder film and other ends represent 6B for the soft film. Hardness of the seventeen pencils is increased as follows.

6B,5B,4B,3B,2B,B,HB,F,H, 2H,3H,4H,5H,6H,7H,8H,9H

Test was carried out according to the ASTM 3363-92a by using pencil hardness tester. A film coated plate is placed on horizontal surface on the tester and pencil is firmly held against the film at an angle of 45° and pushed away from the operator for 6.5 mm. Test continued until the film is not scratched.

4.3.5 Testing flexibility of dried film by conical mandrel

Flexibility of dried film was rated according to ASTM D522-92. Mandrel bend test is used to evaluate the flexibility/resistance to cracking of the dried film on metal plate using standard conical mandrel.

4.3.6 Testing of solvent resistance properties

Solvent resistance properties were determined using an absorbent medium method as per ISO 2812-1. Absorbent discs wetted with test solvent were placed on the dried film in horizontal position and covered with a watch-glass. The time taken to appear any sign of deterioration of the coating was observed.

4.4 Calculation procedure of recipes

Nahar seed oil, Karawila seed oil, pentaerythritol and phthalic anhydride were formulated to obtain alkyd with 65w/w % oil length as follows.

Stoichiometric reaction between free fatty acids and pentaerythritol is 2:1 as shown in figure 4.1. During the oil upgrade process, two moles of free fatty acids are producing two moles of water. Required amount of pentaerythritol was calculated for the oil upgrade process according to that.

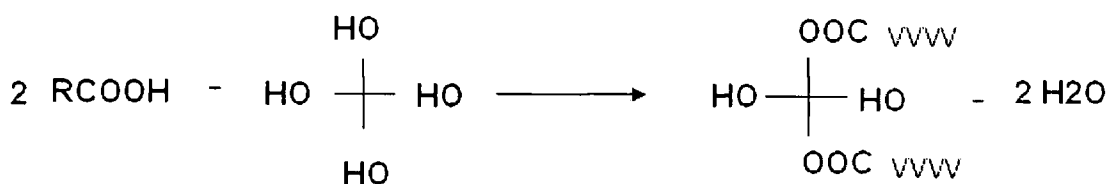


Figure 4.1: Reaction between free fatty acid and pentaerythritol

Stoichiometric reaction between triglycerides and pentaerythritol is 1:1 as shown in figure 4.2 during monoglyceride process. Required amount of pentaerythritol was calculated for the monoglyceride process according to that.

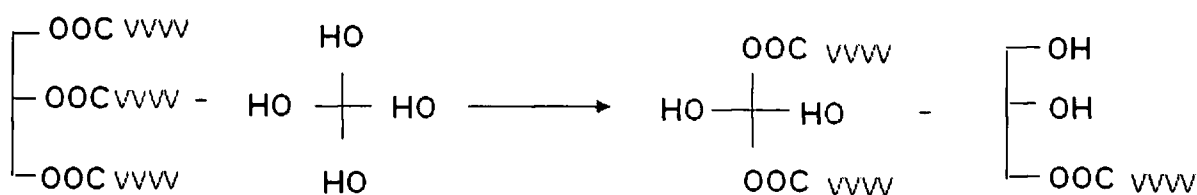


Figure 4.2: Reaction between triglyceride and pentaerythritol

Required amount of phthalic anhydride was calculated based on mass balancing to maintain oil length of 65w/w %. During the polyesterification reaction between monoglyceride and phthalic anhydride, one mole of water is produced by one mole of phthalic anhydride.

Recipe was calculated as follows;

Following symbols were used during the calculation of recipes.

1. M_{KOH} - Molecular weight of KOH
2. $M_{\text{H}_2\text{O}}$ - Molecular weight of H_2O
3. M_{PA} - Molecular weight of phthalic anhydride
4. M_{PE} - Molecular weight of pentaerythritol
5. M_{Noil} -Molecular weight of Nahar seed oil
6. M_{FFA} -Molecular weight of free fatty acid in Nahar seed oil

Table 4.1 Calculation procedure of recipe

No of moles of Karawila seed oil in Y g of oil	=	A
Acid value of the Nahar seed oil	=	a
Amount of free fatty acid in Y g of Nahar seed oil	=	$a \times Y / M_{KOH} \times 1000$
Moles of pentaerythritol required to neutralize free fatty acid in Y g of Nahar seed oil	=	$a \times Y / M_{KOH} \times 1000 \times 2$
Weight of pentaerythritol required to neutralize free fatty acid in Y g of Nahar seed oil	=	$a \times Y \times 3 M_{PE} / M_{KOH} \times 1000 \times 2$
Weight of free fatty acid in Y g of Nahar seed oil	=	$a \times Y \times M_{FFA} / M_{KOH} \times 1000$
Weight of oil in Y g of Nahar seed oil	=	$Y - (a \times Y \times M_{FFA} / M_{KOH} \times 1000)$
Moles of oil in Y g of Nahar seed oil	=	$[Y - (a \times Y \times M_{FFA} / M_{KOH} \times 1000)] / M_{Noil}$
Total No of oil moles	=	$A + [Y - (a \times Y \times M_{FFA} / M_{KOH} \times 1000)] / M_{Noil}$
Moles of pentaerythritol to react with oil	=	$A + [Y - (a \times Y \times M_{FFA} / M_{KOH} \times 1000)] / M_{Noil}$
Weight of pentaerythritol to react with oil	=	$(A + [Y - (a \times Y \times M_{FFA} / M_{KOH} \times 1000)] / M_{Noil}) \times M_{PE}$
Weight of monoglyceride (Z)	=	$\{2Y + (a \times Y \times 3 M_{PE} / M_{KOH} \times 1000 \times 2) + (A + [Y - (a \times Y \times M_{FFA} / M_{KOH} \times 1000)] / M_{Noil}) \times M_{PE}\} - [a \times Y \times M_{H_2O} / M_{KOH} \times 1000]$
From mass balancing for 65% oil length, No of moles phthalic anhydride required is considered as b;		
$2Y \times 100 / 65 = \text{Weight}_{\text{monoglyceride}} + \text{Weight}_{PA} - \text{Weight}_{H_2O}$		
$2Y \times 100 / 65 = Z + b \times M_{PA} - b M_{H_2O}$		
Weight of phthalic anhydride required to balance oil length	=	$(2Y \times 100 / 65) + b M_{H_2O} - Z$
Weight of Water produced during polyesterification	=	$b M_{H_2O}$
Total weight produced during whole synthesis process	=	$b M_{H_2O} + \{(a \times Y / M_{KOH} \times 1000) \times M_{H_2O}\}$

Excess OH was calculated as a percentage to the total number of stoichiometric moles of OH in the monoglyceride process. Four recipes of prepared alkyd resins were summarized as shown in Table 4.2 respectively. Recipe with 12% excess OH is represented as NK12 whereas 18%, 24% and 30% excess OH are represented as NK18, NK24 and NK30 respectively.

