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SYNTHESIS AND CHARACTERIZATION OF BIO RESIN FROM PALM OIL

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ABSTRACT:

Vegetable oil is one of the renewable bioresources which can be used as an alternative of petroleum-based raw materials for the preparation of polymeric materials. In this research work, polyalkyd-based resin was prepared from palm oil by using polycondensation reaction. A two-step method viz. alcoholysis and esterification was conducted to synthesize polyalkyd-based resin,. Prior to alcoholysis, crude palm oil was subjected for catalytic dehydration process to increase its unsaturation for the preparation of good quality alkyd resins. Five different catalysts such as sulphuric acid, para-toluene sulfonic acid, phosphoric acid, sodium hydrogen sulphate and potassium hydrogen sulphate were used for the dehydration of palm oil. In alcoholysis process, the triglyceride-based dehydrated oil was reacted with glycerol to produce monoglyceride. The optimum condition was used to prepare different types of alkyds by using five different types of acid anhydrides such as maleic anhydride, phthalic anhydride, succinic anhydride, 3,4,5,6-tetrahydrophthalic anhydride and cis-1,2-cyclohexanedicarboxylic anhydride. A comparison was drawn among the resins prepared by using different anhydrides. Comparison was also drawn in between aliphatic and aromatic anhydride containing resins. The produced bioresins were characterized for physico-chemical properties such as viscosity, density, iodine value, acid value, saponification value, drying time, non-volatile materials content, specific gravity, colour, etc. The resins prepared from optimum reaction parameters were subjected for curing process by using methyl ethyl ketone peroxide (MEKP), as initiator, and cobalt naphthanate, as dryer. To enhance the resinous property, multi-walled carbon nanotubes were dispersed into the resin at different percentages of loading such as 0.5, 1.0 and 1.5 wt.%. The filler loading was optimized regarding the end properties of the film produced by incorporating them. Finally, in-situ polymerization with carbon nanotubes during esterification was performed by adding optimum percentage of loading. A comparison of the properties of the films was drawn among the optimum loaded nanotube-based film, in-situ reacted nano-tube based film and the films with different percentages of loading and that of without using carbon nano tube. The films were characterized by different testing such as adhesion, chemical resistivity, thermogravimetric analysis, differential scanning calorimetry, field-emission scanning electron microscopy, x-ray diffraction analysis, contact-angel measurement, tensile testing, elongation at break, pencil hardness, gloss etc. Finally, the curing kinetics of the resin was analysed to evaluate the kinetic parameters such as reaction rate, activation energy, degree of conversion in terms of time and temperature. Result analyses through RSM revealed a desirability of 0.985, predicted reaction time of 88.64 min, catalyst concentration of 0.04 wt.%, agitation speed of 584.20 rpm and phthalic anhydride: mono-glyceride (PA:MG) molar ratio of 0.35:1 at reaction temperature 240^{o}C. Moreover, 91.5% fractional conversion was achieved actually, which is close to the predicted value. Analysis revealed that 3,4,5,6-tetrahydophthalic anhydride (TPA)-based resin shows improved resinous property than that of others due to high degree of crosslinking. It was also found that higher amount of aliphatic anhydrides are responsible for high degree of crosslinking density, whereas higher thermal stability was ensured by the inclusion of aromatic anhydride. Finally, incorporation of multi-walled carbon nanotubes (MWCNTs) into the optimum alkyd resin enhanced the overall resinous properties, which boosted up significantly through in-situ reaction. From this project 6 Journals papers, 4 conference papers and 1 patent has been published.

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

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

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

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

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

Vegetable oils are triglycerides, consisting of glycerol molecule connected with three similar or different types of saturated or unsaturated fatty acids. Depending on the unsaturated conditions or unsaturated fatty acids’ percentages in the oil, the route of their modification on functional groups can be decided to produce a potential monomeric molecule (Bailey, 1996). The produced monomer can be subjected for suitable polymerisation process to formulate bio-polymers. The estimated amount of vegetable oils that are being utilized to prepare different kinds of coating materials is one million tonnes (Gunstone et al., 2007).

Among the biopolymers, polyalkyds are being used efficiently in coating industries due to their short drying time, sufficient mechanical strength and acceptable chemical resistivity. There are several advantages of preparing polyalkyds from vegetable oils over traditional monomer based raw materials. Especially, the cost involved to produce plant based polyalkyds is lesser compared to the conventional polyalkyds. Moreover, it is environmental-friendly and associated with low-energy requirement during manufacturing. Furthermore, the polymerisation process is easy to control.

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

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

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

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

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Nature is blessed with abundant number of plant-based resources. Vegetable oil is one of them, which is available in huge quantities in the world. There are several types of vegetable oils available in the nature such as, edible oil (palm oil, sunflower oil, soybean oil, coconut oil, etc.), non-edible oil (rubber seed oil) and essential oil (jasmine oil, sandalwood oil, etc.). These vegetable oils can be utilized to produce polymers and polymeric materials. Many useful polymers like, polyesters, polyurethanes, polyamides, etc. have been prepared from different vegetable oils and studied in previous investigations. Different types of characterization techniques have been performed to evaluate these materials for various types of applications such as, surface coatings, adhesives, inks, paints, industrial chemicals and polymer composites. However, in this chapter, the properties of vegetable oils for the suitability of polymer preparation have been discussed. The polymerization techniques and methods with different features of the prepared polymers are also highlighted. Moreover, palm oil along with other vegetable oils has been studied for the preparation of different kinds of polymers, especially polyalkyds. The curing process, curing kinetics and other related parameters have been discussed based on previous analyses. Finally, incorporation of nano materials for the improvement of the film properties has been summarized at the end of this chapter.

2.2 VEGETABLE OILS AND THEIR PROPERTIES

There are a huge number of vegetable oils available in the world. Nearly, 4000 botanical species have been identified in the planet, from which oil can be extracted (Santori et al., 2012). Depending on the suitability of the growth, weather condition, demand, specific purpose of utilization and ease of plantation, different kinds of oil are produced at varying quantities in various parts of the world. For example, palm oil and palm kernel oil is highly produced in Indonesia and Malaysia; soybean oil is highly produced in USA, Brazil, Argentina and China; rapeseed oil is highly produced in Europe, China, Canada and India.

The annual production of some major vegetable oils per hectare is listed in Table 2.1 (Pahl, 2006). The important sectors of utilization of these vegetable oils are cooking, bioresin, biodiesel, soap, lubricant, detergent, paint, pharmaceutical, coating, ink, adhesive, and oleo-chemical industries. These oils are mainly extracted from the seeds, but the other parts of the plants such as, stem, leaf, fruit shell, flower and fruit-skin also contain a significant amount of oil. However, oil is defined as triglyceride or ester compound, which is, normally, liquid in state at room temperature. They are soluble in xylene, chloroform, toluene and other organic solvents, but insoluble in water. Generally, oils are classified as non-drying oil, semi-drying oil and drying oil, depending on the types of fatty acids present.

Table 2.1: Annual oil yield per cultivated hectare [kg ha^{-1}] (Pahl, 2006).

Crop	Yield	Crop	Yield	Crop	Yield
Maize	145	Lupine	195	Hibiscus	230
Pumpkin	449	Mustard	481	Camelina	490
Opium	978	Rape	1000	Olive	1019
Calendula	256	Sesame	585	Ricin	1188
Cotton	273	Safflower	655	Jojoba	1528
Hemp	305	Rice	696	Jatropha	1590
Soy	375	Walnut	790	Avocado	2217
Coffee	386	Sunflower	800	Coconut	2260
Flax	402	Cocoa	863	Palm	5000
Hazelnut	405	Peanuts	890		

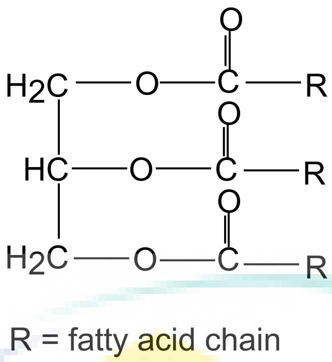
The drying oils become hard and solid film on exposure to atmospheric oxygen. This process is called as oxidation. Due to this property, the drying oils are being utilized in surface coating and oil paint industries over many years. Semi-drying oils, on the other hand, thicken on exposure to air for long time, but do not form a film, whereas, the non-drying oils do not change much in consistency (Sharma, 2002). Generally, these differences are based on the variation of percentages of unsaturated fatty acids and the degree of unsaturation present in the oils. An important term called iodine value, by which the degree of unsaturation as well as the types (drying, semi-drying and non-drying) of oils can be determined. It can be calculated as the amount of iodine in grams consumed by 100 g of oil. Commonly, oils having iodine value more than 130 are referred as drying oil, whereas, 90 to 130 and below 90 are termed as semi-drying and non-drying oil, respectively (Guner et al., 2006). Thus, the more the iodine values of the oils, the more the unsaturation present in the oil.

Except the iodine value, some other important characteristics of oils which may affect directly or indirectly the properties of bio resin such as, density, viscosity, specific gravity, colour, acid value, saponification value, peroxide value, moisture content, *etc.* Acid value is the amount of KOH in mg required to neutralize the free fatty acids present per gram of oil. The determination of acid value is important to measure the free fatty acids or the acidity present in the oil. Additionally, the extent of polymerization reaction or desired level of acidity in the samples can be monitored by this value. Saponification value is the amount of

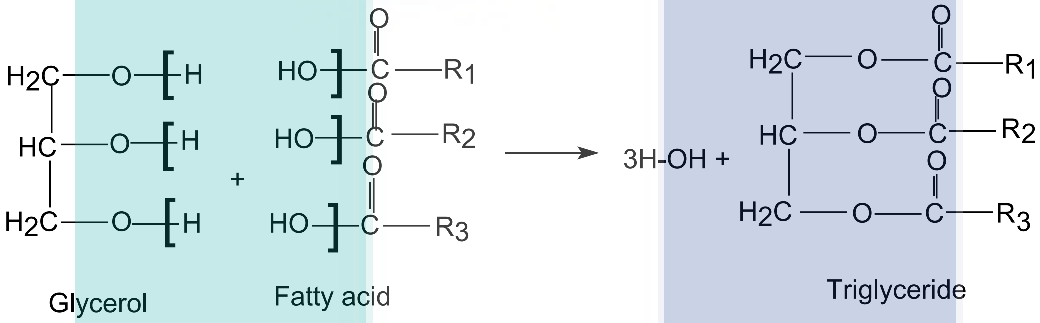
KOH in mg required to neutralize the fatty acids that produced from the hydrolysis of 1 g of oil. The chain length or average molecular weight of the fatty acid present in the oil can be determined by saponification value. The short chain fatty acids in oil have higher saponification value, whereas the long chain fatty acids have the lower value. The peroxide value is determined by the amount of peroxide oxygen present in 1 kg of oil. It is useful to detect the rancidity or freshness of the oil sample. Likewise, the variations of density, viscosity, moisture content as well as specific gravity of the oils also affect the properties of the produced bio resins.

Some other important characterization techniques of vegetable oils are available for the elucidation of their chemical structures, functional groups and natures. Among the characterization techniques, Fourier transform of infrared (FTIR) spectroscopy is an essential measure for the confirmation of particular functional groups and structures. Table 2.3 represents some absorption peaks of jatropha oil for particular functional groups through FTIR analysis (Boruah et al., 2012). Another common method, nuclear magnetic resonance (NMR) spectroscopy, was found to be effective for the evaluation of chemical microstructures of oils and their derivatives. Through NMR techniques at a particular δ, it is convenient to get the proton density for the presence of various linkages such as, $–CH$, $-CH_2$, $-CH_3$, *etc.* in oil and their derivatives. By these data, the fatty acid content in an oil sample can be calculated. The calculation of the surfaces of the peaks corresponding to the methylene groups, for example, gave an assessment of the fatty acid content. High performance liquid chromatography (HPLC) can be used to assess the purity of the samples. The calculation for reaction kinetics, rate constant and activation energy during the bio resin preparation can also be performed by using HPLC. Another technique, gas chromatography, can be used to identify the fatty acids and their relative percentages present in the oil both qualitatively and quantitatively.

Vegetable oils are triglycerides and ester compounds, consist of a glycerol molecule linked with three same or different kinds of saturated or unsaturated fatty acids (Scheme 2.1). A reaction is illustrated below to show the preparation of triglyceride in laboratory (Scheme 2.2).

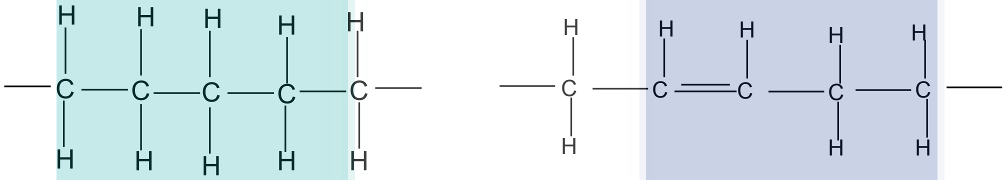


Scheme 2.1: A triglyceride molecule.



Scheme 2.2: Reactions between glycerol and fatty acids to produce triglyceride.

However, a number of fatty acids are available in the plant based vegetable oils. These fatty acids are of different types based on the variation of chain-length, number of carbon atoms, types of carbon-carbon bonds (double/treble bonds), presence and position of these bonds, *etc.* Some fatty acids are saturated, while some are unsaturated. Saturated fatty acid chain contains single bond between carbon atoms with hydrogen atoms attached to the other two sides of the carbon atom, whereas unsaturated one contains double or triple bonds between two carbon atoms along with the regular single bond. The unsaturated fatty acids present in the oils are of two types: mono unsaturated (single double bond) and poly unsaturated (two or more double bonds). The double bonds present in the fatty acid chains are considered as isolated or conjugated with respect to the position in the carbon chain. If the double bond present in the chain is separated by at least two carbon atoms, then the double bond is termed as isolated. On the other hand, if the double bond and single bond are present alternately, then it is termed as conjugated double bond. The number of carbon atoms in the fatty acid chains of almost all the plant based oils is ranged from 8 to 22. The number of carbon atoms present in the plant based vegetable oils is an even number, because the biosynthetic way involves building up the backbone chain with two carbon atoms at a time. Various types of fatty acids chains and their structures are illustrated in Scheme 2.3. They are present in vegetables oils at different proportion. For example, among the fatty acids, stearic acid, oleic acid, linoleic acid and linolenic acids of carbon atom number 18 with an order of increasing unsaturation are present in canola oil, linseed oil and sunflower oil. They contribute more than 90% of total fatty acid content in the oil (Guner et al., 2006). A list of common fatty acids available in various types of oils and their structures and chemical formula is presented in Table 2.5. Table 2.6 represents the fatty acid percentages present in various types of vegetable oils.



(a) Saturated (b) Unsaturated

(c) Isolated (d) Conjugated

Scheme 2.3: Various types of fatty acid chains.

Table 2.5: Common fatty acids, structure and formula.

Acid Name	Scientific Name	Structure	Formula	CN:DB	Type
Caprylic	Octanoic acid	$CH_3(CH_2)_6COOH$	$C_8H_{16}O_2$	8:0	Saturated
Capric	Decanoic acid	$CH_3(CH_2)_8COOH$	$C_{10}H_{20}O_2$	10:0	Saturated
Lauric	Dodecanoic acid	$CH_3(CH_2)_{10}COOH$	$C_{12}H_{24}O_2$	12:0	Saturated
Myristic	Tetradecanoic acid	$CH_3(CH_2)_{12}COOH$	$C_{14}H_{28}O_2$	14:0	Saturated
Palmitic	Hexadecanoic acid	$CH_3(CH_2)_{14}COOH$	$C_{16}H_{32}O_2$	16:0	Saturated
Stearic	Octadecanoic acid	$CH_3(CH_2)_{16}COOH$	$C_{18}H_{36}O_2$	18:0	Saturated
Arachidic	Eicosanoic acid	$CH_3(CH_2)_{18}COOH$	$C_{20}H_{40}O_2$	20:0	Saturated
Palmitoleic	Hexadec-9-enoic acid	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	$C_{16}H_{30}O_2$	16:1	Monounsaturated
Oleic	Octadec-9-enoic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	$C_{18}H_{34}O_2$	18:1	Monounsaturated
Erucic	Docos-13-enoic acid	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$	$C_{22}H_{42}O_2$	22:1	Monounsaturated
Linoleic	9, 12-Octadecadienoic acid	$CH_3(CH_2)_4CH=CH\text{-}CH_2\text{-}CH=CH(CH_2)_7COOH$	$C_{18}H_{32}O$	18:2	Polyunsaturated

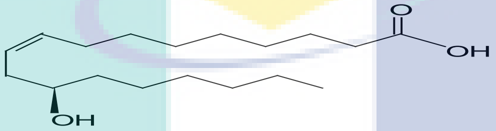
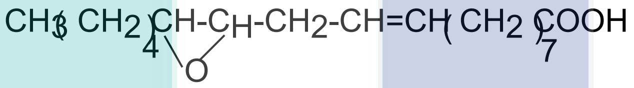
			2		
α-Linolenic	Octadeca- 9, 12, 15-trienoic acid	$CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH(CH_2)_7COOH$	$C_{18}H_{30}O_2$	18:3	Polyunsaturated
α-Eleostearic	Octadeca-9, 11, 13-trienoic acid	$CH_3-(CH_2)_3-CH=CH-CH=CH-CH=CH(CH_2)_7COOH$	$C_{18}H_{30}O_2$	18:3	Polyunsaturated
Ricinoleic	(9Z,12R)-12-Hydroxyoctadec-9-enoic acid		$C_{18}H_{34}O_3$		Polyunsaturated
Vernolic	Cis-12,13-Epoxy-cis-9-octadecenoic acid	$CH_3(CH_2)_4CH-CH-CH_2-CH=CH(CH_2)_7COOH$	$C_{18}H_{32}O_3$		Monounsaturated

Table 2.6: Common vegetable oils and their fatty acid content.

Name of oil	Caprylic acid	Capric acid	Lauric acid	Myristic acid	Palmitic acid	Stearic acid	Arachidic acid	Oleic acid	Erucic acid	Linoleic acid	Linolenic acid	Ricinoleic acid
Palm	-	-	-	1.2	41.8	3.4	-	41.9	-	11.0	-	-
Soybean	-	-	-	-	14.0	4.0	-	23.3	-	52.2	5.6	-
Coconut	6.2	6.2	51.0	18.9	8.6	1.9	-	5.8	-	1.3	-	-
Sunflower	-	-	-	-	6.5	2.0	-	45.4	-	46.0	0.1	-
Rapeseed	-	-	-	-	4	2	-	56	-	26	10	-
Castor	-	-	-	-	1.5	0.5	-	5	-	4	0.5	87.5
Linseed	-	-	-	-	5	4	-	22	-	17	52	-
Naharseed	-	-	-	-	15.9	9.5	-	52.3	-	22.3	-	-

Corn	-	-	-	-	10	4	-	34	-	48	-	-
Olive	-	-	-	-	6	4	-	83	-	7	-	-
Sesame	-	-	-	0.1	8.2	3.6	-	42.1	-	43.4	-	-
Safflower	-	-	-	0.1	6.8	2.3	0.3	12.0	-	77.7	0.4	-

Fatty acid contributes 94 to 96% of the total weight of the triglyceride molecule. Polymeric properties depend on vegetable oils' reactivity or fatty acid properties and their relative percentages (Stenberg, 2004). For example, the dielectric property of oleic acid based polyurethane was assessed by Velayutham and co-workers, and found that the proton, originated from the oleic acid, determines the relaxation mechanism of dielectric properties of polyurethane (Velayutham et al., 2012). They also claimed that the higher oleic acid content produce a higher amount of flexible side change, which results in less compact polymer. It was also found that, the properties of the oil and their derivatives are affected due to the structure of the fatty acids.

Palm oil is major vegetable oil among the plant based oils regarding the productivity worldwide. About 90% of world production comes collectively from Malaysia and Indonesia. In 2011, palm oil made up 32.8% of the global total vegetable oil consumption, ahead in position of soybean oil (28.4%), rapeseed oil (16.0%) and sunflower oil (8.6%). In an average, three quarters of all palm oil go into production of food stuffs, and the remainder go into industrial products such as, chemicals, animal feed and fuels. Total vegetable oil demand is predicted to be double between 2010 and 2050, from 120 to 240 million tonnes annually. As for palm oil, total demand is projected to increase from 51 million tonnes today to 75 million tonnes by 2050. Over the last decade, demand for palm oil has grown by on average of 2.3 million tonnes annually. Indonesia has supplied 62% of the palm oil needed to meet this demand, whereas Malaysia and other countries have supplied 30% and 8%, respectively. This trend is set to continue as total palm oil demand is projected to rise by another 5 million tonnes annually in 2015. The commercial benefit comes to these countries for this huge amount of oil production. The major portion of this oil is being utilized for food product. Like other vegetable oils, this oil can be used for oleochemicals, soap, detergent, pharmaceutical, biofuel and polymer preparation. Some properties of palm oil are as same as other vegetable oils as follows: renewable and biodegradable, high dielectric strength, high pour point, high flash point, high fire point, moderate oxidative stability, lox toxic, high water absorption and poor low-temperature properties.