Table 4.2: Recipe of each alkyd resin

Experiment	Nahar & Karawila seed oil (W/W%)	Pentaerythritol (W/W %)	phthalic anhydride (W/W %)	Water (ml)
NK12	65	11.98	26.48	4.95
NK18	65	13.75	24.46	4.82
NK24	65	13.16	25.14	4.70
NK30	65	12.57	25.81	4.57



University of Moratuwa, Sri Lanka
 Electronic Theses & Dissertations
www.lib.mrt.ac.lk

Chapter 5

Results and Discussion

Physicochemical properties of the Nahar seed oil, Karawila seed oil and prepared alkyd resins were determined as per the standard test methods indicated in section 4.2, chapter 4 and obtained results are tabulated in Table 5.1 and Table 5.3.

Table 5.1: Physicochemical properties of Nahar & Karawila seed oil

Property	Nahar seed oil	Karawila seed oil
Oil content (w/w %)	65	26
Specific gravity	0.910	0.930
Saponification value (mgKOH/g)	234.94	203.94
Free Fatty acid content (w/w %)	11.72	1.34
Acid value (mgKOH/g)	23.75	2.87
Colour	Reddish-brown	Yellowish-brown
Lovibond colour index	50+	35+
Viscosity (Cps)	16	17
Moisture content (w/w %)	0.1	0.1

Oil content of the Nahar seed oil in the present study using solvent extraction process was ~65w/w %. It is closer to the oil content of Nahar seed (~75w/w %) extracted using hydraulic pressing method² but little less because during the hydraulic pressing not only the oil but also other types of polysaccharides, proteins, gum-resins can be extracted. Oil content of the karawila seed was ~26w/w % which is comparable to the literature (~24w/w %) ⁴. Results of the moisture content of the both Nahar and Karawila seed oil confirmed that both oils were properly dried.

Generally free fatty acids in fatty oil are relatively small since most of the fatty acids are in triglycerides form. However acid value can be increased due to the activity of lipase enzyme on triglycerides to hydrolyze it into free fatty acids and other products like monoglycerides, diglycerides⁸. Acid value depends on the origin, weather and soil condition of the tree. Thus acid value of Nahar seed oil origin in India is 34 mgKOH/g⁵ whereas Nahar seed oil used in present study origin in Sri Lanka was around 24 mg KOH/g.

Saponification value obtained for both Nahar and Karawila seed oil in this study were almost same as saponification value of Nahar seed oil (241 mg KOH/g) and Karawila seed oil (190.7 mg KOH/g) in literature^{4, 5}.

Specific gravity of Nahar and Karawila seed oils were almost same as most of the vegetable oils.

In the present study four different types of alkyd resins with varying amount of excess OH were prepared using oil upgrading process, monoglyceride process followed by polyesterification reaction.

Oil upgrading process was carried out to reduce the free fatty acid content in the Nahar seed oil from 23.75 mg KOH/g to 6 mgKOH/g. If the amount of free fatty acid in the fatty oil is high, it is neutralized the basic catalyst used in the monoglyceride process by forming metallic soap. This will reduce the catalytic activity. Metallic soap also can act as a catalyst when it ionized. This ionization is taken place at low fatty acid medium otherwise high fatty acid concentration is suppressed that. Since that it is necessary to reduce acid value to somewhat lower before carrying out the monoglyceride process. As per the figures shown in 5.1, 5.2, 5.3 and 5.4 this process was taken around 120 min. Fatty acids were neutralized with pentaerythritol producing dipentaerythritide and water as shown in figure 4.1. Since that free fatty acid content in the oil was reduced and acid value was decreased.