Palm oil (Elaeis guineensis) is derived from the mesocarp as well as kernel of the fruit of the oil palm. Palm mesocarp oil is of 41% saturated, while palm kernel oil is of 81%. In general, crude palm oil contains 43.5% palmitic acid, 36.6% oleic acid, 9.1% linoleic acid, 4.3% stearic acid, and 1% myristic acid. The properties can vary with different factors such as, weather or climate condition of the cultivated area, fruit quality, ripeness, extraction methods, and degree of purification.

2.3 POLYMERS FROM VEGETABLE OILS

Polymers are being utilized in various technical purposes depending on their diversifying properties. The monomer and architectural organization of the macromolecules simultaneously decide the dominating properties of polymers. The endless numbers of options to create or modify the polymers have made these materials attractive to the researchers. Moreover, high price of petroleum based polymer, their non-biodegradable nature, significant amount of greenhouse gas emission, huge heat consumption during their processing, scarcity of the raw materials, environmental legislations, *etc.* are also responsible for searching bio-based alternatives. Among the bio-based resources, the triglyceride-based vegetable oils are important for polymer synthesis.

Current section reviews the synthesis of vegetable oils-based polymers of different kinds by using different polymerization reactions and techniques. Generally, these polymers are environmental-friendly, inexpensive, and produced from readily available raw materials. These polymers are being utilized as coatings, adhesives, insulators, binders, medicinal sutures and matrixes for the preparation of composites. Figure 2.1 shows various applications of vegetable oils in polymer sectors. The properties of these polymers are comparable to the petroleum based one and sometime even superior to the later.

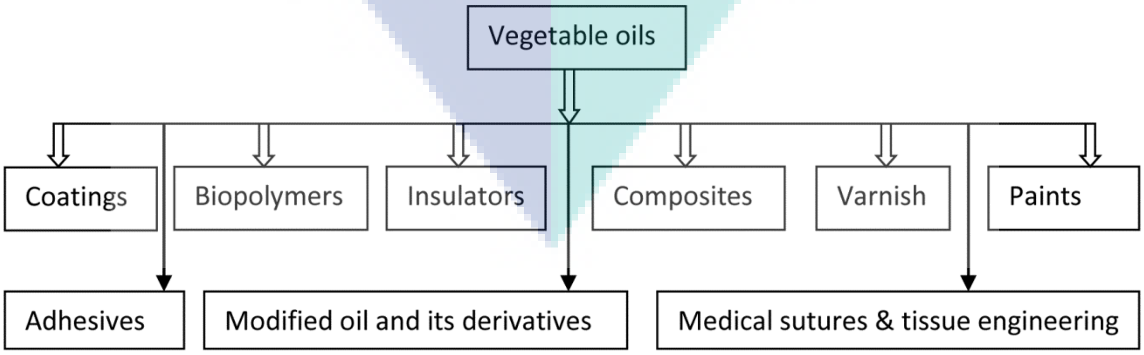


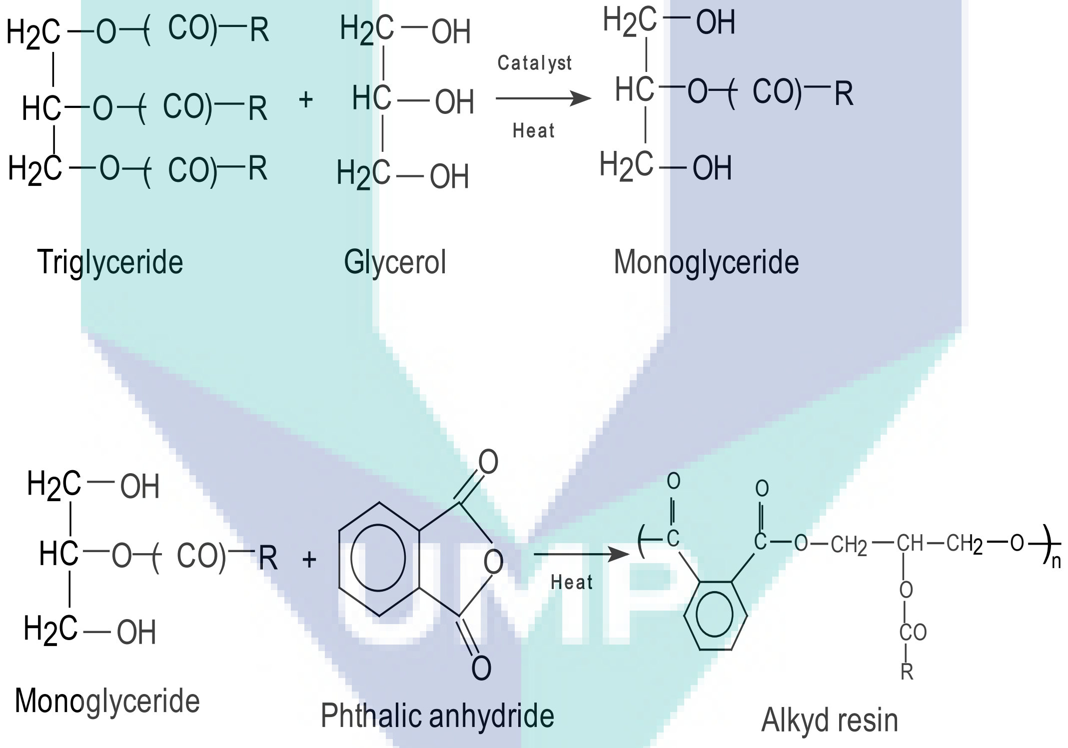
Figure 2.1: Applications of vegetable oil-based polymers.

The fatty acid composition is very important for vegetable oil to be considered as a potential material for bio resin synthesis. More specifically, the unsaturated fatty acids are susceptible for attacking by the chemical reagent on their double or triple bonds. The types of vegetable oil based polymers depend on the functional groups and distinguishable linkages between the constitutional atoms. Some common types of polymers produced from vegetable oils are including oxidative polymers, polyesters, polyurethanes, polyester amides, vinyl polymers and epoxies. The current study deals with polyalkyds (polyesters), which have been highlighted along with other types of polymers in this section. The preparation methods, polymerization reactions and optimization of esterification process have been summarized in the following subsections. Comparative analyses of polyesters prepared from different vegetable oils have been also focused.

2.3.1 Polyesters

Polyesters are polymers which essentially contain ester functional group in their backbone chain. Several billion tons of polyesters are being produced every year for its various types of industrial utilization. The general ways for preparing polyesters are: (1) polycondensation reaction of hydroxyl group (-OH) containing organic or inorganic acids or diacids with a diol; (2) ring opening polymerization of lactones (Yang et al., 2011). Since vegetable oils are very rich source of various kinds of carboxylic acids, so modification of them through esterification reaction are found to be easy way to produce polyester type polymers. Although traditional monomer based polyesters are mostly non-biodegradable, but these polyesters are biodegradable. They can be thermoplastic or thermosetting, but most of them fall into thermosetting category.

Polyalkyd resins have been used as a major binder since the starting of the nineteenth century due to their excellent auto-oxidative, chemical and mechanical properties (Athawale et al., 2011). They were synthesized for the first time by J. Smith in 1901 (Athawale et al., 2011). The first commercialized alkyd paint was Glyptal, made by General Electric in 1926 (Athawale et al., 2011). Alkyds are reaction product of alcohol and carboxylic acids through esterification reaction. It is a polycondensation reaction and the water formed in the reaction must be continuously removed by any means, for example, by azeotrope distillation. The common process to prepare polyesters is the two-steps method includes alcoholysis followed by esterification. In alcoholysis process, the oils or triglycerides are subjected to alcoholysis to produce mono-glycerides (as partial glycerides), catalysed by various acid or base catalysts such as, PbO, NaOH, CaO, $Ca(OH)_2$, $CaCO_3$, para-toluene sulphonic acid (PTSA), etc. After this, the mono-glycerides are subjected to polymerization process with different acid anhydrides such as, aliphatic acid anhydride (glutaric anhydride, maleic anhydride, succinic anhydride, etc.) and aromatic acid anhydrides (phthalic anhydride) to produce polyalkyd based resin. The process is presented in Scheme 2.9. The properties of the polymer change with the incorporation of different kinds of acid anhydrides. The aliphatic polyesters possess low melting point, whereas the incorporation of aromatic compound led to a high heat and moisture resistant product.



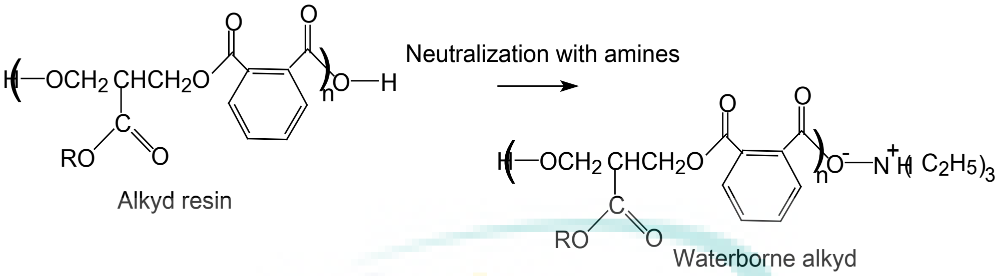
Scheme 2.9: Alchoholysis and poly-condensation reaction of oil with acid anhydride.

There are different kinds of polyalkyds available based on the properties and preparation methods. One of the prominent types of this category is liquid crystal polymers (LCP). LCP shows excellent mechanical performance, high temperature stability and good chemical resistivity. Liquid crystalline alkyd resins were prepared by the following three methods (Chiang et al., 1992; Chen et al., 1988): (a) grafting *p*-hydroxybenzoic acid

(PHBA) to hydroxyl-terminated alkyd resin, (b) grafting PHBA to carboxyl-terminated alkyd resin, and (c) grafting PHBA to an excess succinic anhydride-modified alkyd resin. Dicyclohexylcarbodiimide (DCC) was employed to react with formed water in promoting esterification of PHBA with alkyd at room temperature. The catalytic amount of PTSA was added to suppress side reaction and promote esterification in the presence of pyridine, as a solvent. The grafting efficiency was estimated in the range of 70 to 95%. The character of liquid crystallinity was imparted only when at least two or more aromatic units of PHBA are connected to form the rod-like mesogenic side chain. The advantages of LCPs include reduced viscosity, reduced coating's dry-to-touch time, hardened and toughened coating film and excellent resistance to water and acid. The disadvantages associated with LCP are the high cost and requirement of drying before processing.

Another important type of polyalkyds is high solid content alkyds. High solid content resins are attractive due to their technical aspect and economic benefit (Chen et al., 1988). They reduce the use and emission of volatile organic solvent, which has negative impact in coating industries. In the development of high solid alkyds, the major problem is to reduce the viscosity without deterioration of the property. The problem associated with high gloss decorative paints due to decreasing solvent content can be mitigated by preparing high solid content alkyd resin by decreasing the molecular weight (Lindeboom, 1998). The molecular weight can be decreased by increasing fatty acid content or increasing the ratio of -OH/-COOH groups. Resins prepared by this way perform slow drying rate with weak properties and this problem can be removed to a greater degree of extent by making hyperbranched structure (Lindeboom, 1998; Ma´nczyk et al., 2002). Therefore, star and hyperbranched structured resins were developed based on this phenomenon.

Another new invention of polyalkyds is the water borne category of alkyds. Importance of zero or less volatile organic compound (VOC) in the coating system drives researchers to develop the alternative water-borne resins. In addition, high cost and high emission of organic solvent during drying process are found to be the drawbacks associated with organic solvent-based alkyds. Water-borne or water reducible or water soluble or water thin-able alkyd resins are considered as environmental-friendly materials, which are easily diluted with water. It is important that, after evaporation of water from the coating system, the resulted coating should exhibit the same property as similar as the organic solvent-based one (Murillo et al., 2011). Water borne resin contains water reducible binders. Alkyd resins with high percentages of acid value, upon neutralization of their carboxylic acids with amines, act like water reducible binders. A scheme is illustrated below for the preparation water borne alkyd (Scheme 2.10). The drawbacks of this kind of resin include slow drying and tackiness. This problem can be removed by incorporation of melamine or urea formaldehyde during backing at 150°C for 2 h (Murillo et al., 2011; Nicholas, 2003). Limited hydrolytic stability is another drawback associated with water borne alkyd resin (Wang et al., 2000). The assessment of stability was carried out in a different investigation and found to be impressive. Water borne alkyd resins were prepared with high storage stability from the reaction between acrylic copolymers and monoglycerides formed from soybean oil and trimetylol propane. An excellent stability, with 10% changes in acid number after nine months of storage period, was observed (Wang et al., 2000). Water-borne alkyd resins were prepared by using different percentages of maleic anhydride (2-20%) from rubber seed oil for non-polluting organic coating (Aigbodion et al., 2003). Maleinization of the oil increased the acidity and it can be neutralized with amines, which further subjected for polycondensation reaction with the anhydrides to prepare water-soluble alkyd resin (Aigbodion et al., 2003). Among the properties, high resistivity to chemical entity and very less amount of volatile organic content are mentionable. In another work, linseed oil was used to produce sulfonate based water borne alkyd resin (Rokicki et al., 2001). A transesterification reaction of monosodium di-n-pentyl-5-sulfoisophthalate groups with the partial esters of polyhydroxy alcohols and unsaturated fatty acids prior to traditional polycondensation with phthalic anhydride was claimed as the best for introducing sulfonate group. Small amount (3 wt.%) of sodium sulfonate groups results in good water dispersity and short drying time with good water resistance performance of the coating. In recent work, soybean oil was used to prepare water borne alkyd resin by neutralization with triethyeleamine and modified by butylated melamine formaldehyde (Pathan et al., 2013). Results revealed antibacterial property of the resin, which can be used as food packaging application.



Scheme 2.10: Preparation of water borne alkyds.

Alkyd resin is a product of a chemical reaction of fatty acids, polyol and poly acid. This bio based resin can be cured in a solvent medium in the presence of oxygen or other curing agents to produce thin film with comparable properties. They can be used as a substitute of synthetic resin for coating or others purposes. Petal and co-workers showed a process describing the synthesis of alkyd resin from jatropha and rapeseed oil in their work (Patel et al. 2008). A comparison was drawn among the properties of the resins produced from the individual oils. They produced varnish from that resins for electrical insulation purpose. In the analysis, they recommended the suitability of the varnishes for practical applications, as these materials satisfied the standard requirements.

Few studies have been found utilizing palm oil for alkyd types of resin preparation. An example of producing bio resin form palm oil was described by Ali and co-workers (Ali et al., 2001). They developed two types of polyester acrylate resins through acrylation process for wood coating application, which were ultraviolet radiation-curable. They investigated the resins by gel fraction, swelling ratio and pendulum hardness. The properties were found to be suitable for the coating applications. Saravari and co-workers in their work described the synthesis process of water-reducible acrylic-alkyd resins from modified palm oil (Saravari et al., 2005). They used tung oil as another ingredient to modify the unsaturation condition of palm oil for the suitability of alcoholysis process.

2.3.1.2 Polymerization reactions and techniques

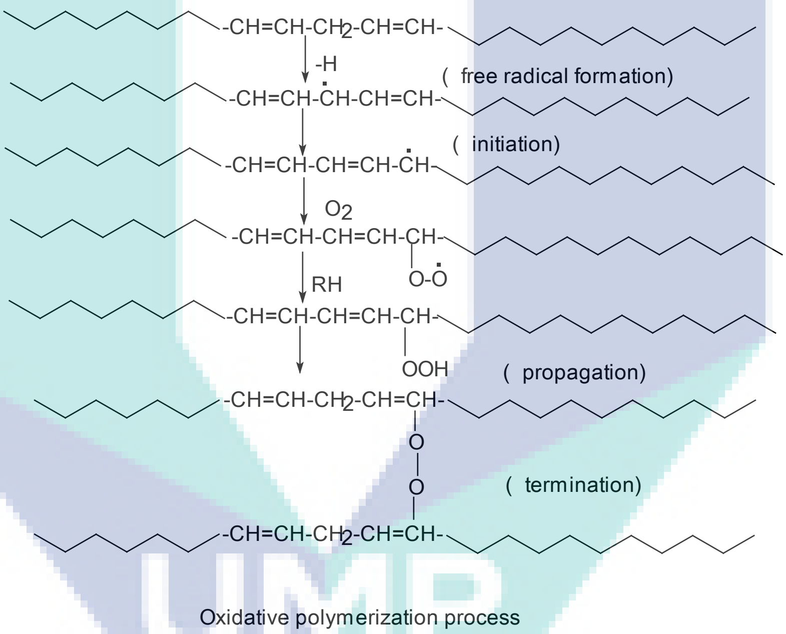
Different types of polymerization process are available to prepare variety types of polymers from potential monomers. To understand the polymerization reactions, some basic terms such as, initiator, propagation, termination, functionality of the monomer and degree of polymerization are needed to be analysed. The extensive studies on many polymers from different polymerization reactions led the researchers to bring in variations in the properties in terms of molecular weight, structure and crystallinity.

Different polymerization reactions such as, step, condensation, addition, ring-opening, amidation and ester interchange are commonly found to produce various kinds of polymers. In step polymerization, the polymer build-up proceeds through a reaction between functional groups of the monomers. The reaction takes place in a step-wise manner, and the polymer build-up is, therefore, a slow process. Step polymerization reactions are mostly accompanied by the elimination of small molecules like water from the monomer or other constitutional ingredients. Polycondensation process is such kind of step polymerisation, commonly used to produce polyalkyds. The major features of polycondensation reaction are stated below.

2.3.2 Other Polymers

2.3.2.1 Oxidative and thermo-oxidative polymers

Oxidation of vegetable oils is a common method which involves the modification of fatty acid chains by oxygen. The preliminary and common experimental characteristics of the oxidation of vegetable oils were summarized by Cloez in 1866 (Cloez, 1866). This process can occur even automatically through atmospheric oxygen at a slow rate during the extraction and processing of the oils from the seeds and during the period of storage. Mostly the drying oils become harden to film like solid materials on exposure to air due to chemical cross linking of the fatty acid chains called oxidative polymerization. This process can be influenced by light, heat, contact with metal catalysts, biological metabolism (enzymatic action) and oxygen containing radicals. This idea makes the drying oils to be used in oil paint formulations or coating applications since long time before. The oil oxidation follows the general free-radical propagation theory (Hess et al., 1950). Utilizing this property, sometime the drying oils can be used as the initiator or cross linker for a polymerization process (Oprea, 2010). Linseed oil was used earlier as an ingredient of coating materials, but development of synthetic high quality alkyd based resin has lessened the use of it. Tung oil was found to be used as the starting materials for paint and varnish preparation due to its highly unsaturation nature and the presence of conjugated double bonds in the backbone chains of the fatty acids (Li et al., 2003). The carbon-carbon double bonds (C=C) in the unsaturated fatty acids present in the oils are mainly responsible for oxidation process. Unsaturated fatty acids like oleic$_{(18:1)}$, linoleic$_{(18:2)}$ and α-linoleic$_{(18:3)}$ can be found in some vegetable oils like linseed, tung, sunflower, walnut *etc.* These fatty acids can easily be attacked on its double bonds by the atmospheric oxygen to produce hydroperoxide free radicals, which is very reactive to attack new unsaturated molecules of fatty acids. Some common peroxides are methyl ethyl ketone peroxide, benzoyl peroxide, acetone peroxide and hydrogen peroxide, have been used for that purpose as initiator in oxidation process. The outcome of this process includes weight gain, formation of three dimensional structure or network and rancidity. The mechanism of oxidation of vegetable oils has been drawn in Scheme 2.11.

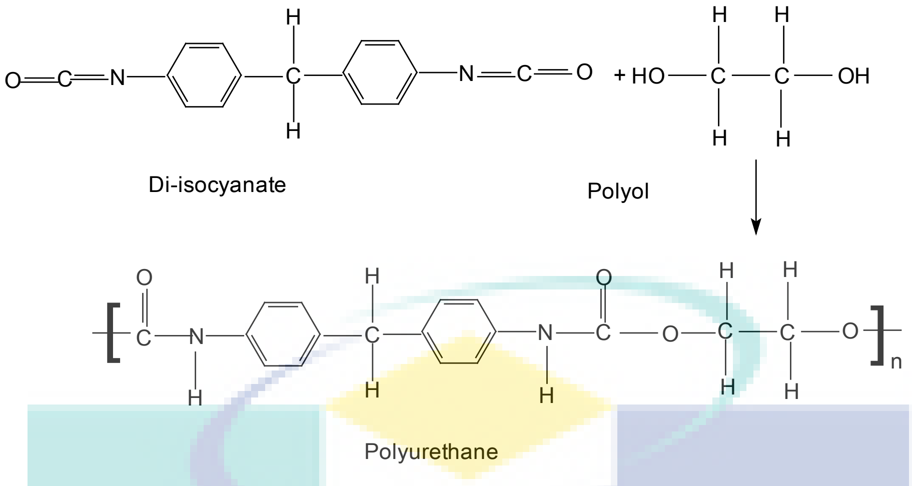


Scheme 2.11: Oxidative polymerization process.

Oxidative polymerization also can be carried out with the help of various metal salts as catalyst or drier. Catalytic oxidation is required as because sometime the drying rate is very slow that cannot be used for fast drying purpose. Catalytic method has been developed and studied for oxidative polymerization for the case of drying, semi-drying and even for non-drying oils. Some examples of metal catalysts which were found to be used for drying purpose as Tn, Ni, Cobalt 2-ethylhexanoate, Zarconium, Calcium/Zarconium etc. (Mallegol et al., 2000).

2.3.2.2 Polyurethanes

Polyurethanes (PUs) are polymers made from the reaction of diisocyantes and hydroxyl functional group containing compounds or polyols. This kind of polymer was discovered for the first time by Bayer through a reaction between polyester diol and a diisocyante (Delebecq et al., 2013). Modified oils or triglycerides can be used as polyol to produce partial glyceride, which may be used in the formulation of polyurethane. The reaction mechanism is shown between methylene-4, 4′-diphenyldiisocyanate and a diol to produce polyurethane polymer in Scheme 2.12. Diisocyanates used to prepare polyurethanes can be aromatic or aliphatic. Polymers belonging to this category show wide range of variations of properties such as, density, flexibility and rigidity, which make them useful in many applications based products including foam, varnish, paint ingredients, adhesives, glue, matrix for composites, *etc.* For example, toluene diisocyante (TDI) and methylene diphenyl isocyanate (MDI) are being utilized for flexible and rigid PU products, respectively. Generally, two physical-chemical processes are responsible for these wide ranges of properties, that is, phase separation between hard and soft segments and hydrogen bonding between the urethane or carbamate bonds. In addition to that, the high reactivity of isocyanate even in viscous system or at low temperature is also responsible for the variations of the properties. The only drawback of this useful material is the inherent toxicity due to isocyanates. A number of research works including vegetable oil based PU have been performed since a few decades ago. Castor oil, canola oil, soybean oil, sunflower oil, neem oil, palm oil, nahar seed oil, tung oil, karanja oil, prosopis juliflora oil, *etc.* have been used to produce polyurethanes based polymers (Tan, 1994; Petrovic´ et al., 2010; Palaskar et al., 2010; Chaudhari et al., 2013; Lee et al., 2007; Deka et al., 2009; Mosiewicki et al., 2012; Palanisamy et al., 2011; Tathe et al., 2013). The types of isocyanates (aliphatic or aromatic) and the polyol used in the preparation have the major controlling roll on the properties of the formulated PU.



Scheme 2.12: Reaction between di-isocyanate and polyol to form polyurethane.

Hyper branched and linear polyurethane resins from sunflower oil were studied by Das and co-workers (Das et al., 2013). A comparison on physico-mechanical properties, thermal stability and biodegradability was drawn between hyper branched polyurethane (HBPU) and linear polyurethane (LPU). HBPU showed better film properties than LPU. In another work, synthesis of aqueous cationic polyurethane dispersions was performed by Lu and co-workers by using methoxylated soybean oil based polyols (Lu et al., 2010). The effect of hydroxyl functionalities on the films was assessed in this work. The range of hydroxyl functionalities was used from 2.4 to 4.0. In a different study, the dielectric properties of the palm oil based polyurethane were analysed by Velayutham and co-workers (Velayutham et al., 2012). The oleic acid content in the polyol and NCO/OH ratio contributes the variation of properties of the polyurethanes. The dielectric properties were found to be in the range of 2.0 to 3.0 and 0.02 to 0.08 in the real permittivity and imaginary permittivity, respectively. A γ-relaxation process was proposed as the probable mechanism for the dielectric behaviour. It was found that the dielectric constant and loss mechanism of the formulated polyurethane is dependent on the NCO/OH ratio as well as the percentage of oleic acid in the polyol.

Vegetable oil based polyols have been used since long time ago for the preparation of PU. The modification or change in the fatty acid chain is possible in the unsaturated double bond location or to the carboxylic functional group. Thus development of new PU with different property is based on the modified polyols and hybridization of them with other compatible functional groups of other compounds (Desroches et al., 2011; Allauddin et al., 2013). In this purpose, rapeseed oil was functionalized to prepare a polyol by thiol-ene coupling for the preparation of PU based on 1, 6-hexamethylene diisocyanate and methylene diphenyl-4, 40-diisocyanate. The produced elastomeric product showed comparable thermal property based on commercially available polyol based PU. In another work, a novel methodology was undertaken to prepare PU-urea-silica based hybrid coating by using modified castor oil through $-Si-OCH_3$ groups in the backbone chain with isophorone diisocyanate (Allauddin et al., 2013). Improved mechanical and viscoelastic property were claimed by the authors. The hydrophobic character of the hybrid coating and glass transition temperature (T_g) were found to be increasing with the increase of NCO/OH ratio. The swelling property and contact angle was also found to be dependent with that ratio.

The structure and concentration of elastically active network chain of PU were determined by rubber elasticity theory (Zlatanic et al., 2002; Kong et al., 2007). Vegetable oils based PU network is a heterogeneous composition and its structure–property relationship was examined by Zaitanic and co-workers (Zlatanic et al., 2002). The authors prepared PU-network model through the reaction between triolein (triglyceride of oleic acid) and 4, 4'-diphenylmethane diisocyanate. According to the authors, due to cross linking, the middle part of the fatty acid chains remain in the structure as hanging part. Through metathesis, the swing part of the chain in another PU structure was removed. Analyses revealed that the PU structure without dangling chain shows a decreased viscosity and glass transition temperature. The dangling chain acts as a plasticizer and removal of that increases the solvent resistivity of the PU-structure model. Higher triol content canola oil was used to prepare a new generation PU by introducing a mild solvent (ethyl acetate) and zinc as a reductive reagent. The prepared aliphatic diisocyanate (1, 6-hexamethylene diisocyanate) based-PU showed higher T_g, tensile strength, tensile modulus and longer elongation break at same OH/NCO molar ratio (Kong et al., 2007). In an advanced level of work, linear saturated diisocyanate was derived from fatty acid to prepare different types of PUs from canola oil (Hojabri et al., 2009). Petroleum based polyol and commercially available 1, 6-hexamethylene diisocyanate were used to prepare PU, and a comparison was drawn with canola oil based PU. Comparative properties with acceptable tolerance were showed by canola oil based PUs.

Recent developments of producing non-isocyanate based polyurethane (NIPU) are attracting the researchers due to the scope of avoiding the toxic isocyanate from the PU structure (Li et al., 2008; Wilkes et al., 2004). NIPU can be prepared by the reaction between cyclo-carbonates and amines. Commercially available amines such as, ethylenediamine, hexamethylenediamine, and tris (2-aminoethyl) amine were used to prepare NIPU (Li et al., 2008; Wilkes et al., 2004). The improvements were observed for different properties such as, porosity, water absorption, chemical and thermal resistivity for the case of NIPU compared to isocyanate based one.

Water borne PUs is environmental-friendly. The researchers have interest on them over the traditional/organic solvent-soluble PUs because the later pollutes the environment with VOC during their application and formulation, through evaporation process. The toxic and expensive volatile organic solvents were replaced by water in the formulation of polyurethane dispersions (PUD), resulting in minimal VOC contents (Wilkes et al., 2004; Dieterich et al., 1970; Eisenberg, 1970; Visser et al., 1991; Kim et al., 1991; Kim et al., 1996; Coutinho et al., 1996; Chen et al., 1997; Jhon et al., 2001; Narayan et al., 2006). Water-borne PU dispersion can be used in various purposes such as, coatings for various fibres, adhesives for alternative substrates, primers for metals, caulking materials, emulsion polymerization media for different monomers, paint additives, defoamers, associate thickeners, pigment pastes, and textile dyes (Guo et al., 2012; Yao et al., 2012; Scrinzi et al., 2011; Wicks et al., 2001; Yang et al., 2009; Asif et al., 2005; Durrieu et al., 2005; Parmar et al., 2005; Tanaka et al., 1999). Novel bio-renewable, waterborne and castor oil-based PUDs were successfully synthesized via homogeneous solution polymerization in methyl ethyl ketone followed by solvent exchange with water (Madbouly et al., 2013). A detailed rheological behaviour of PUD as a function of angular frequency, solid content, and temperature, were evaluated through small-amplitude oscillatory shear flow experiments. The solid content and temperature significantly affected the rheological behaviour of the PUDs. The composition dependency of the complex viscosity (η^*) was described by the Krieger−Dougherty equation. Although the viscoelastic behaviour of the PUDs was well-described by the time−temperature superposition (TTS) principle in a temperature range lower than the gel point, but TTS failed to represent the behaviour of the PUDs at temperatures near the critical gel point.

Interpenetrating polymer networks (IPNs) are polymer blends can be prepared by permanent entanglement between two or more distinctly cross-linked polymers and possess' excellent properties due to interlocking of polymer chains (Sperling, 1981). There are many kinds of IPNs, among which sequential IPNs and simultaneous interpenetrating networks (SINs) are the two most important types (Nayak et al., 2009). Soybean oil (Nayak et al., 2009; Praharaj et al., 2004; Nayak et al., 2004), canola oil (Kong et al., 2008a) and castor oil (Das et al., 2011; Yenwo et al., 1977; Devia et al., 1979; Patel et al., 1987a; Patel et al., 1987b; Patel et al. 1987c) were studied for the preparation of IPN type polyurethanes. Castor oil based polyurethanes and styrene monomers were used to prepare IPNs with tough elastomeric properties (Das et al., 2011; Yenwo et al., 1977). A series of IPNs based on castor oil with acrylic monomer were studied by Suthar and co-workers (Patel et al., 1987a; Patel et al., 1987b; Patel et al. 1987c). The produced IPNs showed elastomeric and good mechanical properties.

Sequential interpenetrating polymer networks (SIPNs) were prepared using polyurethane synthesized from canola oil-based polyol with terminal primary functional groups and poly (methyl methacrylate) (PMMA) (Kong et al., 2008a; Kong et al., 2008b). The mechanical properties of the SIPNs were found superior to those of the constituent polymers. The new SIPN material covered a broad spectrum of useful properties such as, sound and vibration damping, and was found to be valuable substitutes for existing materials (Kong et al., 2008b).

CHAPTER THREE

MATERIALS AND METHODS

3.1 INTRODUCTION

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

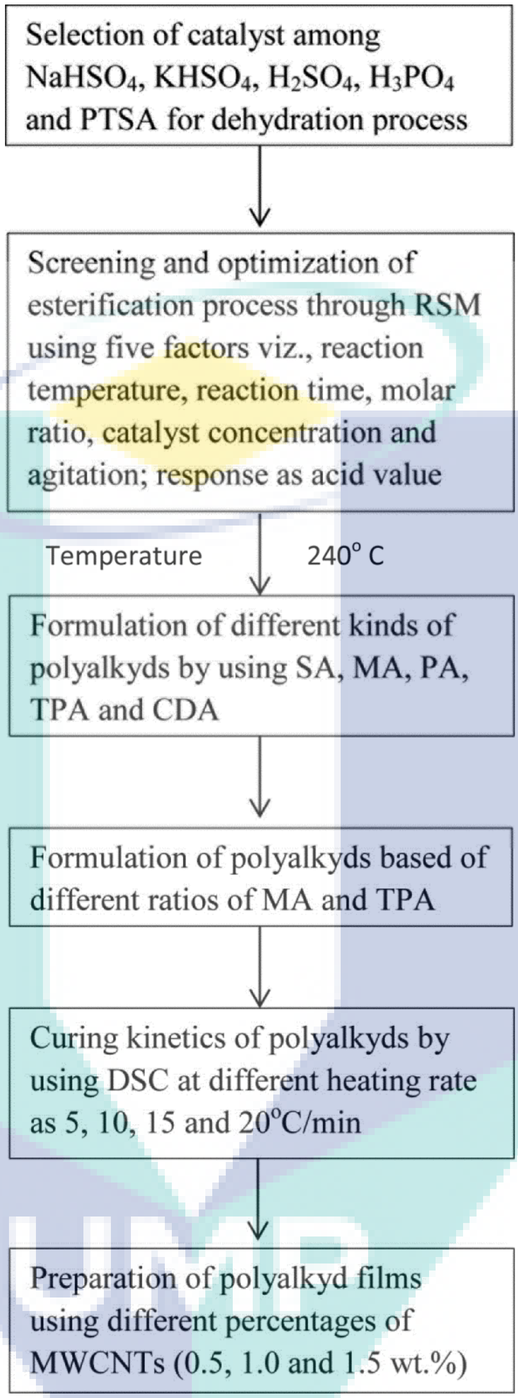


Figure 3.1: Process flow diagram.

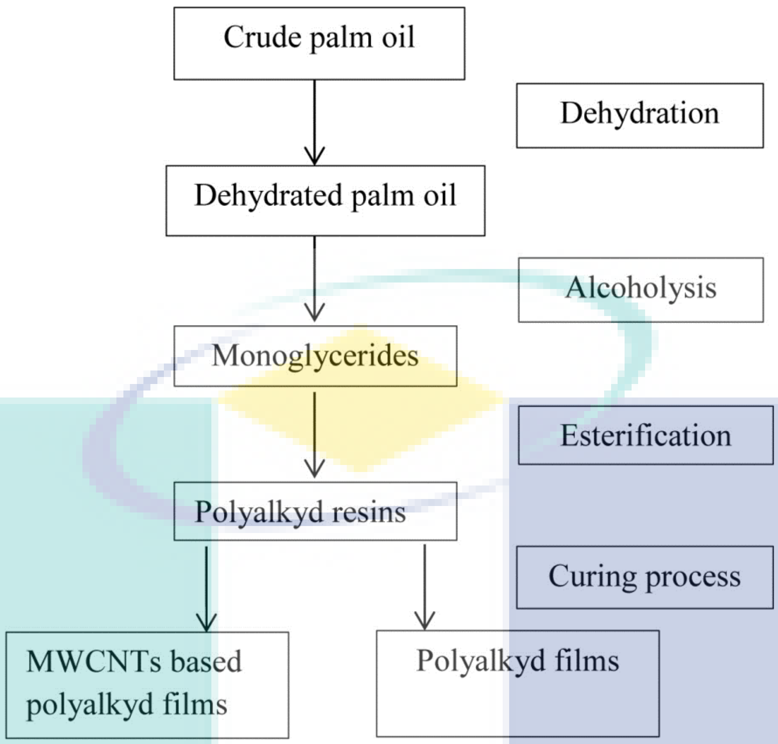


Figure 3.2: Experimental design of the research.

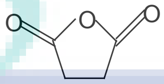
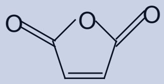
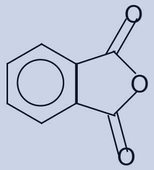
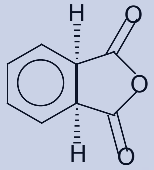
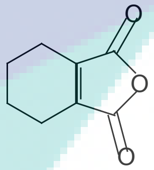
3.2 MATERIALS

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

Table 3.1: List of chemicals and raw materials used in this research.

Name	Manufacturer and loaction
Crude palm oil	Malaysian Palm Oil Board (MPOB).
Glycerol ($C_3H_8O_3$) (purity > 99%), xylene, starch indicator	Aladdin Chemistry Co. Ltd, Shanghai, China.
Phthalic anhydride ($C_6H_4(CO)_2O$) (PA) (with minimum assay > 97%), 3,4,5,6-tetrahydrophthalic anhydride ($C_8H_8O_3$) (TPA) (98%), succinic anhydride ($C_4H_4O_3$) (SA) (98%), cis-1,2-cyclohexanedicarboxilic anhydride ($C_8H_{10}O_3$) (CDA) (99%), methyl ethyl ketone peroxide ($C_8H_{18}O_6$) (MEKP) (purity 99%).	Aladdin Industrial Corporation, Shanghai, China.
Para-toluene sulfonic acid (PTSA) (purity > 99.5%)	Shanghai lingfeng chemical reagent Co. Ltd, Shanghai, China.
Cobalt-naphthenate 6%, toluene, butanol, ethanol, methanol, styrene, acetone, potassium hydroxide, sodium hydroxide and hydrochloric acid.	Sigma Aldrich, USA.
Calcium oxide (CaO)	Aladdin Chemistry Co. Ltd., Shanghai, China.
Sulphuric acid (H_2SO_4) (98%), phosphoric acid (H_3PO_4), sodium hydrogen sulphate ($NaHSO_4$), potassium hydrogen sulphate ($KHSO_4$),	Fisher Scientific, USA.
Maleic anhydride (MA).	Acros Organics, New Jersey, USA.
Highly pure nitrogen gas.	Air Products, Malaysia.
Iodine mono chloride, potassium iodide, di-ethyl-ether, chloroform, phenolphthalein indicator and sodium thiosulphate.	Merck, Germany.
Multi-walled carbon nano tubes (MWCNTs) diameter less than 8 nm, length of 10 to 30 µm and carbon purity of 95%.	Timesnano, Chinese academy of science, China.

Table 3.2: Different types of acid anhydrides and their properties.

Types of acid anhydrides	**Type**	**Molecular weight (g/mol)**	**Chemical formula**	**Structure**	**Density (g/cm^3)**	**Boiling point (^{o}C)**
Succinic anhydride	Saturated aliphatic	100.07	$C_4H_4O_3$		1.23	261
Maleic anhydride	Unsaturated aliphatic	98.06	$C_4H_2O_3$		1.48	202
Phthalic anhydride	Saturated aromatic	148.1	$C_8H_4O_3$		1.53	295
Cis-1,2-cyclohexanedicarboxylic anhydride	Saturated aromatic	154.16	$C_8H_{10}O_3$		1.18	158
3,4,5,6-tetrahydro phthalic anhydride	Unsaturated aromatic	152.15	$C_8H_8O_3$		-	-

3.3 METHODS

3.3.1 Oil Characterization

3.3.2.1 Acid value

The acid value is also called as neutralization number or acid number. It is the measure of free fatty acid content in 1 g of oil, and accounted as the amount of potassium hydroxide (KOH) in mg required to neutralize the alkali-reactive groups of oil. In other sense, it is the measure of carboxylic acid present in fatty acids or a mixture of compounds. The more the acid value, the more the free faty acid present in the sample. Acid value is an important measurement to determine the acidity present in the product after a particular reaction. It can be used to indicate the completion of a reaction, or sometimes, as a mean of checking the required or desired value of a reaction product. The standard method to measure the acid value of oil as stated in ASTM D1639 was used in this study. According to the procedure, about 5 g of oil sample with 12.5 ml of ether and 12.5 ml of methyl alcohol were added in a flask and mixed properly. After that, 1 ml of alcoholic solution of phenolphthalein indicator was added. The solution was then titrated using 0.1 N solution of potassium hydroxide till the faint pink colour obtained. For this measurement, conical flask, burette, pipette, water bath, 0.1 N KOH, ether, methyl alcohol and phenolphthalein (ph.ph) indicator solution (10g/L) was required. The equation 3.1 was used to calculate the acid value.

$$\mathrm{AV} = \mathrm{V} \times \mathrm{N} \times \frac{56.1}{\mathrm{W}} \tag{3.1}$$

Where, AV = acid value, V = volume of KOH required for titration, N = normality of KOH solution as 0.1, molecular weight of KOH = 56.1 and W = weight of oil sample.