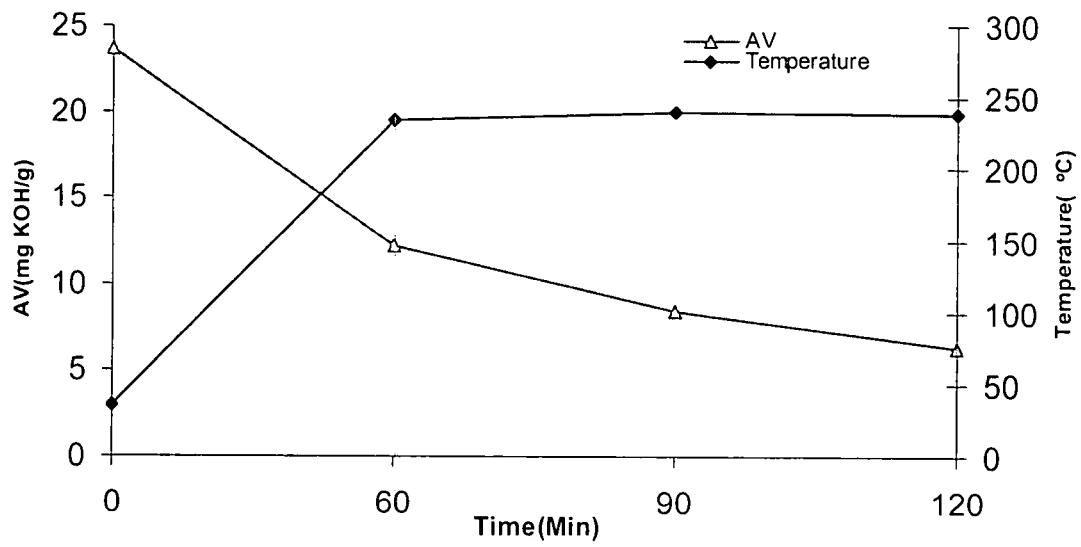


Figure 5.1: Acid value & temperature Vs Time during oil upgrade process for NK12

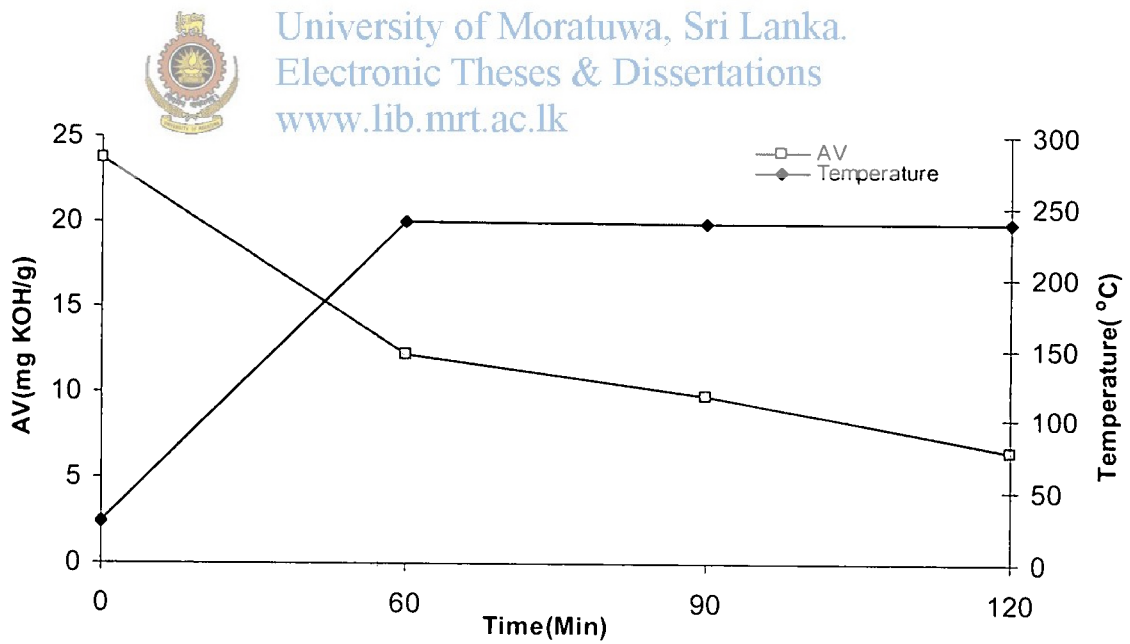


Figure 5.2: Acid value & temperature Vs Time during oil upgrade process for NK18

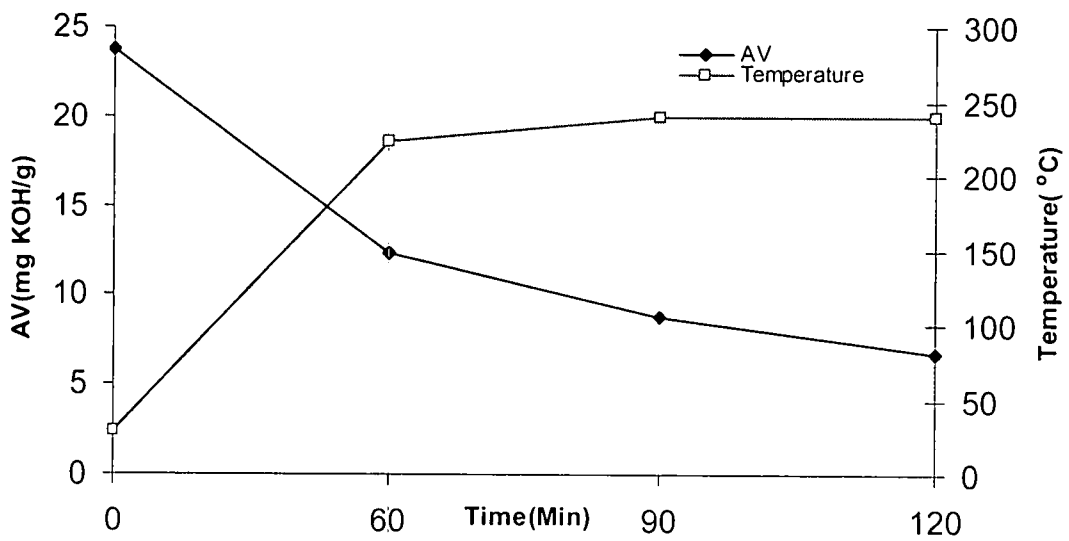


Figure 5.3: Acid value & temperature Vs Time during oil upgrade process for NK24

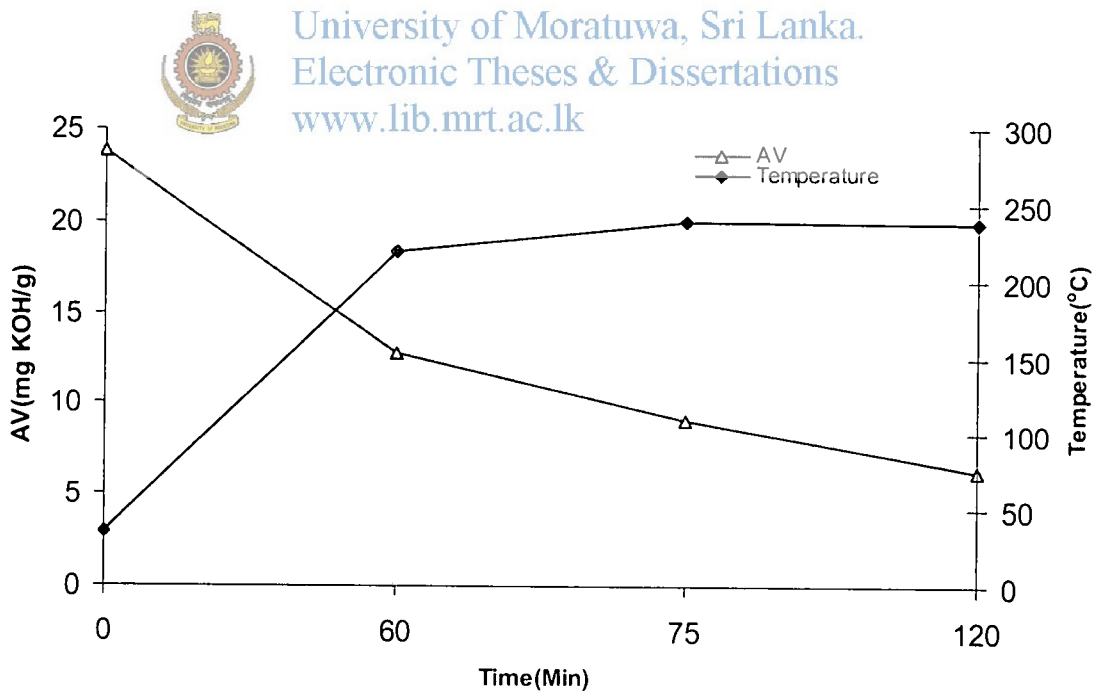


Figure 5.4: Acid value & temperature Vs Time during oil upgrade process for NK30

For the synthesis path of alkyd resin, monoglyceride process was used due to the comparatively low acid value of Nahar and Karawila seed oil. Heating rate was major process parameter during the synthesis of alkyd resin since heating rate up to 240 °C was affected the yield and time requires to complete the monoglyceride process as well as to prevent sublimation of pentaerythritol inside the reaction flask. Sublimation of pentaerythritol was also inversely affected the yield of monoglyceride. 5 °C/min and 1650±10 rpm were considered as optimum heating rate and stirrer speed respectively.

Monoglyceride process was carried out to form homogeneous mixture of less polar oil and relatively more polar polyol and dibasic acid. As per the figures shown in 5.5, 5.6, 5.7 and 5.8 this process was taken around 90 min. During this process fatty oil was reacted with pentaerythritol and produced monoglyceride and dipentaerythritide as shown in figure 4.2. This process was carried out at 240 °C to achieve maximum amount of monoglyceride within short period of time with relatively low amount of ether formation from polyols.