3.3.2.2 Iodine value

Iodine value or iodine number is the amount of iodine in grams is consumed-up by 100 g of oil. It is the measure of the degree of unsaturation in oil. The saturated part of the oils does not react with iodine, but the unsaturated fatty acids have double or triple bonds which can readily attacked by the iodine. The more the iodine values, the more the unsaturated fatty acid present in the oil. The standard method as stated in ASTM D5554-2011 was followed in this work to measure the iodine value of oil. According to the procedure, 10 ml of oil sample was added into an iodination flask. After that, 20 ml of iodine monochloride reagent was added into the flask. After mixing the solution properly, the flask was then kept in the dark for incubation at room temperature for 30 minutes. A blank sample was also prepared by following the same procedure followed by incubation for 30 minutes at room temperature. After incubation, 10 ml of potassium iodide was added in the test iodination-flask. Then, it was required to add 30 ml of distilled water in the flask. The solution of the test flask was then titrated by 0.1 N sodium thiosulphate till the colour of the solution turned from dark red brown to pale straw colour. After that, 1 ml of starch solution was added in the flask. The colour of the solution was then turned to purple blue. The titration was continued until the solution turned to colourless. The same process was repeated for the case of blank solution. Iodination flask, burette, burette stand, glass pipette, measuring cylinder, iodine monochloride reagent, potassium iodide, 0.1 N sodium thiosulphate, starch indicator solution, chloroform and distilled water was required for the test. The iodine value of the sample was calculated by using the following formula:

$$\frac{\text{Equivalent weight of Iodine} \times \text{Volume of sodium thiosulphate used in ml} \times \text{Normality of sodium thiosulphate} \times 100 \times 1}{\text{Weight of oil sample used for analysis (g)}} \qquad (3.2)$$

Where, the equivalent weight of iodine is 127, and normality of sodium thiosulphate is 0.1.

3.3.2.3 Density

A gas pycnometer (Model-micromeritics, AccuPyc II 1340) was used to determine the density of the samples. The equipment was operated by inert helium gas. Approximately, 2 to 3 g of each sample was measured up to four decimal by using a digital balance machine. Five replicates of analysis were measured for each category of sample, and an average value was considered for data analysis.

3.3.2.4 Viscosity

The viscosity of the liquid samples was determined at 25±2^{o}C using Brook-field viscometer (Model RVT, Brookfield Engineering Laboratories Inc., Stoughton, MA) with spindle no. 18 and 12 rpm. The viscosities of the samples were measured according to ASTM D1084-97.

3.3.2.5 Fourier transform of infrared (FTIR) spectroscopy

The functional groups of the samples were examined by a Fourier transform of infrared spectrophotometer (Model- Thermo SCIENTIFIC, NICOLET AVATAR 370DTGS, USA). The KBr method was employed for the analysis with scanning range of 400 to 4000 cm^{-1}.

3.3.2.6 Nuclear magnetic resonance (NMR) spectroscopy

The H^1 NMR spectra of the liquid samples were recorded on a Nuclear Magnetic Resonance 500 MHz (Model: FT-NMR Avance III, Bruker, Switzerland) by dissolving them in the deuterated chloroform.

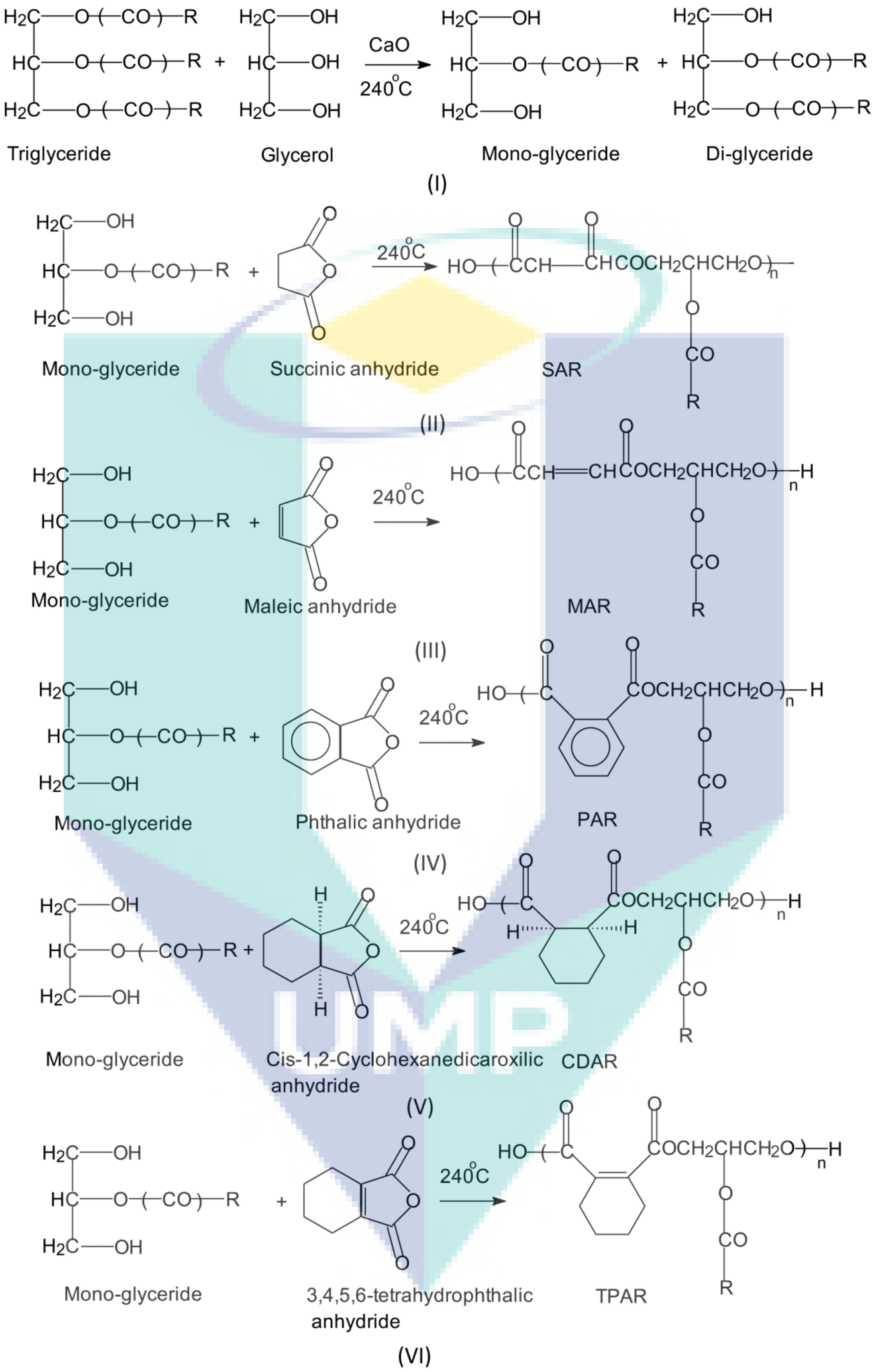
3.3.3 Resin Preparation and Characterization

3.3.3.1 Preparation of bio resin

The reaction was performed in a four-necked round bottom flask. A magnetic heater was used to heat the reaction mixtures. A dean-stark apparatus was attached with the condenser to collect the water produced from the condensation reaction. Nitrogen gas flow was ensured to avoid oxidation reaction during preparation of resin. The arrangement for the reaction is presented in Figure 3.3. A fixed amount of dehydrated oil and glycerol was reacted in the presence of catalyst (calcium oxide) for alcoholysis process, at 240^oC for nearly 1 h. The completion of the reaction was ensured by the complete solubility of the prepared monoglyceride in methanol as a ratio of 1:3 (v/v). Then, the mixture was cool down to 120^oC and the mono-glyceride prepared from the alcoholysis was brought into contact with different types of acid anhydrides to produce glyceride phthalate (alkyd resin) via polyesterification reaction. The general reactions for alcoholysis and esterification process are shown in Scheme 3.1. The details of the ingredients for the alcoholysis process of palm oil are listed in Table 3.4. The amount of ingredients was selected by the collision theory of the reaction between oil and glycerol molecule.

Table 3.4: Reactants for the alcoholysis process of palm oil.

Raw materials	Used amount
CaO	0.02- 0.08 wt.% (respect to oil)
Oil	33.2 g
Glycerol	7.36 g



Scheme 3.1: Alcoholysis (I) and esterification reaction (II-VI).

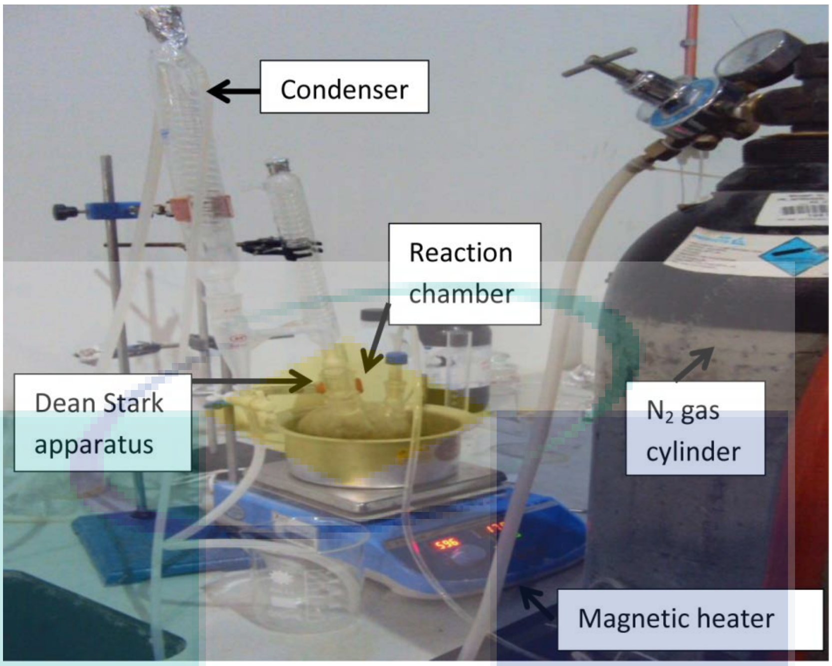


Figure 3.3: Reaction set up for polyalkyd preparation.

Table 3.7: Amount of different acid anhydrides for the esterification reaction for the preparation of polyalkyds.

Sample name	Amount used (g)
SAR	11.62
MAR	11.62
PAR	11.62
TPAR	11.62
CDAR	11.62

Table 3.8: Mixing details for the esterification reaction for the preparation of polyalkyds based on different ratios of aromatic and aliphatic acid anhydrides.

Sample name	TPA:MA	TPA (g)	MA (g)
MA0	100:0	11.62	0
MA50	50:50	5.81	5.81
MA75	25:75	2.91	8.71
MA100	0:100	0	11.62

3.3.3.3 Curing process of resin

The curing process of the liquid resins involves the formation of linkages among the polymeric chains through their unsaturation. In this process, MEKP, cobalt nephthenate and styrene were mixed with a fixed amount of resin, and agitated manually at 60^{o}C for 10 min. The mixing details of the ingredients are listed in Table 3.9. After that, the resins were poured onto a Petridis and put in an oven for curing process. The samples were checked frequently for the dryness by using the finger-tip. Only spot-free samples were considered as cured polymeric films for further characterization. The time for curing was recorded as drying or curing time of the resins.

Table 3.9: Mixing details of the curing process.

Ingredients	Amount used (g)
Resin	10.0 g
MEKP	0.4 g
Cobalt-naphthenate	0.2 g
Styrene	3.0 g

3.3.3.5 Non-volatile materials content

To calculate the non-volatile materials content, three specimens were placed in the oven within 30 minutes in previously weighted steel plate, and heated for 2 h at 140^{o}C. The non-volatile mater was calculated from the difference of the weight of the plates, which were recorded initially and finally. The mean value of the three results was reported as the percentage of non-volatile matter.

$$PDI = \frac{M_w}{M_n}$$

3.3.4.1 Nano composite film preparation

Nano composite films were prepared by incorporation of MWCNTs with the assistance of sonication technique by using an ultrasound bath (Daihan Ultrasonic Bath, CREST-ultrasonics). Different percentages of MWCNTs such as 0.5, 1.0 and 1.5 wt.%

were loaded. Almost similar amount of carbon nanotubes (0 to 1.0 wt.%) were also used for the preparation of castor oil based polyurethane nanocomposite films (Ali et al., 2014). The nano particles were dispersed into styrene with the help of ultrasound techniques for 30 min. The nano particles incorporated styrene was then added with resin and stirred for another 30 min at 60^{o}C. After that, MEKP and cobalt naphthanate was added and stirred for 30 min more. Then, the mixture was poured onto Petridis and kept inside the oven at 120^{o}C. The samples were checked frequently with finger-tip for the dryness. The time for the drying was recorded and the films were subjected for further analysis. The optimum loading was confirmed by the resinous property, and the best loading percentages was considered for in-situ reaction during esterification.

3.3.4.2 Scanning electron microscopy

The morphological images of the films were analysed by using scanning electron microscope (model-ZEISS, EVO 50). The samples were air dried before testing. For the testing, the samples were put onto a metal based holder with the help of double sided sticky carbon tape. Prior to SEM observation, samples were coated with gold with the help of vacuum sputter-coater for the ease of conduction. The coated samples were then subjected for microscope images at 300 kV. The microstructures of materials were compared by observing the surfaces of films.

3.3.4.3 Thermogravimetric analysis

A thermogravimetric analyser (TA instrument, model- TA-Q500), was used to determine the thermal behaviour of the polymeric films. Nearly, 5 mg of the sample was considered for the testing. The holder of the sample was made of platinum. The samples were heated from 25 to 600^{o}C with a heating rate of 20 ^{0}C/min. The weight loss was recorded in against of temperatures. Nitrogen gas was used during the testing to avoid oxidation.

3.3.4.4 Differential scanning calorimetry

A TA instrument, Q-1000, was used for DSC analysis with a heating rate of 20^{o}C/min. The ramp method was applied using aluminium pan with a temperature range

25-410^{o}C. Approximately 3 to 4 g of the sample was considered for this test. The melting points of the films were observed by the analysis.

3.3.4.6 Tensile properties

A fresh portion of the cured film was also used to determine tensile properties such as tensile strength, tensile modulus and elongation at break using a universal testing machine (model: Instron 4505), with a load cell of 5 KN. The method was followed according to ASTM D 638. A cross head speed was fixed at 1 mm/min during the testing. Tensile strength (TS) and tensile modulus (TM) were reported for the mechanical properties of the film produced from different formulations.

3.3.4.10 Chemical resistivity

For chemical resistivity, nearly 0.5 g of each type of films was immersed in various solutions of different chemicals, such as hydrochloric acid (5%), sodium hydroxide (5%), sodium chloride (5%) and distilled water for 24 h, at room temperature. After that, the weight loss was measured and recorded for analyses. A relative expression of the measurements such as, excellent (not affected), fair (less affected) and poor (affected) were used to indicate the chemical resistivity of the films based on their weight losses. The chemical resistivity testing was adopted from ASTM D1647. For the assessments of MWCNTs-filled films, the time was extended from 24 h to 48 h and changes were observed and recorded.

3.3.4.11 Gloss

Gloss (at 60^{o}) of the cured films was measured in accordance with ASTM D523-08. The test method is important for comparing of different films for understanding the relative properties of the films prepared from different formulations. The surface capacity of different films to reflect light in direction close to the specular are measured through these testing. Two results of a single determination was considered for the desire result of a film and testing was carried out for several times until the value is reached more than the limit of maximum acceptable differences as stated in the method (0.9 for both the ceramic tiles and painted tiles for a single determination within laboratories). According to Richart the gloss are categorized with respect to their values as stated in Table 3.10 (Richart, 1999).

Table 3.10: Different gloss categories at 60^{o} (Richart, 1999).

Category	Gloss value (60^{o})
High	➢ 85
Standard	70 to 85
Semi	40 to 70
Low	15 to 40

3.3.4.12 Adhesion

Adhesion testing was conducted based on the ASTM D3359 test method. The dried films were cut by cross hatch cutter and the coating flakes were cleaned using a brush. A scotch tape was adhered onto the film and peeled of quickly at 180^{o}C angle. The peeled off grid of areas on the tape were observed by a magnifier.

3.3.4.13 Solubility

The solubility of the resins was measured by using different organic solvent like ethanol, butanol, methanol, xylene and toluene. The behaviour was observed and time was recorded for different resins for different solvents.

3.3.4.14 Pencil hardness

The cured films were subjected for pencil hardness testing to determine the hardness of the films as pencil hardness. The sharpened edge of the pencil was pressed slowly along the surface with a force of 5 N. Tests on three specimens were carried out to see whether the pencil is capable of scratching on the film surface or not. The pencil hardness of the cured resin was measured with the help of a pencil hardness tester (Model-

B-3084), in scale of 6B to 6H of a standard set of pencils. The test was performed by dragging the pencil along the films by following ASTM D3363-05 method. The hardest pencil grade which fails to scratch the coating was recorded. The ability to scratch is termed as Fail, whereas non-ability is termed as Pass in this research. A set of calibrated drawing lead of the following scale of hardness is presented in Figure 3.4.

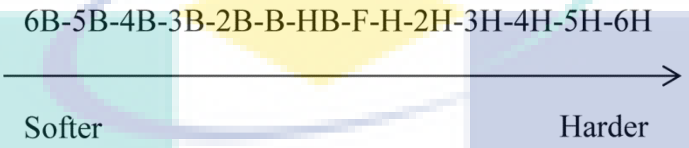


Figure 3.4: Scale of pencil hardness testing from softer to harder hardness.

This process is rapid and inexpensive for the measurement of film hardness. It is being commonly used by the coating industry for many years both for clear and pigmented organic coating films. The film was coated on an aluminium plate and the plate is placed on a plane surface of a table. The pencil is placed firmly on the surface of the film at 45^{o} angle and pushed away in a 6.5 mm stroke. Pencil hardness was measured by the type of pencil as it failed to cut the film is referred as pencil hardness. The result was confirmed by the two results performed by two operators when the difference of the results is by one unit of the scale.

3.3.4.15 Wettability

The wettability of the films was measured by contact angle measurement by using a contact angle meter (Goniometer, China). Water was used as the probe liquid for the measurement. The static contact angle of water on the surface of the films was determined. About 5.00 μl of water droplet was allowed to rest on the polymeric films by using a 10-ml Hamilton positive displacement syringe and images were captured. During measurement the surrounding temperature was 25^{o}C and relative humidity of 65%. Fifteen images at different locations of the surface were analysed for each sample with the help of contact angle software (model- JY-82), and average of ten images result were computed to obtain the contact angle.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 INTRODUCTION

In this chapter, the effects of dehydration of oil by using different types of catalysts such as, H_2SO_4, $NaHSO_4$, $KHSO_4$, PTSA and H_3PO_4 have been analysed. The optimization through RSM for esterification reaction and the effects of various variables have been summarized. In addition, the properties of polyalkyds prepared from different types of acid anhydrides viz., succinic anhydride, maleic anhydride, phthalic anhydride, 3,4,5,6-tetrahydrophthalic anhydride and cis-1,2-cyclohaxanedicaroboxylic anhydride have been studied and compared with each other. Additionally, the effects of aromatic and aliphatic content have also been highlighted. The curing kinetics of the formulated resin have been focused and discussed. Moreover, the film properties of the cured resins have been analysed. Finally, nanocomposite coating films have been produced by the incorporation of different percentages of MWCNTs, and reinforcement characteristics have been studied.

4.2 EVALUATION OF POLYMERIZATION REACTION AND TECHNIQUE

The esterification process is a polycondensation reaction, which proceeds under step polymerization technique. Usually, in this process, the building of polymers happens as step-wise and through the functional groups of the monomers. Once the polymerization starts, it takes time to be completed. Thus the esterification process of palm oil was completed in longer time as tabulated earlier. The two important functional groups, carboxylic (-COOH) and hydroxyl (-OH) are involved in this reaction. The basic reaction is shown in Scheme 4.1. There is a benefit of using triglyceride and tri-ol or polyol for esterification reaction: the polymerisation can happen as long as carboxylic functional group present in the product of the reaction. As the functionality of glycerol is three (3), thus the possibility to build up a three dimensional network structure of polymer is very high. Moreover, a favourable reaction condition may raise the growth of polymeric chain in a faster and spontaneous manner. Thus sometime if the ratio of bi-functional and trifunctional monomer is not competent to each other, possibility of the formation of insoluble and infusible mass of three dimensional products is high. Generally, the insoluble or infusible mass is called “gel”. To avoid the gel formation, the ratio of the ingredients is very important in the process.

Scheme 4.1: Basic mechanism for a polycondensation reaction between carboxylic and hydroxyl functional group containing compound.

The polymerization technique was used in this research can be considered as emulsion polymerization, where the anionic compound and R-COOCa are considered as surface active agent or surfactant. Here, the monomer, glyceride phthalate, is dispersed in aqueous phase in emulsion form. The surfactant lower the surface tension at the monomer/water (produced during the reaction) interface, which facilitate the overall emulsification process. Although the water generated in polycondensation reaction, was eventually, withdrawn from the reaction chamber by dean-stark apparatus, but it helped effectively the emulsification process for polyalkyd formation.

4.3 ANALYSES OF RESIN PROPERTIES: EFFECTS OF THE TYPES OF ACID ANHYDRIDES

The optimum reaction conditions, obtained from RSM analysis, were used to formulate different types of polyalkyd resins based on various acid anhydrides like succinic anhydride (SA), maleic anhydride (MA), phthalic anhydride (PA), 3,4,5,6-tetrahydrophthalic anhydride (TPA) and cis-1,2-cyclohaxanedicarboxylic anhydride (CDA). Various physicochemical properties of the resins such as, acid value, iodine value, yield, density, specific gravity, molecular weight, polydispersity index, non-volatile material content, drying time, colour, etc. were tested by using different standard methods. The cured films were tested for thermogravimetric analysis, gloss, gel-content, swelling ratio, pencil hardness, chemical resistivity, adhesion characteristics, X-ray diffraction and surface morphology. Moreover, hydrophobicity of the cured films was observed by contact angle measurement. A comparison was drawn among the resins prepared from different acid anhydrides. Analysis revealed that the TPA-based resin shows improved resinous property than others.

4.3.1 Physicochemical Properties

The physicochemical properties of the resins are listed in Table 4.6. The density of all the resins was found to be in the range of 0.9145 to 0.9623 g/cm^3, and increased from crude oil (0.8886 g/cm^3) and dehydrated oil (0.8010 g/cm^3). Among the resins, TPAR and CDAR showed higher density compared to others. The higher density of TPAR and CDAR is probably due to the higher molecular weight of TPA and CDA. The same trend of result was found for the case of viscosity measurement, as higher density is responsible for higher viscosity. However, the viscosity of the resins was found to be in the range of 89.4 to 104.45 mPa.s, which is higher than that of crude (86.4 mPa.s) and dehydrated oil (35.4 mPa.s). The viscosity of the resins based on aromatic acid anhydrides showed slightly higher value than aliphatic acid anhydride-based resins due to their higher molecular weight. Higher crosslinking in the polymers are important determinate for the viscosity, which is probably best for the case of TPAR compared to others.

The acid value of crude oil was found to be 54 mg KOH/ g of oil sample, whereas all the resins showed values in range of 29 to 34 mg KOH/g of sample. The iodine value of the resins was found to be increased than crude oil (49 g I_2/ 100 g of oil). Thus the unsaturation was found to be increased due to the dehydration process as well as incorporation of unsaturated aliphatic (MA) and aromatic acid anhydrides (TPA). The highest unsaturation was showed by TPAR with iodine value as maximum as 80. The specific gravity of the resins was found to be in the range of 0.9712 to 0.9767. The lower value of specific gravity indicates the absence of any heavy metal in the produced bio-resins. The colours of the resins were observed to be dark brown, whereas the oil was light yellow. The non-volatile material content of the resins was found to be as high as 96.4 to 98.5%, which is indicating the solid portion of the resins and categorizing them as non-polluting materials (Patel et al., 2008).

The yield percentage of the polyalkyds was found to be 81 to 88. The drying time of SAR, MAR, PAR, TPAR and CDAR were found to be 5 h 37 min, 4 h 43 min, 5 h 32 min, 4 h 28 min and 4 h 57 min, respectively. The shortest drying time was showed by the MAR and TPAR due to the unsaturation nature of the acid anhydrides. The drying time was found to be reduced almost by 50 to 60 % compared to that of crude oil based resin

(11 h 9 min). Due to the presence of high amount of saturated fatty acid (nearly 51%), the drying time of crude palm oil based resin was found to be longer. The GPC technique was used to determine the number average molecular weight (Mn), weight average molecular weight (Mw) and polydispersity index (PDI). The Mn of SAR, MAR, PAR, TPAR and CDAR were found to be 2603, 3100, 3204, 3598 and 3485, respectively. The Mw for the resins was found to be 3615, 5628, 6828, 8450 and 7964, whereas the PDI was found to be 1.38, 1.81, 2.13, 2.34 and 2.28, respectively. The molecular weight was found to be increased in an order of higher molecular weight of acid anhydride incorporated in the polyalkyd chain and partly due to the crosslinking density of the resins. The higher PDI and molecular weight of TPAR is probably due to higher crosslinking density present in the polymeric chain. Thus the polydispersity index was found to be increasing in an order of TPAR > CDAR > PAR > MAR > SAR.

Table 4.6: Properties of various types of resins based on different acid anhydrides.

Properties	**SAR**	**MAR**	**PAR**	**TPAR**	**CDAR**
Density (g/cm^3)	0.9145	0.9311	0.9445	0.9623	0.9543
Viscosity (mPa.s)	89.4	92.30	101.10	104.45	103.41
Acid value (mg KOH/g)	34	29	31	33	30
Iodine value (g I_2/ 100 g)	65	78	70	80	75
Specific gravity	0.9712	0.9756	0.9767	0.9722	0.9712
Colour	Light Brown	Dark Brown	Dark Brown	Dark Brown	Dark Brown
Non-volatile material content (%)	96.4	96.8	97.2	98.2	98.5
Yield (wt.%)	81	87	86	88	85
Drying time	5 h 37 min	4 h 33 min	5 hr 32 min	4 h 28 min	4 h 57 min
Number average molecular weight (M_n)	2603	3100	3204	3598	3485
Weight average molecular weight (M_w)	3615	5628	6828	8450	7964

Polydispersity index (PDI)	1.38	1.81	2.13	2.34	2.28

4.3.2 Structural Properties

The functional groups and structure of the resins were determined by FTIR analysis (Figure 4.7). From the figure, different functional groups and important linkages can be seen. Among the linkages, ester functional group and double bonds in olefins are noticeable. The absorbance peak at around 714 to 726 cm^{-1} was due to -CH bending vibration, whereas the peak at 884 and 902 cm^{-1} because of C-C stretching vibration. C-O-C stretching vibrations can be depicted by the peaks at around 1130 and 1250 cm^{-1} for aliphatic and aromatic compound, respectively. For all the resins, the peak at around 1741 cm^{-1} due to the carbonyl group (C=O) stretching vibration in oil (Figure 4.1), which was found to be shifted to a region of 1733 to 1735 cm^{-1}, confirming the changes around the peak because of esterification reaction (Patel et al., 2008; Issam et al., 2009; Saravari et al., 2005). This change is probably due to the modification around the carbonyl group for the presence of aliphatic and aromatic acid anhydride compound in the backbone chain of the polymer. Next to carbonyl group, the asymmetric and symmetric vibration for -CH$_2$ can be ensured by the peak at around 2850 cm^{-1}, while that at 2920 cm^{-1} helped to anticipate the starching vibration for –CH moiety (Brioude et al., 2007).

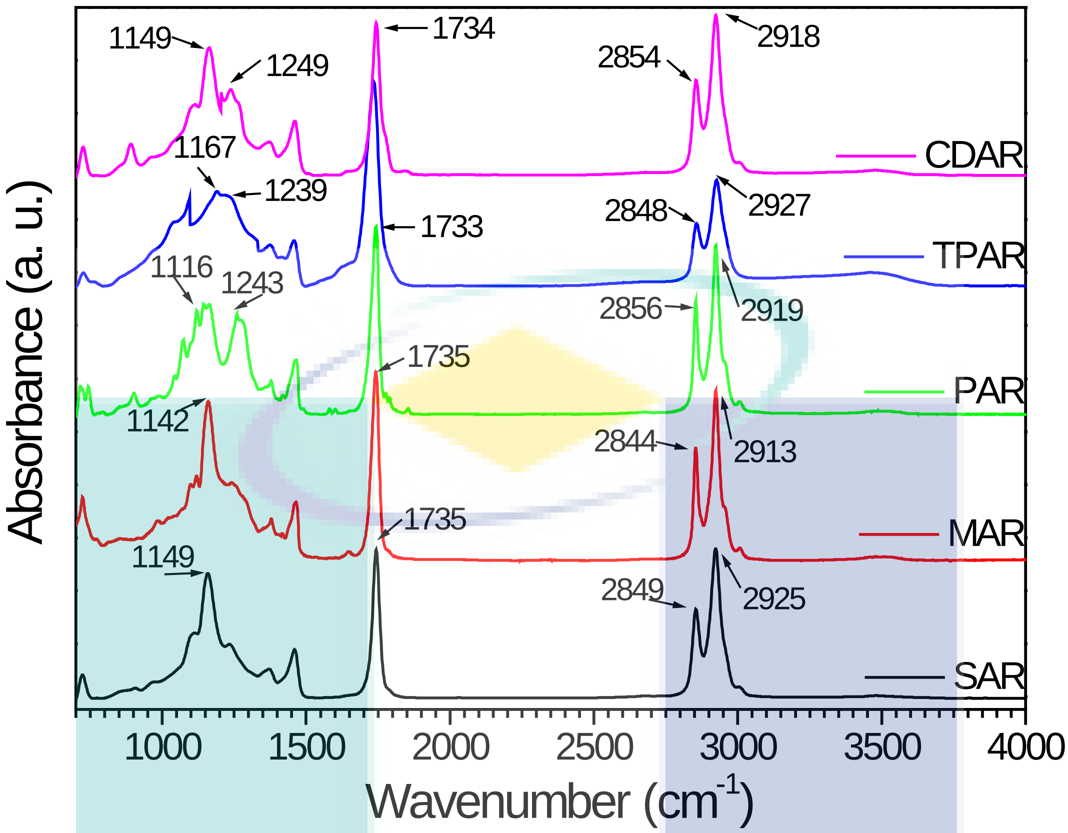


Figure 4.7: FTIR spectra of the resins based on different acid anhydrides.

The information for proton density of different moieties can be depicted in the Figure 4.8, 4.9, 4.10, 4.11 and 4.12 by ^{1}H NMR spectra of the SAR, MAR, PAR, TPAR and CDAR, respectively. The proton for terminal methyl groups of fatty acids was confirmed by the peak at around ∂ 0.87. Peaks at around 1.25 to 1.30 were due to the protons of all -CH_2 present in the chain. Peaks appeared at 4.2 to 4.4 probably due to the methylene protons of glycerol molecule and that at 5.25 to 5.4 because of the unsaturated carbon. The peak appeared at 6.25 to 6.85 ppm was probably for the presence of -CH in glycerol molecule. The proton for the aromatic ring can be depicted by the peak at ∂ 6.8–7.5.

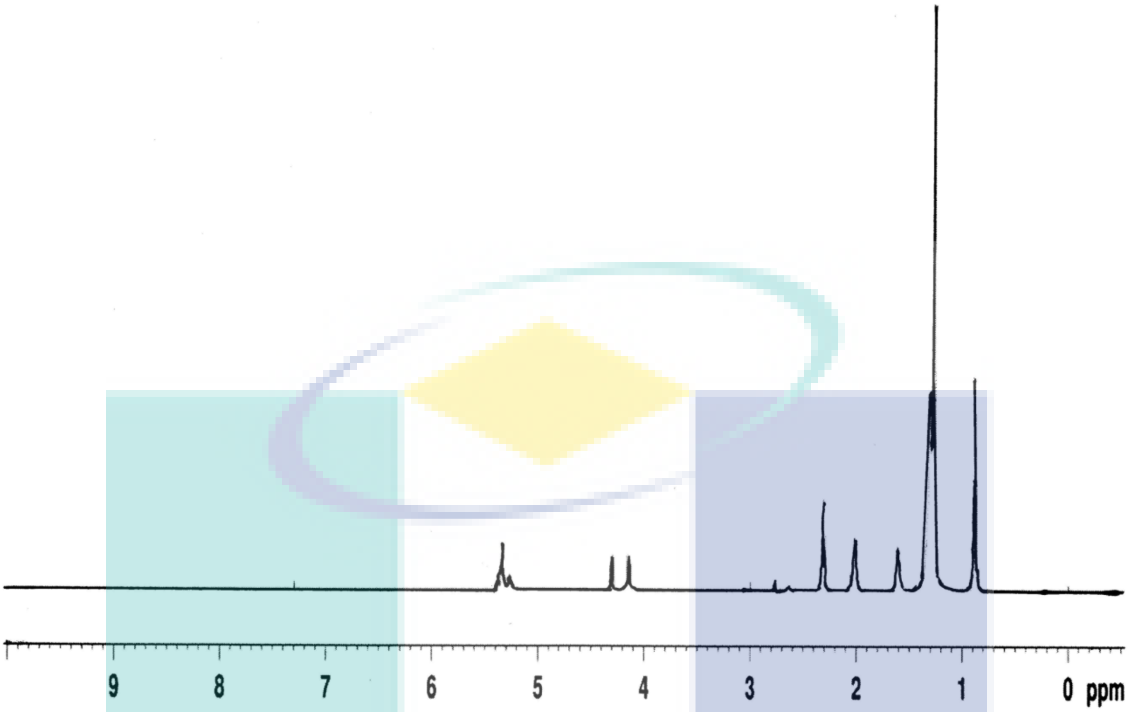


Figure 4.8: ^{1}H NMR spectrum of SAR.

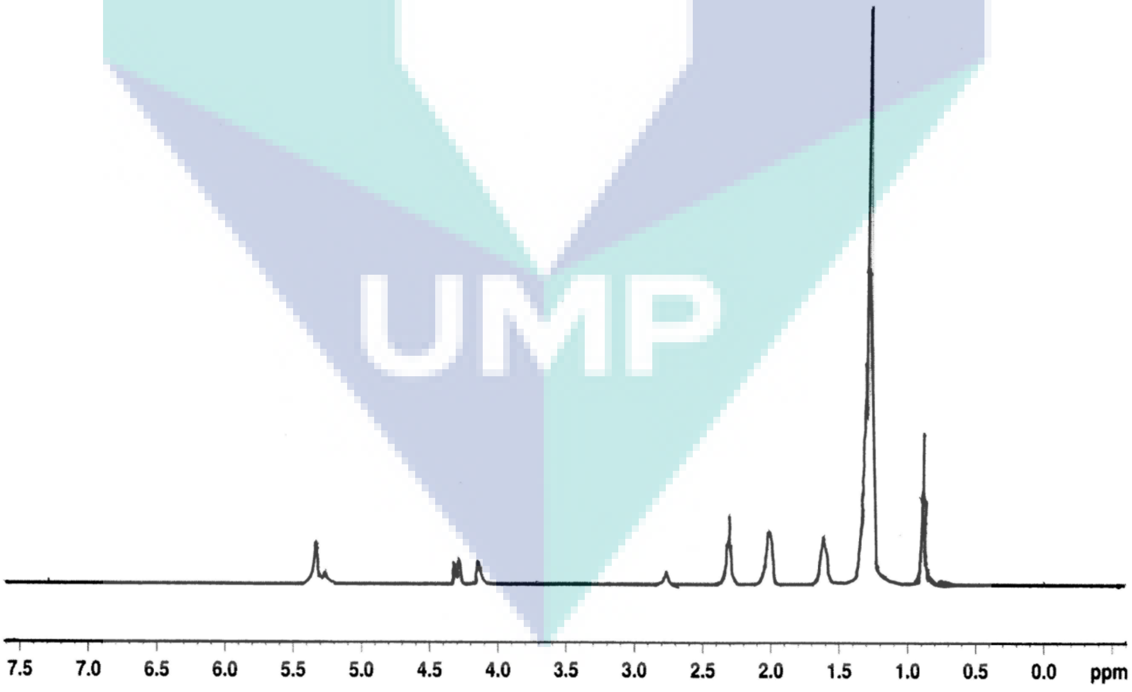


Figure 4.9: ^{1}H NMR spectrum of MAR.

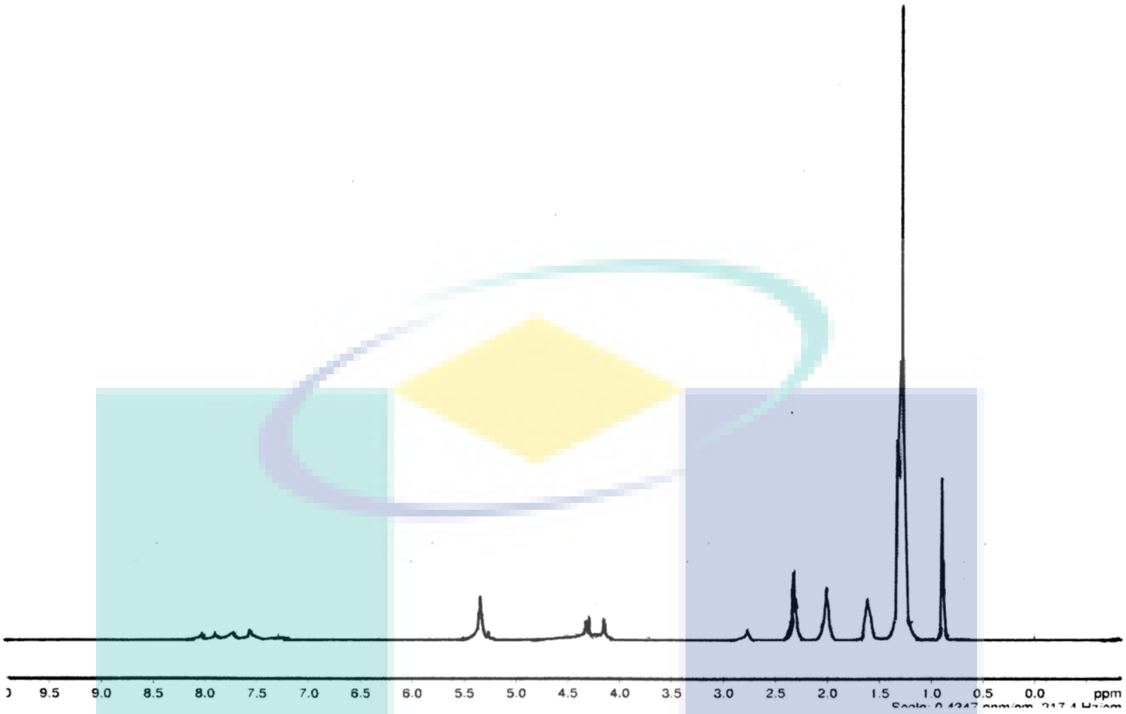


Figure 4.10: ^{1}H NMR spectrum of PAR.

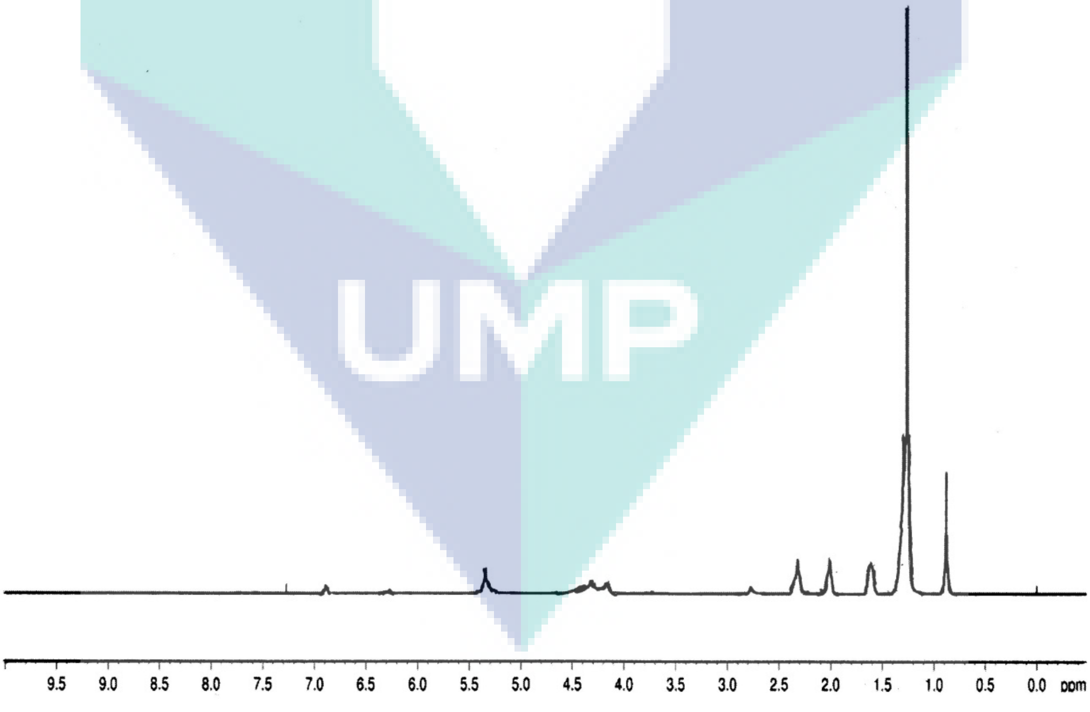


Figure 4.11: ^{1}H NMR spectrum of TPAR.