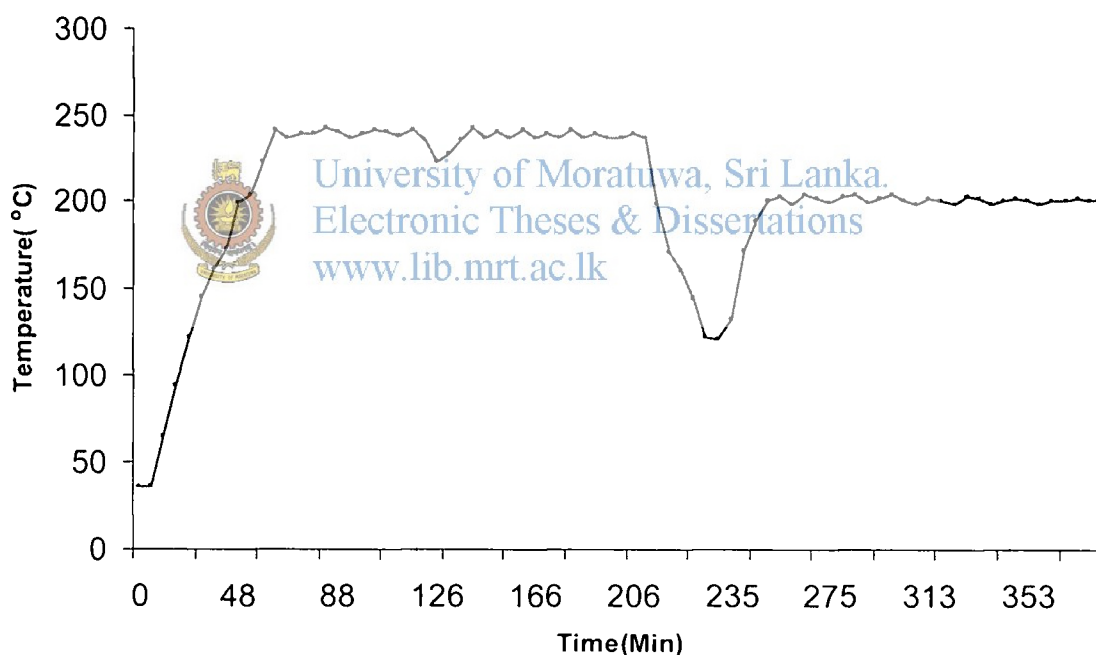


Figure 5.5: Temperature profile for NK12

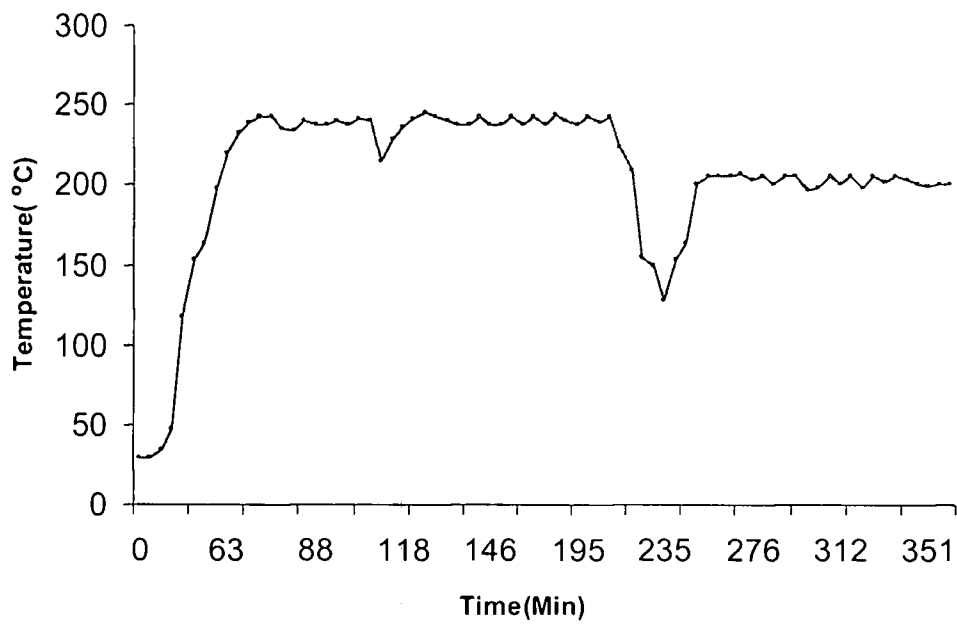


Figure 5.6: Temperature profile for NK18



University of Moratuwa, Sri Lanka.
 Electronic Theses & Dissertations
www.lib.mrt.ac.lk

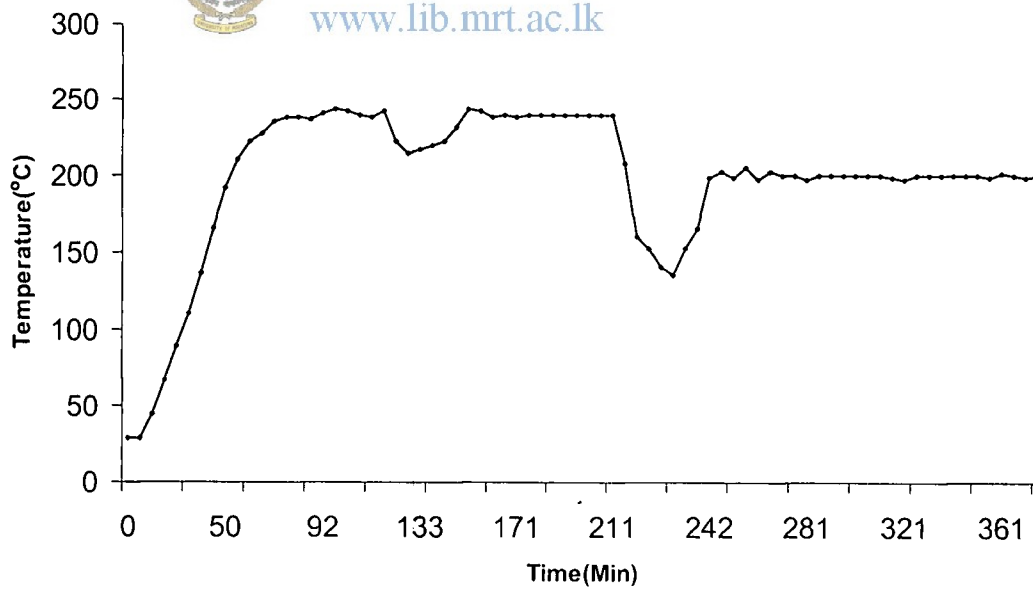


Figure 5.7: Temperature profile for NK24

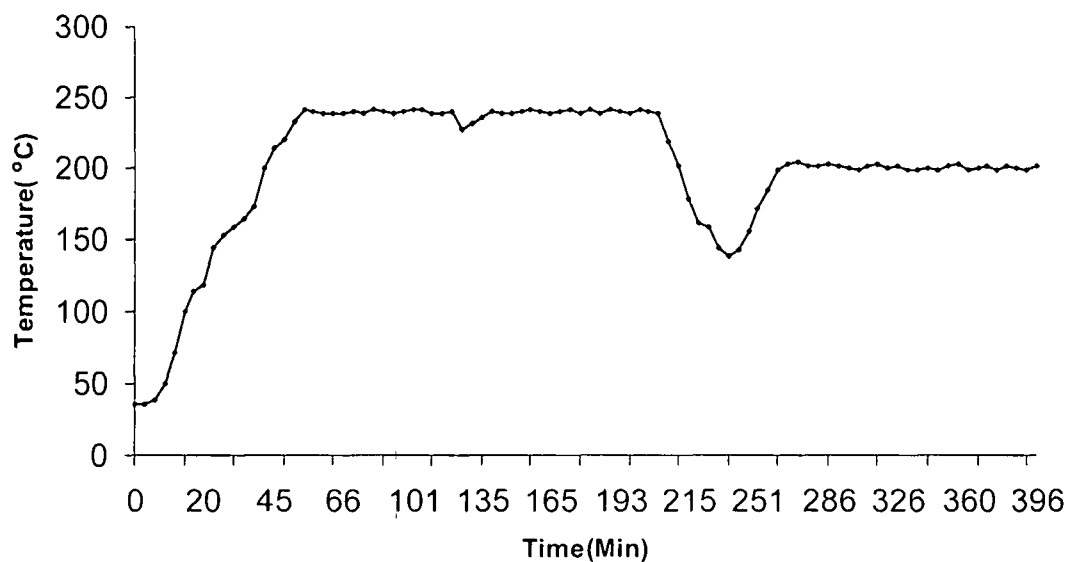


Figure 5.8: Temperature profile for NK30



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

Before starting the polyesterification reaction temperature of the reaction mixture was reduced to 160 °C and phthalic anhydride was added at that temperature. This was help to reduce the rate of polyesterification reaction during the addition period of phthalic anhydride. As per the figures shown in 5.9, 5.10, 5.11 and 5.12 further reductions in temperature about 25-30 °C were observed during the each addition of pentaerythritol and phthalic anhydride at the beginning of monoglyceride process and polyesterification reaction respectively.

Normally polyesterification is conducted at temperature 200- 260 °C. As per the figures shown in 5.9, 5.10, 5.11 and 5.12 this process was carried out at 200 °C since the time taken to complete the polyesterification reaction was reasonably low (2 1/2 hours) for all four recipes. This indicates that rate of condensation reaction for these recipes were quiet high at even 200 °C. During the polyesterification reaction acid value was decreased as per the figures shown in 5.9, 5.10, 5.11 and 5.12 due to formation of ester linkages from carboxylic groups. Thus the final acid value of the reaction mixture is an indication of the extent of polymerization near gel point.

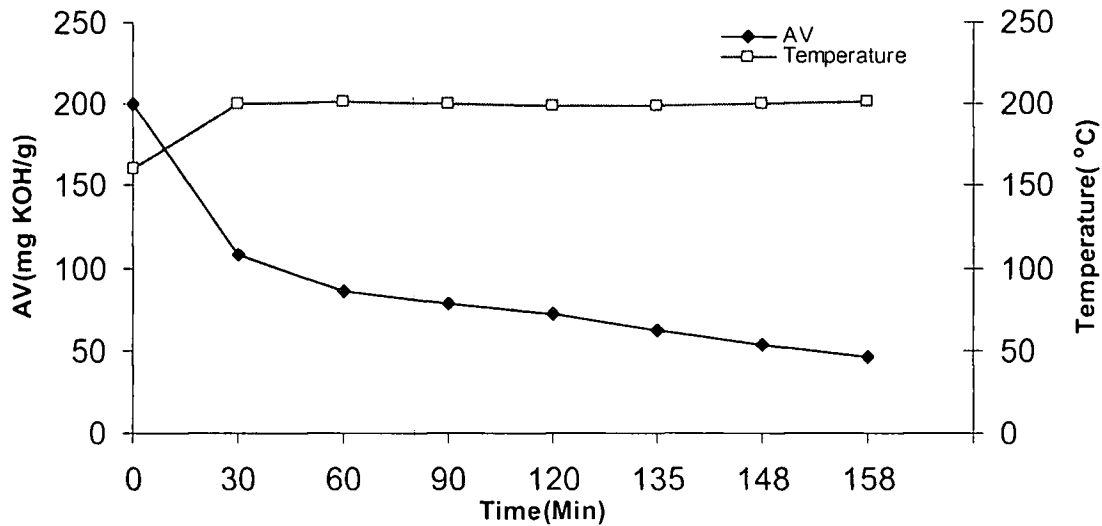


Figure 5.9: Acid value & temperature Vs Time during polyesterification reaction for NK12



University of Moratuwa, Sri Lanka.
 Electronic Theses & Dissertations
www.lib.mrt.ac.lk

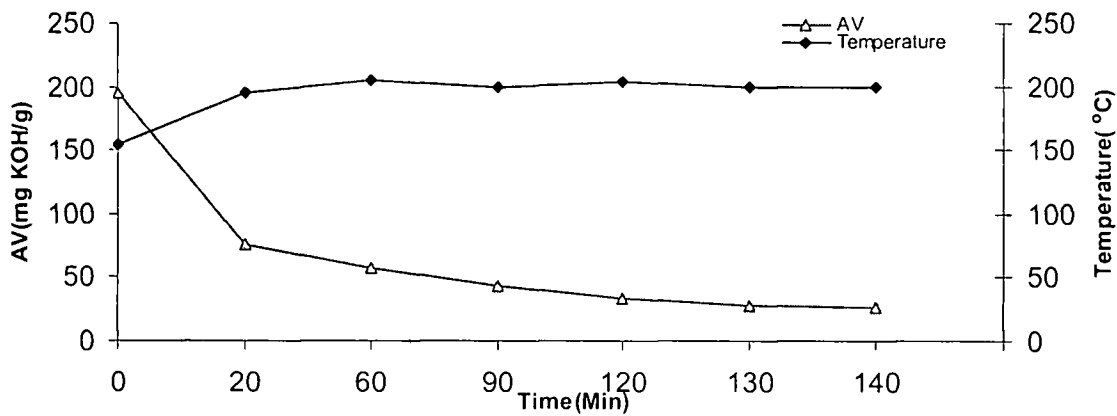


Figure 5.10: Acid value & temperature Vs Time during polyesterification reaction for NK18