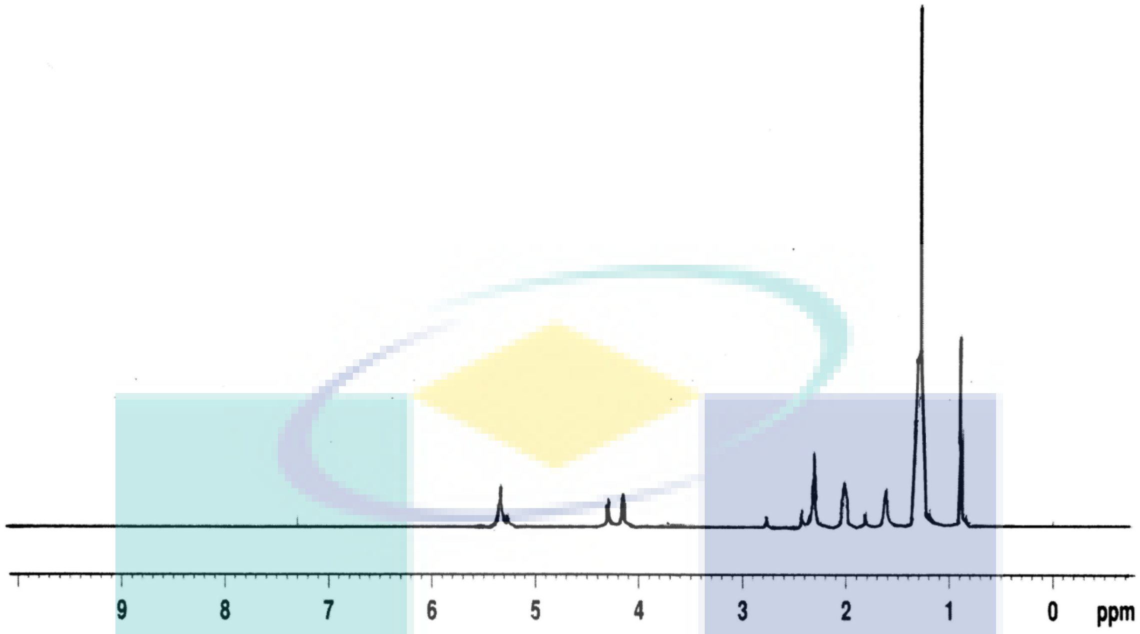


Figure 4.12: ^{1}H NMR spectrum of CDAR.

4.3.3 XRD

Figure 4.13 shows XRD patterns of different films prepared from different acid anhydrides. The plot is showing intensity vs. scattering angle curves. The values of scattering angle, d-spacing, crystalline size and crystallinity of different films are listed in Table 4.7. The scattering angles in between 19.36^o and 19.84^o was found to be apparent because of the crystalline and amorphous region of the polyalkyd resin, as shown by the medium sharp peak. The same characteristic peak for TPA-based film was found to be a little sharp at around 21.43^o. This is probably due to the extra amount of unsaturation and crosslinking density which is favourable for mesomorphic or crystalline organization (Brioude et al., 2007). The crystalline size of the films was found to be in the range of 12.76 to 15.5 nm. The d-spacing or intra-chain segment distance was calculated by using Bragg’s law, and found to be in the range of 4.14 to 4.58 Å (Azaroff, 1968). The similar result was observed by the other investigators in a different study (Brioude et al., 2007). Although the lattice spacing changed a little, but it can be predicted that the variations in the spacing is probably due to different nature of the acid anhydrides that build the polymer. In addition, the change in lattice spacing depends on the curing time and temperature (Dean et al., 2005; Mohon et al., 2005; Montserrat et al., 2002). The overall crystallinity was varied a little bit due to different acid anhydrides as seen in Table 4.7.

Table 4.7: XRD parameters for different types of resin based on different acid anhydrides.

Resin types	Peak position (2θ)	d (Å)	Crystalline size (nm)	Crystallinity (%)
SAR	19.36	4.58	15.98	43.31
MAR	19.67	4.50	12.76	44.89
PAR	19.84	4.47	13.45	40.54
TPAR	21.43	4.14	15.50	39.85
CDAR	19.35	4.58	15.50	39.78

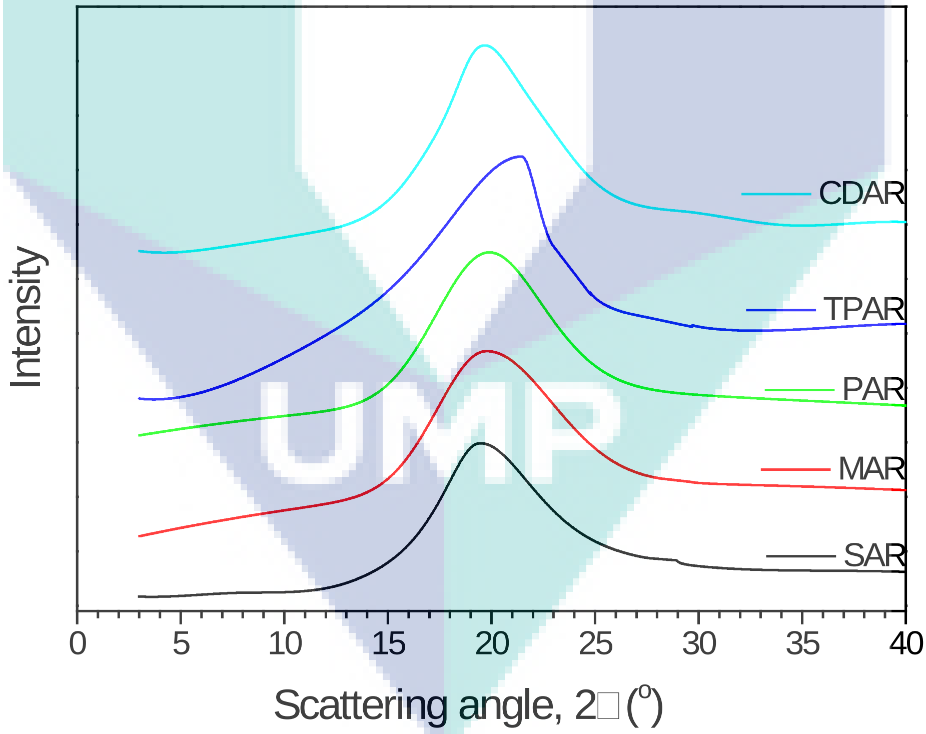


Figure 4.13: XRD profiles of different films based on different acid anhydrides.

4.3.4 Surface Property

Figure 4.14 shows the contact angle images of different resin based films. The contact angle of TPAR was found to be maximum (90^o) among the films produced from different acid anhydrides. The hydrophobicity of aromatic anhydride based films was found to be better than the aliphatic acid anhydride-based one. This may be due to the slow rate of hydrolyse process of aromatic acid ester than aliphatic based one (Zeno et al., 2007). Although the unsaturation present in aliphatic anhydride did not take part to increase the contact angle compared to saturated aliphatic anhydride based film, but that in aromatic acid anhydride showed a higher contact angle by 15^o. The conformational changes thought to be a reason for higher contact angle (Nie et al., 2010). The polar group may appear on the surface easily and lower the contact angle of aliphatic based polyesters (Kronberg et al., 2014). Additionally, the unsaturated aromatic acid anhydride may increase the degree of crosslinking density in the polymeric chain.

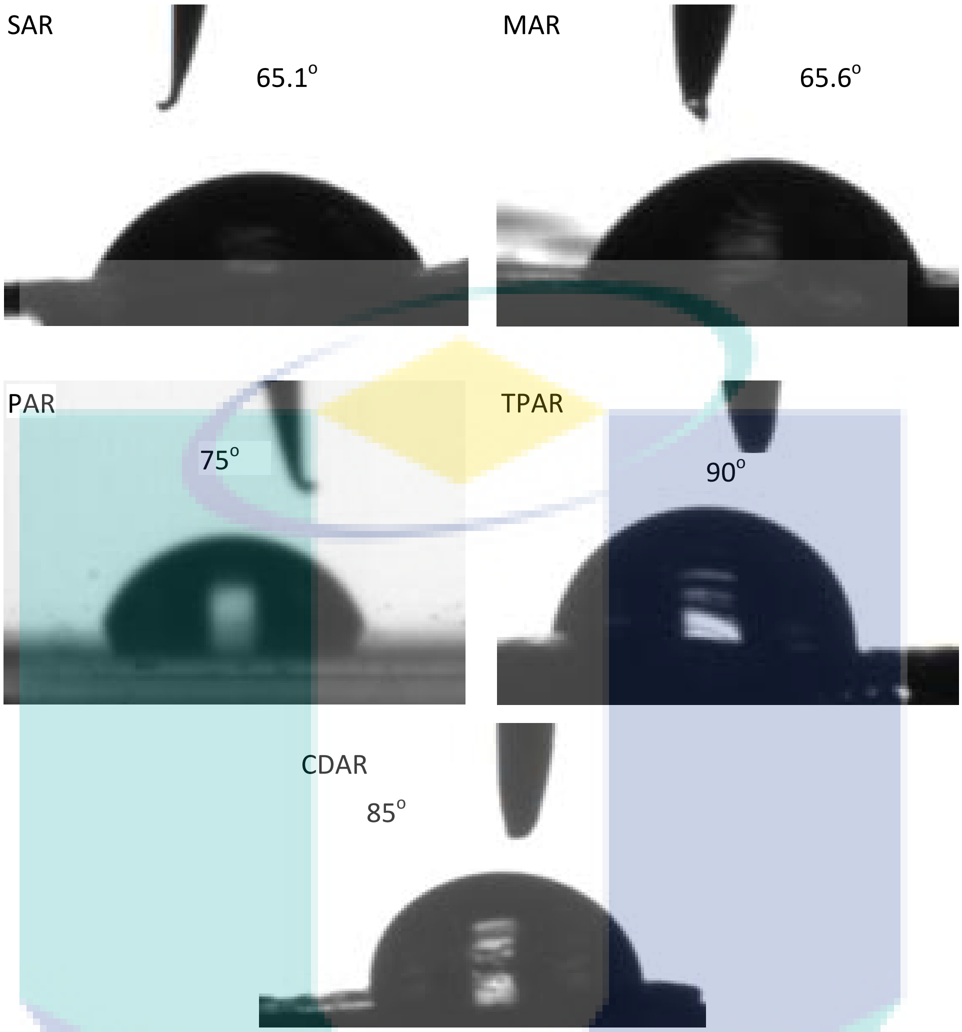


Figure 4.14: Contact angle of different acid anhydrides-based films showing the wettability.

The gloss property was measured for different films and the results are listed in Table 4.8. The gloss at 60^o was measured for all the films prepared from the resins. Acceptable gloss was showed by the resins of values 65, 67, 70, 75 and 72 for the case of SAR, MAR, PAR, TPAR and CDAR, respectively (Richart, 1999). The similar values were found to be in previous investigation which was claimed as acceptable gloss property (Schmidhau, 2001).

Table 4.8: Gloss, gel content, swelling ratio, crosslinking density and adhesion properties of different resins prepared from different acid anhydrides.

Resin types	**Gloss (60^o)**	**Gel content (%)**	**Swelling ratio**	**Crosslinking density x 10^4 mol cm^3**	**Adhesion (%)**
SAR	65	70	1.43	2.3	90
MAR	67	80	1.33	3.7	98
PAR	70	72	1.41	2.5	95
TPAR	75	87	1.25	4.1	100
CDAR	72	74	1.35	3.1	95

The adhesion property of different films produced from different acid anhydrides is listed in Table 4.8. It was found that all the films based on unsaturated acid anhydrides (MARR and TPAR) showed higher value compared to saturated acid anhydrides-based film, and it was as maximum as 100% for the case of TPAR. The better adhesion was observed due to better film forming property by the dehydrated palm oil. The additional unsaturation created during dehydration process as well as the unsaturation in the polymer chains, which are more susceptible for atmospheric oxygen attack and responsible for increasing the adhesion property of the resins.

Figure 4.15 shows the surfaces of the films produced from different resins. The surface of Resin A was found to be spotted, which probably due to the presence of saturated aliphatic acid anhydride (SA). On the other hand, a relatively smooth surface was observed for the case of MA-based resin (MAR) due to unsaturated aliphatic acid anhydride, although few spots are apparent. The surface of MAR, PAR and CDAR were found to be relatively darker compared to aliphatic anhydride based resins, although few spots were also observed for PAR and a little curly surface for TPAR. However a smooth surface was noticed for TPAR. This is probably due to better crosslinking density present in TPA based film.

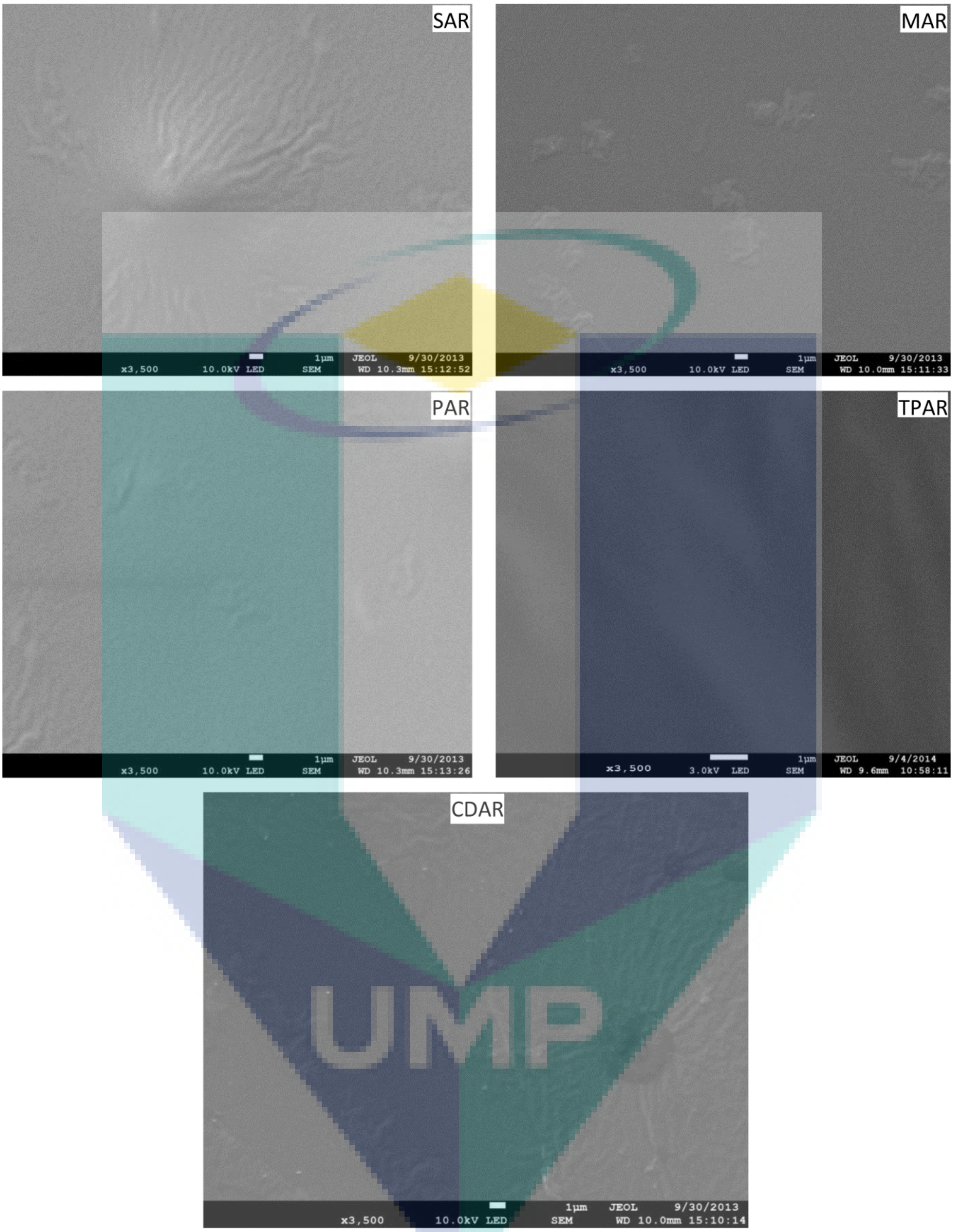


Figure 4.15: The FE-SEM images of the surfaces of different films prepared from different resins based on different acid anhydrides.

4.3.5 Crosslinking Density

The gel content of the films produced from different resins based on various acid anhydrides was measured, and the data is listed in Table 4.8. The gel content was found to be high for all the resins, indicating the presence of sufficient amount of crosslinking in the film’s structure. However, a comparison among the films helps to depict the best film produced from TPA showing the maximum value 87%. The MA based resin also showed higher gel content (80%), whereas the for SA and PA based films showed 70 and 72%, respectively, which are close to that of CDA based resin (74%). The gel content of different films affects the swelling ratio in a similar manner. The values for swelling ratios were found to be 1.43, 1.33, 1.41, 1.25 and 1.35 for the case of SAR, MAR, PAR, TPAR and CDAR, respectively (Table 4.8). This is a common phenomenon that the films with higher gel content show lower swelling ratio. The crosslinking density of the polymers were measured and found to be maximum for the case of TPA based film, 4.1 x 10^4 mol cm^3. The values for the crosslinking density of the polymers followed the order of gel content of the same. The crosslinking density was found to be 2.3 x 10^4, 3.7 x 10^4, 2.5 x 10^4 and 3.1 x 10^4 for the case of SAR, MAR, PAR and CDAR, respectively.

4.3.6 Solubility

The solubility of different resins was observed in different organic solvent like ethanol, butanol, methanol, xylene and toluene. The solubility of the polymer depends on the mobility of the polymer chains, hydrogen bonding and van der Waals force. However, all kinds of resins were found to be soluble in butanol, xylene and toluene. Similar observations were found in previous research (Bora et al., 2014). Among the solvents, xylene was found to be capable of dissolving polymeric resins efficiently at shorter time, while butanol and methanol found to be least in dissolving performance. The solubility was found to be affected due to different types of acid anhydrides. Generally, aliphatic compound takes longer time to dissolve in aromatic solvent like xylene and toluene, which was found to be faster for aromatic compound. The solubility also depends on the molecular weight of the resins. The higher molecular-weighted polymer or resins showed longer time to dissolve in the solvent, although they were found to be soluble completely after 10 h (in methanol and ethanol).

4.3.7 Pencil Hardness

The hardness of the polymeric films was measured by pencil hardness tester. The results were found to be different for different acid anhydride based films (Table 4.9). The analysis showed that aromatic anhydrides are responsible for better hardness of the polymeric films. Due to high crosslinking density, the unsaturated acid anhydride in the polymeric chain was also found to be effective to improve the property. However, from the result analyses it was found that all the films were found to be passed the hardness tested for 2B type of pencil. The differences in result were observed for B-type of pencil testing. The result showed that aromatic acid anhydride-based film showed positive result, whereas that of aliphatic anhydride failed. This is probably due to the presence of stable benzene ring in the polymeric chain based on aromatic acid anhydrides (Oldring, 2000; Sharma et al., 2001). Finally, HB-type of pencil was applied on the surface of all the films and only TPAR was found to be passed. This may be due to higher percentage of crosslinking density contributed by the unsaturated acid anhydride (TPA) and presence of stable aromatic groups in the polymer chains.

Table 4.9: Pencil hardness of various types of cured resins based on different acid anhydrides.