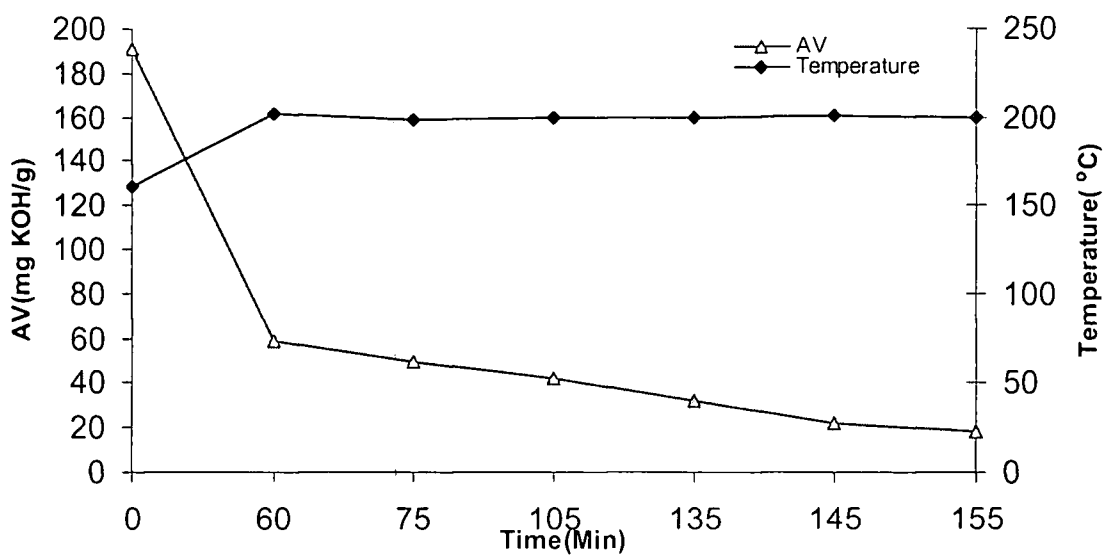


Figure 5.11: Acid value & temperature Vs Time during polyesterification reaction for NK24

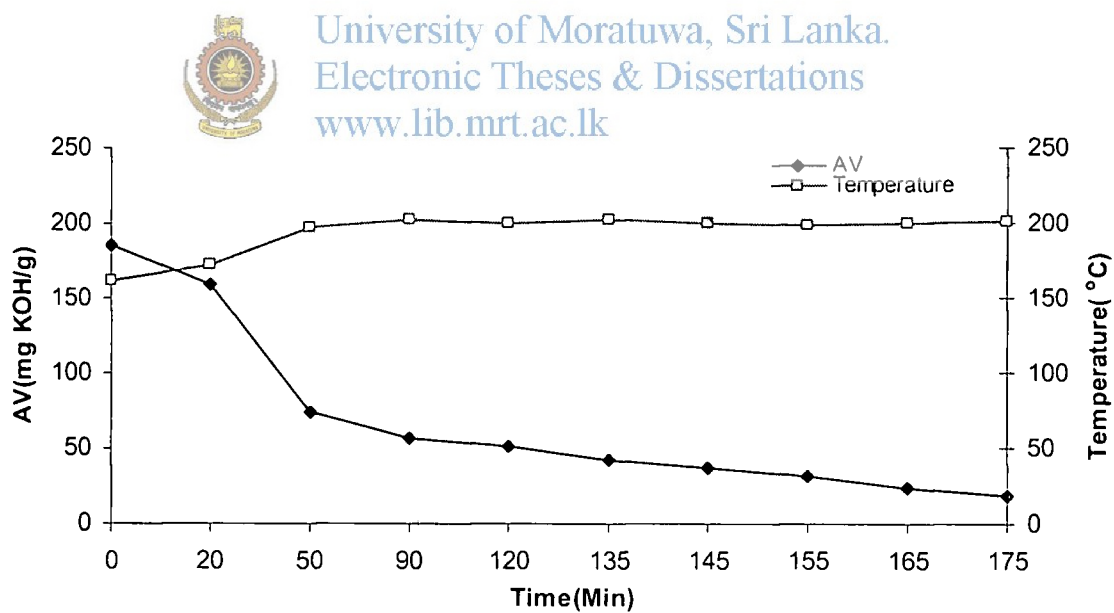


Figure 5.12: Acid value & temperature Vs Time during polyesterification reaction for NK30

OH/COOH ratio and Patton constant were increased with the increase of excess OH as indicated in Table 5.2. Average functionality (f_{av}) was also increased with the increase of excess OH since more and more functional groups were adding to the reaction mixture. Extent of the polymerization (p) was also increased with the increase of excess OH since excess OH can be shifted the equilibrium of the polyesterification reaction to forward direction.

Table 5.2: Experimental data obtained for resulted alkyd resins

Experiment	OH/COOH ratio	Patton constant	f_{av}	P
NK12	0.9056	0.9477	2.0513	0.7719
NK18	0.9789	0.9718	2.0768	0.8623
NK24	1.0564	0.9972	2.1025	0.9036
NK30	1.1379	1.024	2.1283	0.8988



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations

Table 5.3: Physicochemical properties of resulted alkyd resins

Property	NK12	NK18	NK24	NK30
Acid value (mgKOH/g)	45.79	26.92	18.36	18.76
Colour	Dark-brown	Dark-brown	Dark-brown	Dark-brown
Lovibond colour index	90+	90+	90+	90+
Viscosity (Sec)	720	509	371	270
Non Volatile Matter(w/w%)	91.52	93.50	93.49	93.17
Yield (w/w %)	87.81	93.83	85.33	89.57



The yield of the resins found to be very high (80-90w/w %) from the theoretical yield of the each resin.

During the increase of excess OH from NK12 to NK30, increase the OH/COOH ratio in the system. Since that increase the probability of forming more ester linkages and decrease the amount of free COOH groups in the system. Hence final acids value of the resultant alkyd resins were decreased from 45 mgKOH/g to 18 mgKOH/g. Extent of the polymerization (P) of each alkyd resin was calculated based on final acid value. P increased with increased amount of excess OH. This may be due to the presence of excess OH, equilibrium of the polyesterification reaction can be shifted to forward direction to reduce the concentration of OH in the reaction mixture.

Bubble viscosity was decreased with the increased amount of excess OH confirmed that highly branched alkyd molecules were formed and branching were increased with the excess OH since this was supplied by multifunctional polyol. Highly branched architecture can be achieved using multifunctional monomers which help to reduce the viscosity of the resultant alkyd mixture due to loose packing of branched molecules than its linear counterpart.

Lovibond colour index for all alkyd resins are 90+, whereas Karawila seed oil showed 35+ and Nahar seed oil showed 45+. Colour intensity of the alkyd resins was higher than the corresponding oils.

Film properties and solvent resistant properties of prepared alkyd resins were determined as per the standard test methods indicated in section 4.3, chapter 4 and obtained results are tabulated in Table 5.4 and Table 5.5.

According to the observed results indicated in the Table 5.4 set-to-touch drying time and dry-to-touch drying time are comparatively low for all four alkyd resins. Even though Nahar seed oil is a non drying oil, resultant alkyd shown good drying properties after 50:50w/w% blends with good drying oil of Karawila seed. This remarkable drying property of karawila seed oil is due to the presence of ~65w/w% of eleosteric acids. Eleosteric acids contain three conjugated double bonds at 9th, 11th and 13th carbon atoms⁴. Fast drying is attributed through the formation of 1,4 and 1,6 diradicals with O₂ in the presence of air on the eleosteric acid. These diradicals can be reacted with the unsaturation groups on the oleic and linoleic acid in the Nahar seed oil and can be formed -C-C- and -C-O-O-C- cross links in-between polymer molecules. This may be the reason for fast drying of Nahar seed oil after blending with Karawila seed oil.

Table 5.4: Film properties of resulted alkyd resins

Experiment	Set to touch drying time/Min	Dry to touch drying time/Min	Clarity	Scratch Hardness (After 48 hours)	Bend Test
Reference	40	80	Water clear	3H	Pass
NK12	29	74	Water clear	H	Pass
NK18	44	104	Water clear	2H	Pass
NK24	64	126	Water clear	3H	Pass
NK30	89	151	Water clear	H	Pass

Set-to-touch drying time was increased with increased amount of excess OH from pentaerythritol due to the formation of highly branched structure with lower viscosities. During the film formation, alkyd resin molecules are loosely packed due to the highly branched structure. This will automatically reduce the film compactness. This may lead to difficulties in forming inter-molecular interactions between polymer molecules caused increased set-to-touch drying time from NK12 to NK30. In addition to that reduced the rate of O₂ penetration inside the film due to the formation of highly branched network structure may also cause the increased set-to-touch drying time.

Dry-to-touch drying time was also increased with addition of excess OH. Since pentaerythritol was used as a polyol for stoichiometric amount of OH as well as the excess OH, amount of excess OH increased means increased the amount of tetrahedral branching units in the reaction mixture. Since that highly branched alkyd molecule can be produced. Intra molecular cyclization can be occurred in branched loops and solvent molecules can be entrapped in the cyclic structures may cause longer dry-to-touch drying time with increase the percentage of excess OH from NK12 to NK30.

Improved scratch hardness of all four types of alkyd resins indicated that forming of rigid network structure due to the presence of tetrahedral branching sites in alkyd resins as a

result of pentaerythritol. Scratch hardness was improved from NK12 to NK24. Since excess OH has supplied by pentaerythritol, with the increase amount of excess OH rigidity of the net work may be increased due to the formation of more and more branching structures. However scratch hardness was decreased in NK30 may be due to the formation of intra molecular cyclization over inter molecular cross linking. Intra molecular cyclization within the branch loops may hinder the formation of inter molecular interactions. This may be reduced the strength of the forming network results lower scratch hardness. This is indicated that degree of branching needs to be optimized to achieve the superior film properties.

Even though all alkyds form highly branched network structure, films were flexible enough to pass bend test as per ASTM D522-92.

Clarity of all alkyd resin solutions were almost comparable to water clarity indicated that resins were properly formed without any particulate matters.

Table 5.5: Solvent resistance properties of resulted alkyd resins

Experiment	Water resistance/Min	0.5M HCl Resistance/Min	0.5M NaOH Resistance/Min
Reference	White patches observed after 3hrs	White patches observed after 3hrs	Film damaged after 1 hr
NK12	White patches observed after 1hr	White patches observed after 1hr	Film damaged after 15 min
NK18	White patches observed after 2hrs	White patches observed after 2hrs	Film damaged after 20min
NK24	White patches observed after 3hrs	White patches observed after 3hrs	Film damaged after 45 min
NK30	White patches observed after 21/2hrs	White patches observed after 21/2hrs	Film damaged after 30min

Water and acid resistance properties were increased from NK12 to NK24 and NK24 was almost comparable to reference sample as shown in the Table 5.5. Even though

OH/COOH ratio was increased with the addition of excess OH, extent of the polymerization was increased by reducing the final acid value. Since that most of the polar groups (OH & COOH) are involved to form ester linkages. Hence that water and acid resistance were increased with the addition of excess OH. It also indicated that the forming of more and more branched structures with the addition of excess OH which can prevent the penetration of water and acid molecules through the surface of dried film. With compared to the solvent resistance between NK24 and NK30, NK24 was superior to the NK30 was also confirmed the results obtained for scratch hardness. That means rigidity of the net work depends on the number of branching on the polymer chain.

The poor alkali resistance of all four alkyd resins was due to the presence of alkali hydrolysable ester groups. Alkali resistance was slightly increased from NK12 to NK24 as indicated in Table 5.5 also confirmed that the forming of highly branched net work structure which can prevent reach of alkali molecules to the ester linkages. Alkali resistance of NK24 was also inferior to the reference sample. Alkali resistance data were also confirmed the weaken of net work structure in NK30 due to the formation of intra molecular cyclization within the branched loops.



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

Chapter 6

Conclusion and future work

6.1 Conclusion

This research project is mainly focused on using a non drying natural fatty oil to produce a long oil air drying alkyd resin combined with a good drying oil. According to the literature most of the locally available fatty oils are non drying oils. Nahar seed oil was selected as a non drying oil since Nahar seed has high oil content. Karawila seed oil was selected as drying oil since it was identified as a good drying oil from a previous research³. Remarkable drying property of karawila seed oil is due to the presence of considerable amount of eleosteric acids.

Physicochemical properties were determined in both Nahar and Karawila seed oils for selecting the synthesis path of alkyd resin. Monoglyceride process is recommended to synthesis alkyd resin due to the comparatively low acid value of Nahar and Karawila seed oil. Heating rate is major process parameter during the synthesis of alkyd resin. Heating rate up to 240 °C is affected the yield and time requires to complete the monoglyceride process as well as to prevent sublimation of pentaerythritol inside the reaction flask. Sublimation of pentaerythritol may be also inversely affected the yield of monoglyceride. 5 °C/min and 1650±10 rpm were considered as optimum heating rate and stirrer speed respectively.

Considering the four recipes, final acid value was decreased with increasing amount of excess OH. However final acid value was 18 mgKOH/g even in NK30. This is somewhat higher than the acid value of normal air drying alkyd resins which is around 10 mgKOH/g.

Formation of highly branched structure with increase amount of excess OH supplied by pentaerythritol was confirmed by the gradual reduction of viscosity. Gradually increased of drying time and hardness with the increase of excess OH also indicated that the forming of more and more rigid net work through branching up to some extent.