Pencil type	**SAR**	**MAR**	**PAR**	**TPAR**	**CDAR**
2B	Pass	Pass	Pass	Pass	Pass
B	Fail	Fail	Pass	Pass	Pass
HB	Fail	Fail	Fail	Pass	Fail

4.3.8 Thermal Properties

The thermal stability and degradation profile of various cured films are presented in Figure 4.16 (weight vs. temperature curves) and Figure 6.17 (derivative weight vs. temperature curves). From the thermogravimetric analyses (Figure 6.16), it was found that nearly 1 to 2 wt.% of moisture was removed during heating above 100^{o}C for all the films (Brioude et al., 2007). The removal of moisture and corresponding weight loss was confirmed by the isothermal heating of the polymers at 110^{o}C for 2 h, which indicates the same amount of weight loss without any change in chemical structure as observed by FTIR spectroscopy. It was found that all the types of films showed higher thermal stability and the initiation of the degradation started at about 306^{o}C. This is the property as observed from other aliphatic polyesters (Zorba et al., 2007; Chrissafis, et al., 2006; Aoyagi et al., 2002; Arvanitoyannis et al., 1995). It was found that TPAR showed the highest thermal stability among the resins based on different acid anhydrides. Table 4.10 shows the thermal properties of different films based on different acid anhydrides. The onset degradation temperatures were found to be 224, 253, 264, 317 and 286^{o}C for the case of SAR, MAR, PAR, TPAR and CDAR, respectively. The order of thermal stability was found to be as follows: TPAR > CDAR > PAR > MAR > SAR. The higher thermal stability of aromatic acid anhydride based resins is probably due to the presence of aromatic moiety in the alkyd chains. The highest stability of TPAR is probably due to the higher amount of crosslinking density and the presence of stable aromatic ring in the polymeric chains of the poly alkyds (Boruah et al., 2012). The residues after 600^{o}C for all the samples were found to be in the range of 2-10 wt.%. The amount of residue depends on the stability of the polymeric chain due to high temperature. The T_{max} was found to be 357, 364, 365, 374 and 371^{o}C, respectively, for SAR, MAR, PAR, TPAR and CDAR (Figure 4.17). Thus the thermal stability of these resins was found to be high enough to be used for any type of high-temperature applications.

Table 4.10: Thermal properties of different resins based on different acid anhydrides.

Resin types	**T_{onset} (^{o}C)**	**T_{max}**	**Residue (%)**	**T_m (^{o}C)**
SAR	224	357	10	300
MAR	353	364	6	334
PAR	264	365	7	346
TPAR	317	374	4	360
CDAR	286	371	2	345

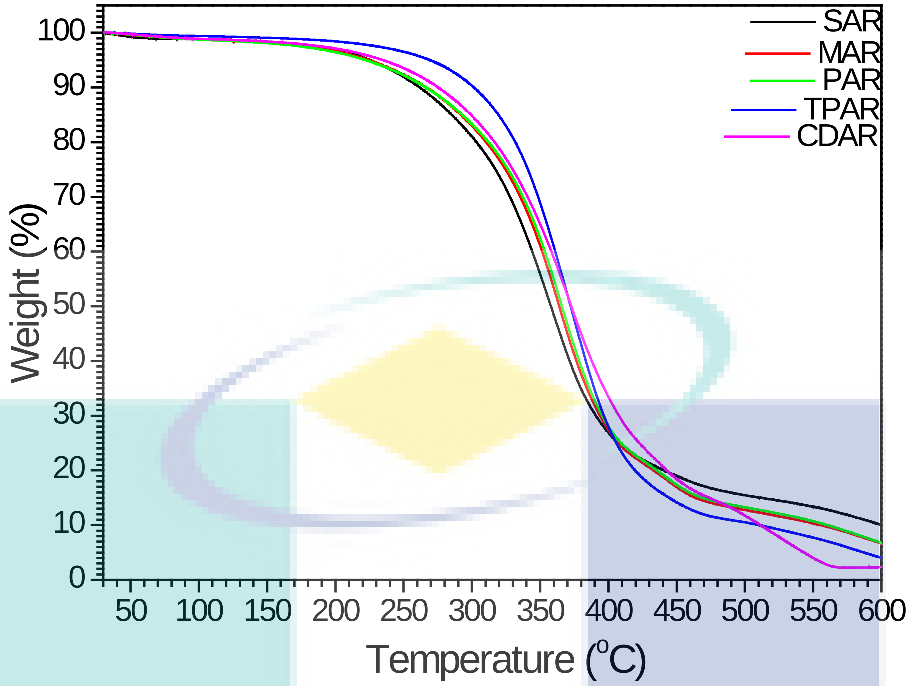


Figure 4.16: Weight vs. temperature curves of different resins based on different acid anhydrides.

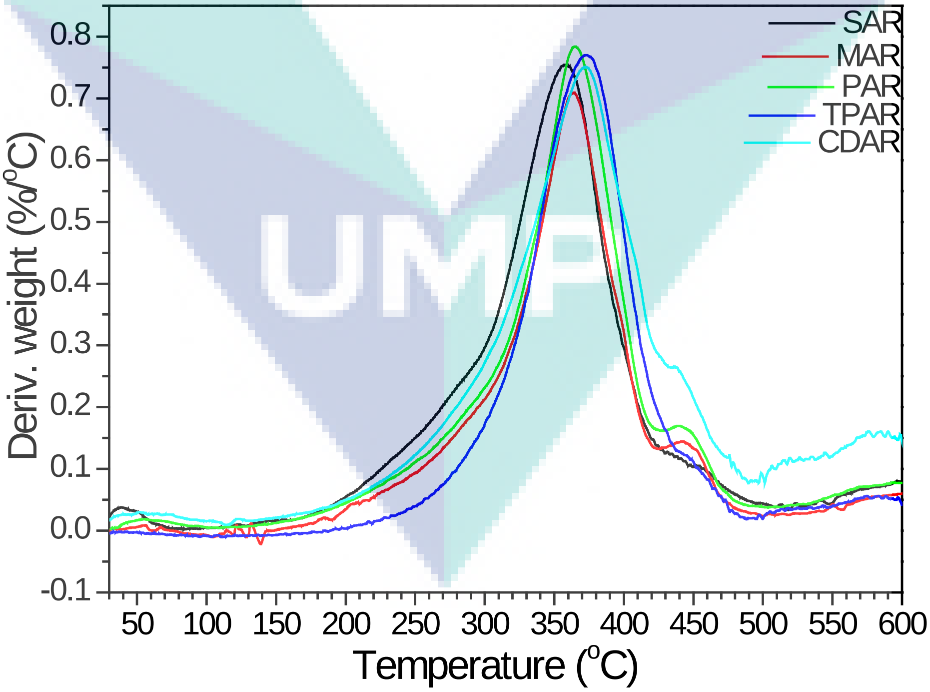


Figure 4.17: Derivative weight vs. temperature curves of different resins based on different acid anhydrides.

The DSC thermograms of the films are illustrated in Figure 4.18. From the graph, a general idea can be depicted about the melting temperature of the cured resins. The thermosetting resins showed a broad region close to the melting point. The melting temperature found maximum (360°C) for the case of TPAR, whereas SAR, MAR, PAR and CDAR showed that of 300, 334, 346 and 345°C, respectively. The higher melting point of PAR, TPAR and CDAR is due to the presence of stable aromatic ring in the backbone chain of the polymer. The highest melting temperature for TPAR is probably due to the higher crosslinking density.

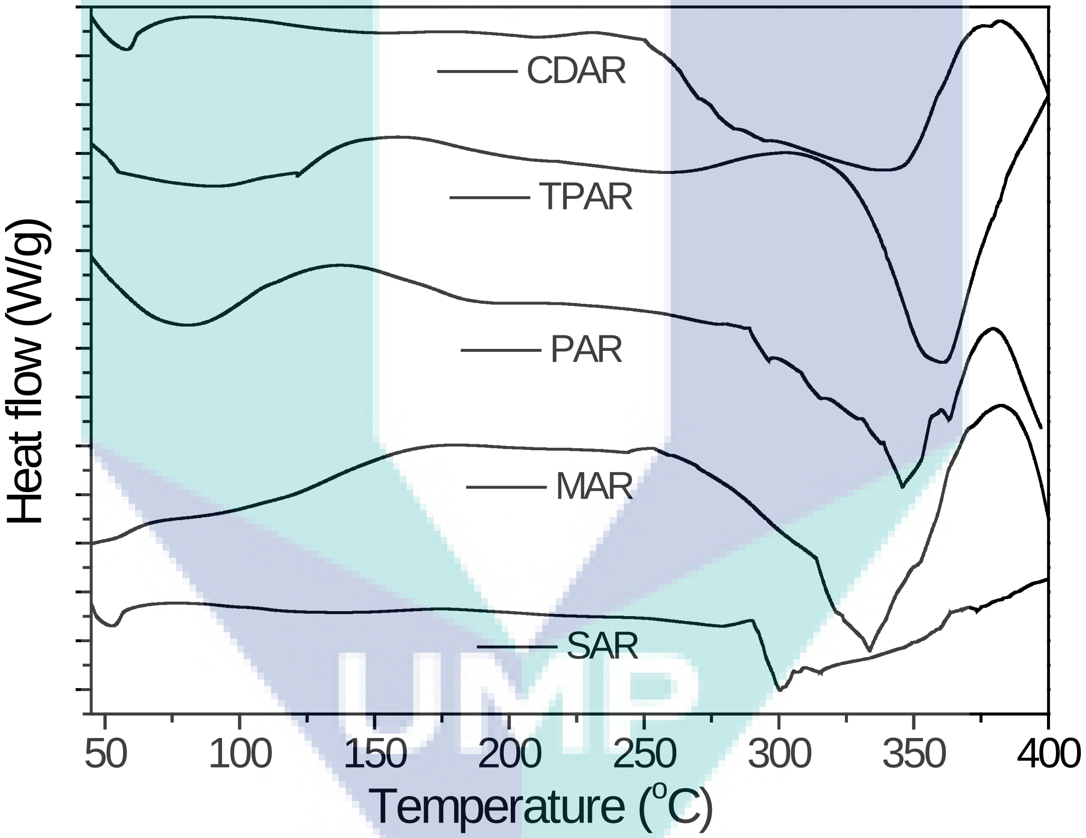


Figure 4.18: DSC thermograms of the various resins based on different acid anhydrides.

4.3.9 Chemical Resistivity

The chemical resistivity of various cured films is presented in Table 4.11. It was observed that all kinds of films were unaffected and highly resistant to distilled water, aqueous sodium chloride and hydrochloric acid during the immersion period. The chemical resistivity of the films was found to be different for sodium hydroxide solution. Among the resins based on different acid anhydrides, SAR and MAR showed poor resistivity to alkali solution due to their hydrolysable aliphatic ester group, but aromatic acid anhydride based resins, viz. PAR, TPAR and CDAR showed comparatively fair resistivity to the same solution. The better property of the aromatic acid anhydride based resins may be due to the presence of stable aromatic ring in the poly alkyd chains. The similar observation was found in previous study (Dutta et al., 2004).

Table 4.11: Chemical resistivity of various types of resins.

Solution	**SAR**	**MAR**	**PAR**	**TPAR**	**CDAR**
Distilled water	Excellent	Excellent	Excellent	Excellent	Excellent
5%HCl (aq.)	Excellent	Excellent	Excellent	Excellent	Excellent
5%NaOH (aq.)	Poor	Poor	Fair	Fair	Fair
5%NaCl (aq.)	Excellent	Excellent	Excellent	Excellent	Excellent

4.4.10 Summary

Palm oil-based polyalkyds were prepared using different types of acid anhydrides, viz. succinic anhydride, maleic anhydride, phthalic anhydride, 3,4,5,6-tetrahydrophthalic anhydride and cis-1,2-cyclohexanedicaroboxilic anhydride. Different resinous properties of the resins were characterized and compared with each other. The FTIR and ^{1}H NMR technique was used to elucidate the structural property and proton density of the resins. The properties of the resins were found to be influenced significantly with the variations of the types of acid anhydrides used to formulate them. The crosslinking density was affected by the unsaturation present in the anhydrides. Resin prepared with TPA showed shorter drying time, highest thermal properties with excellent chemical resistivity among the types of resins. Overall, moderate gloss, good hardness, sufficient molecular weight and PDI were obtained by the resins.

4.4 ANALYSES OF RESIN PROPERTIES: EFFECTS OF ALIPHATIC ACID ANHYDRIDE CONTENT

Palm oil based polyalkyds were prepared through alcoholysis and esterification reaction by using unsaturated acid anhydrides such as, 3,4,5,6-tetrahydrophthalic anhydride (TPA) and/or maleic anhydride (MA). The acid anhydrides were reacted with monoglycerides to prepare different types polyalkyd resins. The prepared resins were cured thermally by using methyl ethyl ketone peroxide (MEKP) and cobalt-naphthanate at 120^{o}C. These resins were characterized for density, viscosity, acid value, iodine value, solubility, molecular weight, polydispersity index, colour and structural properties, whereas the cured films were tested for adhesion, gel content, swelling ratio, surface morphology, chemical resistivity, structural and thermal properties. Moreover, the wettability of the films was also determined by contact angle measurement. The curing kinetics was analysed by differential scanning calorimetry (DSC). The rate of reaction, activation energy and degree of conversion were measured by the analysis. In addition, the aromatic and aliphatic acid anhydride content was optimized by the performances showed by different resins. Analysis revealed that higher amount of aliphatic anhydrides is responsible for high degree of crosslinking density whereas, aromatic anhydride is suitable for higher thermal stability.

4.4.1 Physicochemical Properties

Table 4.12 represents the physicochemical properties of different resins. The density of the resins was found to be different according to the molecular weight of the acid anhydrides and in the range of 0.9311 to 0.9623 g/cm^3. The maximum density was observed for the case of MA0 and the minimum density was showed by Resin MA100. The highest density of MA0 was obtained because of higher molecular weight of TPA. The viscosities of the resins were found to be in an order of similar manner of density as higher density is responsible for higher molecular weight. However, the viscosity of the resins was found to be 104.45, 103.71, 101.35 and 92.30 mPa.s for the case of MA0, MA50, MA75 and MA100, respectively. The acid value of the resins was found to be 33, 31, 22 and 29 mg KOH/g of sample, respectively, for the case of MA0, MA50, MA75 and MA100. The iodine value of the resin was found to be in the range of 78 to 88 g I_2/100 g of sample. The unsaturation was found to be different and increased compared to crude oil, indicating the increment of double bonds due to dehydration of oil and incorporation of unsaturated aliphatic (MA) and aromatic anhydrides (TPA). The highest unsaturation was showed by MA75 (iodine value of 80). This result was found to be higher than that of PA and MA incorporated yellow oleander based alkyd resin (Bora et al., 2014). The specific gravity of the resins was found to be 0.9722, 0.9734, 0.9757 and 0.9757 for the case of MA0, MA50, MA75 and MA100, respectively. Thus aromatic and aliphatic acid anhydride and their mixture did not show any significant effect on the specific gravity of the resins. The colours of the resins were found to be dark brown. Processing improves the colour of alkyds, which may turn it from yellow (oil’s colour) to brown (Odetoye et al., 2010), and dehydration with strong sulphuric acid made the colour as dark brown. The non-volatile material content was found to be 96.8 to 98.7%, thus indicating high solid part of the resin. The yield percentage was found to be in between 87 to 89. The drying time of MA0, MA50, MA75 and MA100 was found to be 4 h 28 min, 4 h 10 min, 3 h 50 min and 4 h 33 min, respectively. The shortest drying time was achieved by the MA75 due to higher crosslinking density by the use of increased amount of MA (75%). The drying time was found to be reduced almost 65 % compared to that of crude oil based resin (11 h 9 min). The GPC technique was used to determine the different molecular weights viz. number average molecular weight (M_n) and weight average molecular weight (M_w). The polydispersity index (PDI) (M_w/M_n) was also calculated by using the aforementioned molecular weights. The M_n of MA0, MA50, MA75 and MA100 was found to be 3598, 3167, 3200 and 3100, respectively. The M_w for the resins was found to be 8450, 6789, 6578 and 5628. Thus the calculated PDI was found to be 2.34, 2.12, 2.07 and 1.81, respectively. The molecular weights of the resins depend on the molecular weights of the acid anhydrides incorporated in the polymer chains. The higher PDI and molecular weight of MA0 is probably due to higher molecular weight of TPA in the polymeric chain. Thus the polydispersity index was found to be increasing as an order of MA0 > MA50 > MA75 > MA100.

Table 4.12: Physicochemical properties of various types of resin based on aromatic and/or aliphatic acid anhydrides.

Properties	**MA0**	**MA50**	**MA75**	**MA100**
Density (g/cm^3)	0.9623	0.9465	0.9355	0.9311
Viscosity (mPa.s)	104.45	103.71	101.35	92.30
Acid value (mg KOH/g)	33	31	22	29
Iodine value (g I_2/ 100 g)	80	82	88	78
Specific gravity	0.9722	0.9734	0.9757	0.9756
Colour	Dark Brown	Dark Brown	Dark Brown	Dark Brown
Non-volatile material content (%)	98.2	97.3	98.7	96.8
Yield (wt.%)	88	88	89	87
Drying time	4 h 28 min	4 h 10 min	3 hr 50 min	4 h 33 min
Number average molecular weight (M_n)	3598	3200	3167	3100
Weight average molecular weight (M_w)	8450	6789	6578	5628
Polydispersity index (*PDI)*	2.34	2.12	2.07	1.81

4.4.2 FTIR and ^{1}H NMR

The FTIR spectra of different resins are illustrated in Figure 4.19. The important functional groups are marked in the figure. Among the functional groups, the carbonyl group in ester and unsaturated carbon-carbon double bonds are mentionable. The -CH bending vibration was confirmed by the absorbance peak at around 714 to 736 cm^{-1}. The C-C stretching vibration was ensured by the peak at 884 and 902 cm^{-1}. The stretching vibration for C-O-C for aliphatic compound was confirmed by the peak at around 1152 cm^{-1}, while the same for aromatic compound was suspected by the peak at 1250 cm^{-1}. The changes was observed at the peak at around 1741 cm^{-1} (Figure 4.1) due to esterification and found to be shifted to a region of 1733 to 1749 cm^{-1}(Figure 1b) for C=O stretching vibration. The asymmetric and symmetric vibration for -CH_2 was visualised by the peak at around 2850 to 2864 cm^{-1}. Finally, the starching vibration for –CH was suspected by the peak remarked at 2915 to 2923 cm^{-1}.

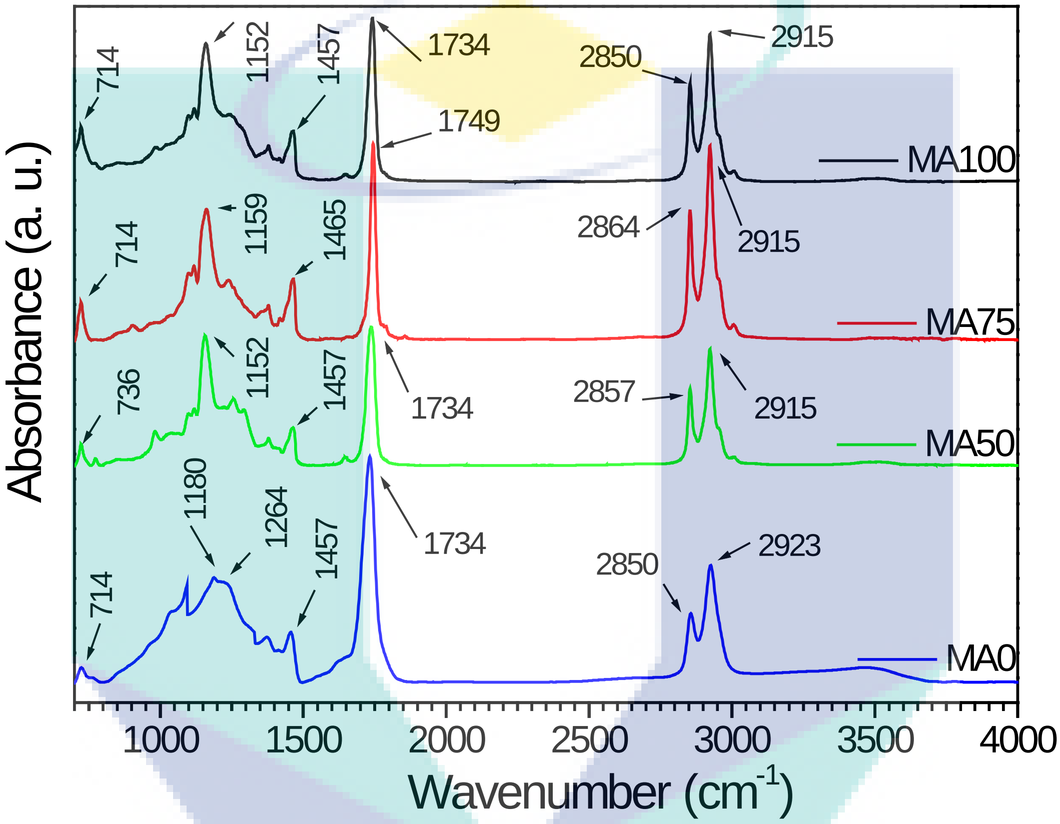


Figure 4.19: FTIR spectra of the resins based on different aromatic and/or aliphatic acid anhydrides.