Alkali resistance was poor in all types of alkyd films compare to the reference sample due to the presence of alkali hydrolysable ester linkages. Water and acid resistance were improved with the increase amount of excess OH up to some extent and NK24 was comparable with reference sample. This is also indicated that the formation of branched

net work structure which can prevent the entering of solvent molecules through the surface of the film.

However scratch hardness results and solvent resistance results were indicated that branching needs to be optimized to achieve superior film properties.

Among the formulated four recipes, resin NK24 and NK30 showed satisfactory viscosity, drying properties, hardness and solvent resistance properties. Since that present study can be concluded resins formulated between 1.0564 to 1.1379 OH/COOH ratios and 0.9972 to 1.024 alkyd constants are considered as general guideline for preparing a long oil air drying alkyd resin with better film properties using blend of Nahar and Karawila seed oils together with pentaerythritol and phthalic anhydride.

6.2 Future work

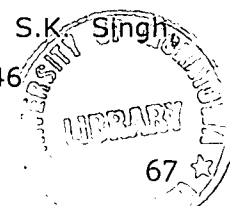
- 1) Final acid value of the resin need to be further reduced to 10 mgKOH/g by partially replacing pentaerythritol from glycerol in the two recipes NK24 and NK30.
- 2) Monoglyceride process needs to be optimized to achieve high yield of monoglyceride within short period of time without formation of unnecessary reactions like etherification. Volume fraction, stirring speed, heating rate and temperature of monoglyceride process to be studied using conductivity data to optimize the monoglyceride process.
- 3) Solvent is used to recover sublimed phthalic anhydride. Effects of solvent for the synthesis process and film properties have to be studied.
- 4) Evaluation of rheological behavior of alkyd and the diluted varnishes at different solid content prepared with different types of multifunctional polyol has to be studied to identify the optimum solid content of varnish with brushable viscosity to curtail the emission of organic solvents.

6.3 References

1. Joel R. Fried, polymer Science & Technology, Prentice – Hall Inc., 1995, Page 675-687
2. Henry Fleming Payne, Organic Coating Technology, Vol 2, John Wiley & Sons Inc, 1961, page 675-690
3. Jan w. Gooch, Emulsification and polymerization of alkyd resins, Kluwer Academic/plenum publishers, Page 1-25
4. M.A.B. Prashantha, Synthesis and characterization of novel alkyd resin based on Karawila seed oil, PhD thesis, 2007, page 1-160
5. N.Dutta, N.Karak, S.K.Dolui, synthesis and characterization of polyester resins based on Nahar seed oil, Progress in organic coating, 2004, 49, page 146-152
6. S. Ogunniyi, T.E. Odetoye, Preparation and evaluation of tobacco seed oil-modified alkyd resins, Bioresource Technology, 2008, 99, page 1300-1304
7. M.D.Dassanayake A revised hand book to the common trees and shrubs of Sri Lanka, Page 106-107
8. Allen J.St. Angelo, Aaron M. Altschul, Plant physiology, 1964, page 880-885
9. D.M.A. Jayaweera, Medicinal plants (Indigenous & Exotic) used in Ceylon, part 3, page72-73
10. Mark Anton, Savitri Gunatilaka, Neela de Zoysa. M.D. Dassanayaka, Nimal Gunatilaka, Siril Wijewardana, A field guide to the common trees and shrubs of Sri Lanka1997, Page 139
11. Luisella Verotta, Erminio Lovaglio, 4-Alkyl and 4-phenyl coumarins from Mesua ferrea as promising multidrug resistant antibacterials, 2004, page 1143-1144
12. H.K. Kakrani, antimicrobial and anthelmintic activity of essential oil of Mesua ferrea Linn, Ind drugs 21 (6), 1984, Page 262-621
13. S.R.Jain, H.R. Jain, Effect of some common essential oil on pathogenic fungi, Plant Med 24, page 127-142
14. M.B. Bhide, Studies on the antiasthmatic activity of Mesua ferrea, Bull Haff Inst 5,27,1977, page 1122-1124
15. Rupa Mazumder, Sujata G. Dastidar, S.P. Basu, Avijit mazumder, S.K. Singh, Antibacterial potentiality of Mesua ferrea Linn. Flowers, 2004, page 1245-1246



University of Moratuwa, Sri Lanka
Electronic Theses & Dissertations
www.lib.mrt.ac.lk



16. D.M.A. Jayaweera, Medicinal plant (Indigenous and Exotic) used in Ceylon, Part 3, page 154-155
17. www.spectrumingredients.com/product/gen_info/oil_extract.html, 2008/10/13
18. Bhupesh C. Roy, Motonobu Goto & Tsutomu Hirose, International Journal of food Science & Technology, 2003, volume 31, issue 2, page 137-141
19. G.P.A. Turner, Introduction to paint chemistry & principles of paint technology, 3rd edition, Chapman and Hall Ltd, 1988, page 148-161
20. C.Stewart Ferguson, Jesse E. Sellar, Protective & Decorative coatings, New York John Wiley & Sons Inc., vol 1, Page 338-359
21. Swaraj Pawl, Surface coating, Wiley interscience publication, 1985, page 70-134
22. Zeno W. Wicks, Frank N. Jones, S.Peter Pappas, Organic coating science & technology, Vol2, John Willey & sons Inc,194, Page197-207
23. Gardner Sward, Paint testing manual ASTM special technical publication, 500, 1972, Page 55-58
24. Robert H. Runk, Industrial and engineering chemistry, 1952, Vol 44, page 1124-1126
25. Painting and decorating craftsman's manual and text book, 4th edition, painting & decorating contractors of America Inc, 1965, page 57-78
26. Gordon Fettis, Automotive paints and coatings, VCH publishers, 1995, Page 76-85
27. Baboo Lal Aggarwal, Technology of paints, varnishes, lacquers and driers, small business publications, page 106-131
28. Swaraj Pawl, Surface coating, Wiley interscience publication, 1985, page 452-457
29. George Odian, Principle of polymerization, Wiley Inter science publication, 2nd edition, page 109-127
30. A.R.Anderson, I.M. Thomas, Encyclopedia of chemical technology, 2nd edition, Vol 1, Page 851-864
31. Krzysztof Maczyk, Pawel Szewczyk, progress in organic coating, 2002, Vol 44, page 99-109
32. Syed Haseebuddin, Randhir Parmar, Gulzar Waghoo, Swapan K. Ghosh, Progress in organic coating, 2002, Vol 44, page 99-109

33. K.H.Zebel, R.P.Klaasen, W.J.Muizebelt, B.P.Gracey, C.Hallett, C.D. Brooks, progress in organic coatings, 35(1999), page 255-264

34. Zeno W. Wicks, Frank N. Jones, S.Peter Pappas, Organic coating science & technology, Vol2, John Willey & sons Inc,194, Page10

35. Dieter Stoye, Werner Freitag, Resins for coating, Henser/Gardner publication Inc., 1996, page 60-78



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