The ^{1}H NMR spectra of different resins viz. MA0, MA50, MA75 and MA100 are demonstrated in Figure 4.20, Figure 4.21, Figure 4.22 and Figure 4.23, respectively. The peak at around 0.87 indicates the proton density for the terminal methyl groups of fatty acid chains. The protons for -CH_2 was confirmed by the peaks at around 1.25 to 1.30. The methylene protons of glycerol molecule was suspected by the peaks appeared at 4.2 to 4.4, while the unsaturated carbon was pointed by the proton density at 5.25 to 5.4. The proton for -CH in glycerol molecule and that for aromatic ring was confirmed by the proton density at 6.25 to 6.85 ppm and 6.8–7.5 ppm, respectively.

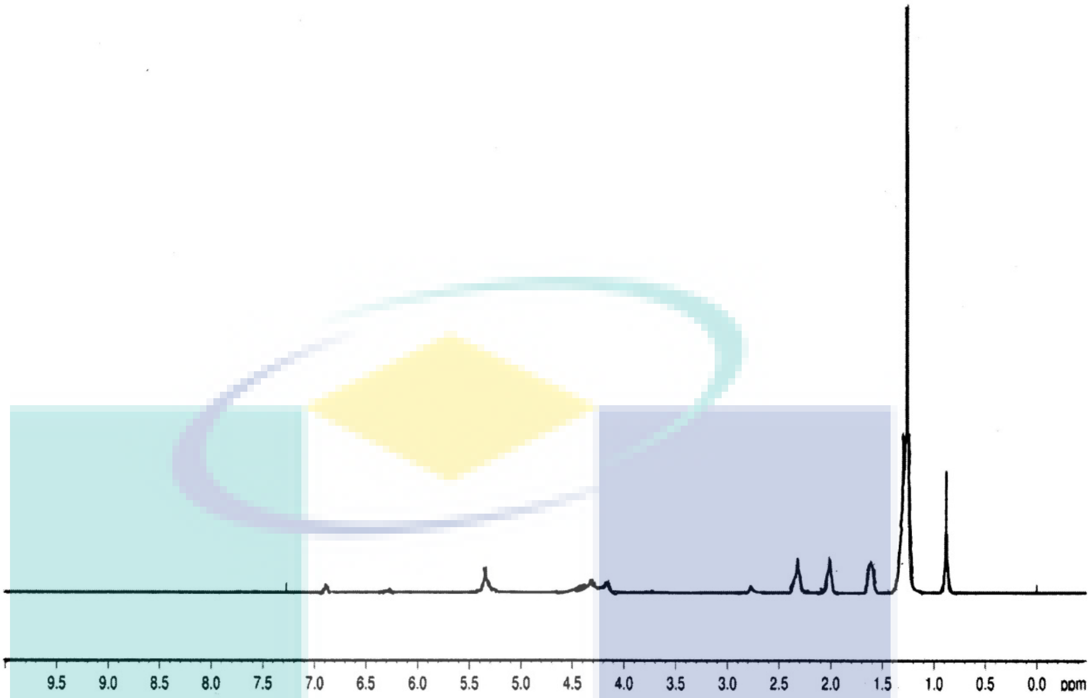


Figure 4.20: ^{1}H NMR spectrum of MA0.

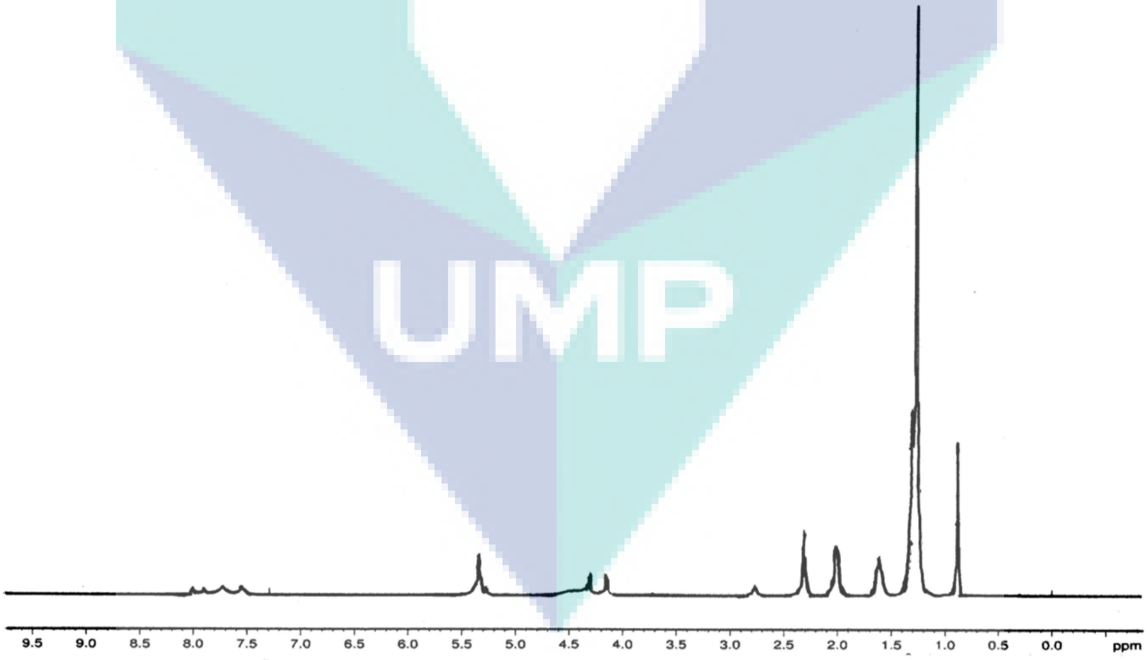


Figure 4.21: ^{1}H NMR spectrum of MA50.

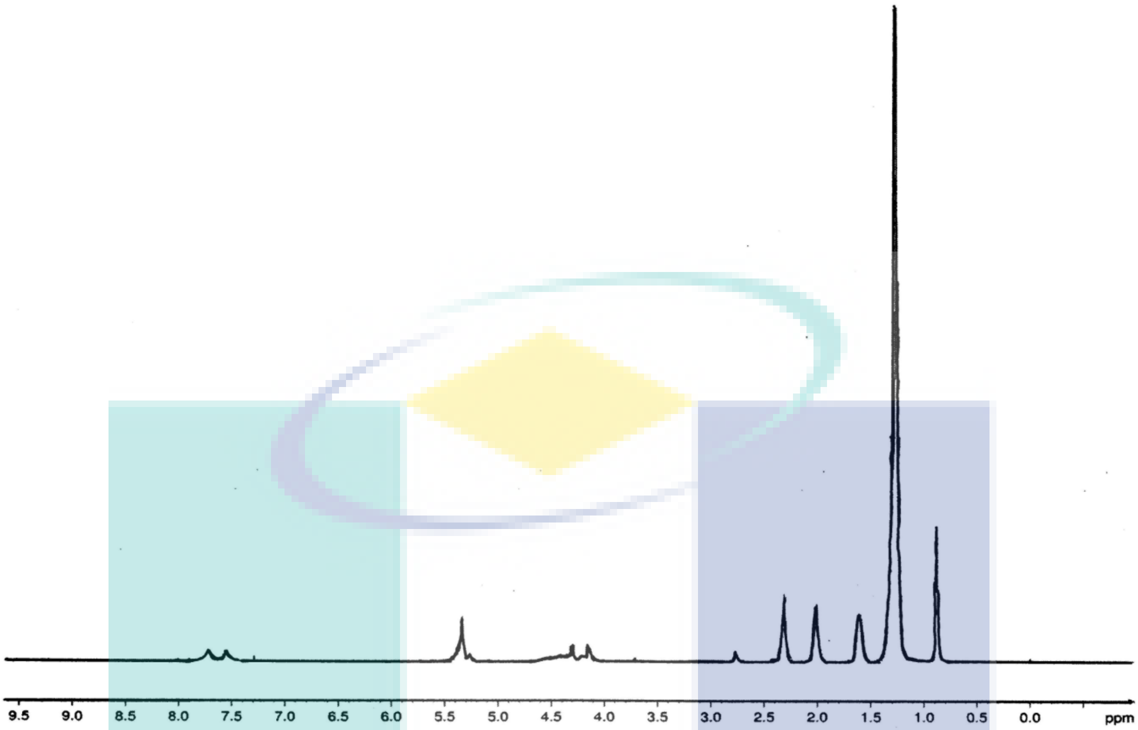


Figure 4.22: ^{1}H NMR spectrum of MA75.

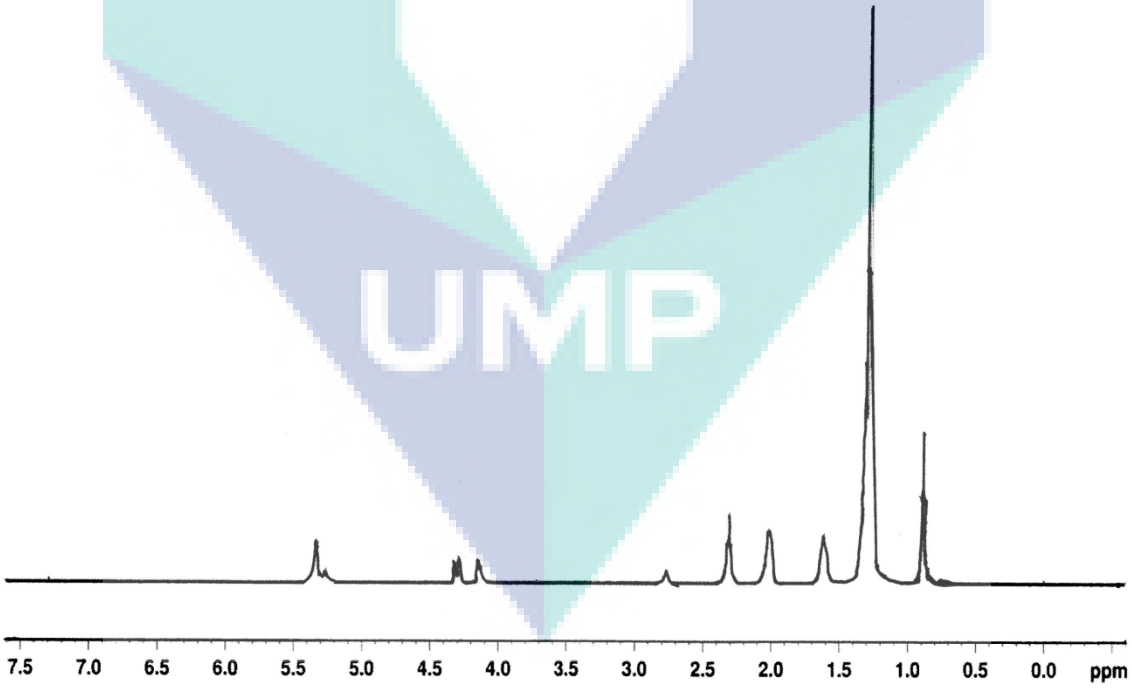


Figure 4.23: ^{1}H NMR spectrum of MA100.

4.4.3 Curing Kinetics

The heat flow vs. temperature curves for different heating rates such as 5, 10, 15 and 20^{o}C/min are shown in Figure 4.24. Two exothermic peaks were found to be appeared in the DSC thermograms. The first peak is probably due to the curing reaction among the initiator and chain, whereas the second peak is due to the crosslinking among the chains due to higher temperature. The influence of the heating rates can be observed in the figure. When the heating rates increases, the area for the first peak also increases. From the figure the onset, peak and final temperature of the curing process can be depicted. Table 4.13 enlists the onset temperature, the exothermic DSC peak temperatures T_{peak1}, T_{peak2} and the heat of reaction ΔH_R per unit of mass. It can be seen that the amount of heat produced per unit of mass is independent of β. Similar results were observed by the previous researchers (King et al., 1974; Sourour et al., 1976). The value of ΔH_R was calculated. Basically, the reaction heat, ΔH_R is caused by the crosslinking between styrene double bonds and unsaturated polyester double bonds. However, the decomposition of organic peroxide is a highly exothermic reaction and different amount of initiator can provide different values of ΔH_R (Severini et al., 1985). The onset, peak1, peak2 and final temperature during the curing process were found to be 48, 72, 131 and 96^{o}C, respectively for the heating rate of 5^{o}C/min. The heat of reaction was recorded as 11.48 J/g for exothermic reaction at 5^{o}C/min of heating rate. The reaction heat can be varied by use of different types of polyesters and the amount of initiators used.

Table 4.13: Total heat of reactions, onset, peak and final temperatures at different heating rates.

Heating rate, (^{o}C/min)	T_{onset} **(^{o}C)**	T_{peak} **(^{o}C)**	T_{final} **(^{o}C)**	H_R **(J/g)**
5	48	72	96	11.48
10	53	87	128	33.19
15	54	99	131	34.29
20	63	99	140	20.76

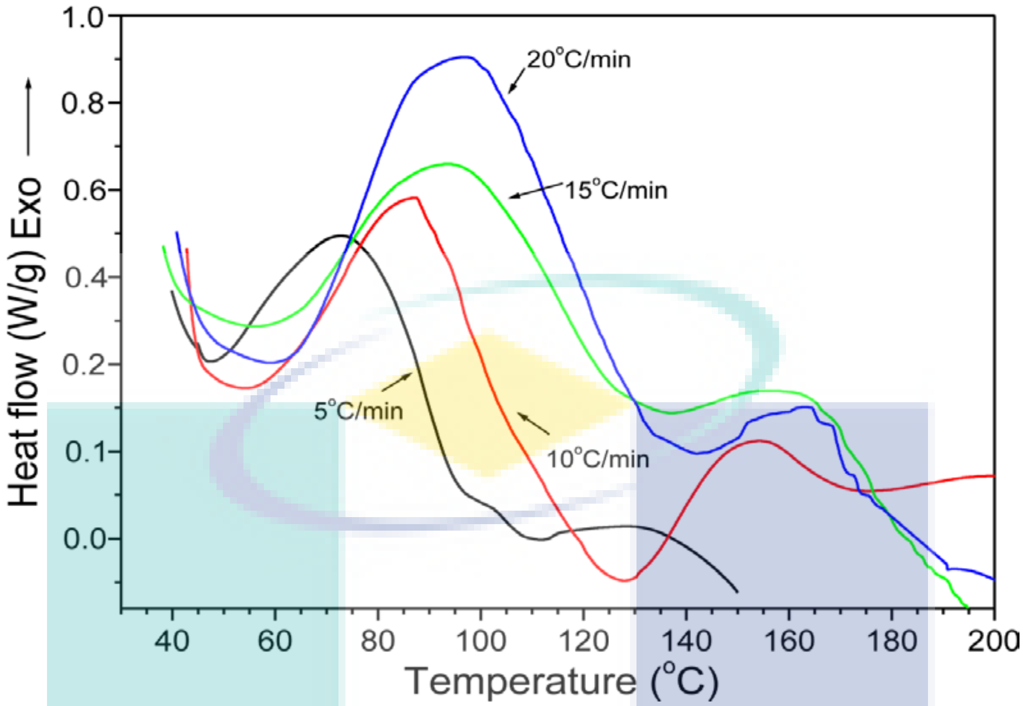


Figure 4.24: Heat flow vs. Temperature curves for different heating rates.

Figure 4.25 demonstrates the degree of conversion vs temperature, whereas Figure 4.26 illustrates conversion vs. time of the curing process for different heating rates. It was found that the degree of conversion versus the cure temperature is shifted to the right hand side when the heating rate is increase. Hence, this indicated that higher temperature is needed to achieve same amount of conversion for the higher heating rate. On the other hand, Figure 4.26 shows the vice versa of the previous observation. Shorter time is required to reach the same amount of conversion for the case of higher heating rate. The rate of reaction vs. temperature and rate of reaction vs. time is represented for different heating rates in Figure 4.27 and Figure 4.28, respectively. The reaction rate for the curing process was calculated. The heating rate has a great impact towards the area of the peak. When the heating rate increases, the area of the peak is also increases.

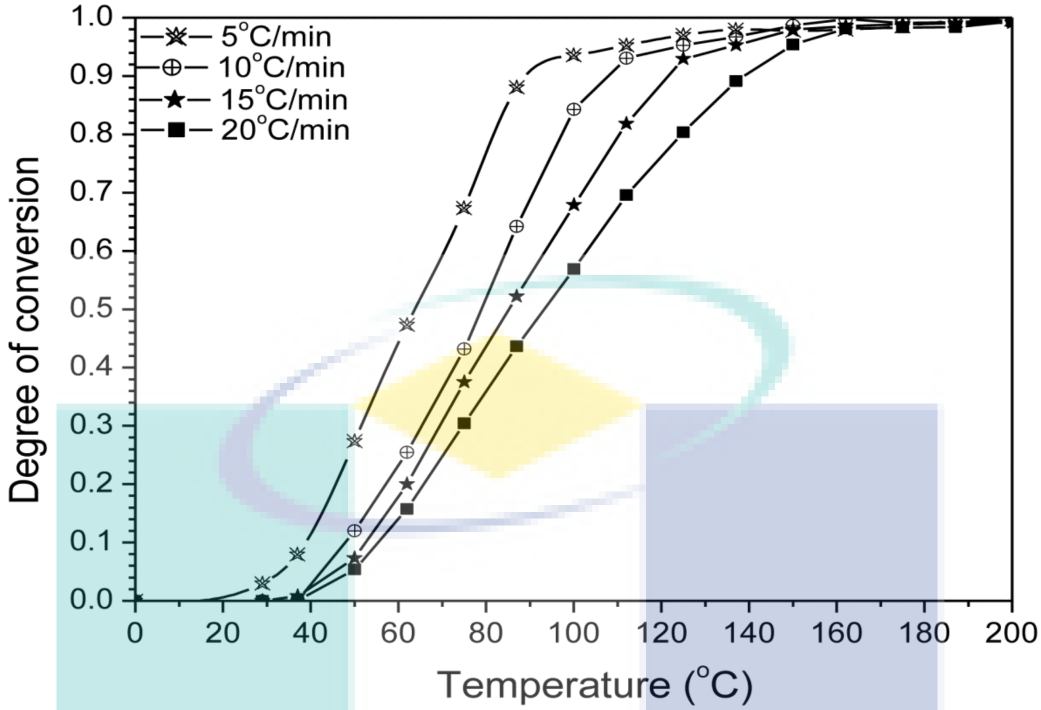


Figure 4.25: Degree of conversion vs. temperature plot for the curing process of palm oil based alkyds.

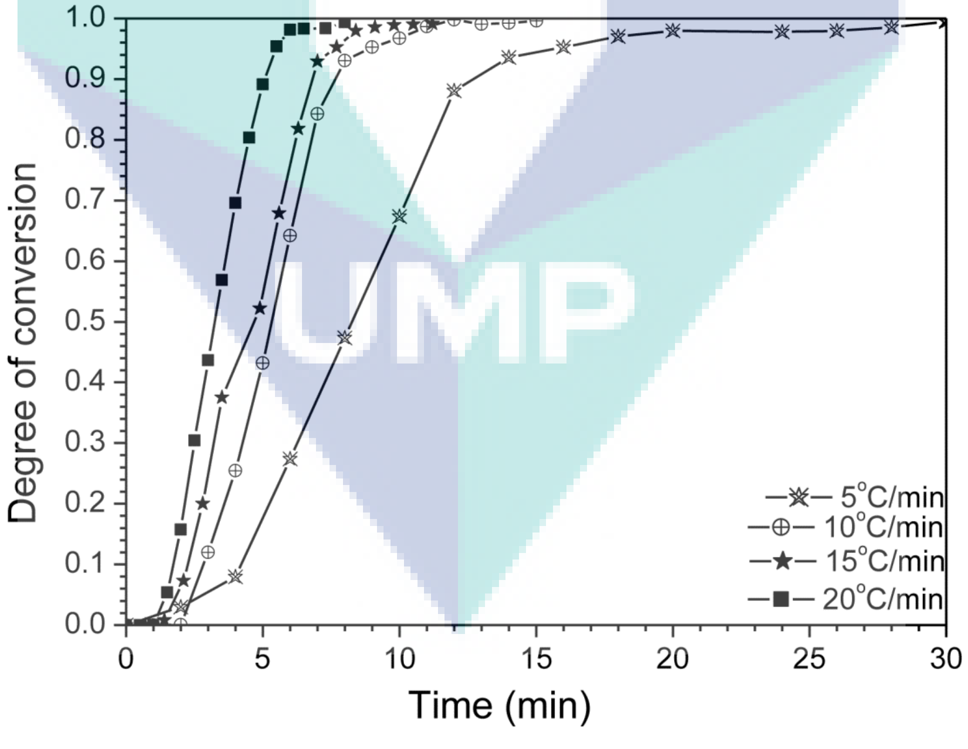


Figure 4.26: Degree of conversion vs. time plot for the curing process of palm oil based alkyds.

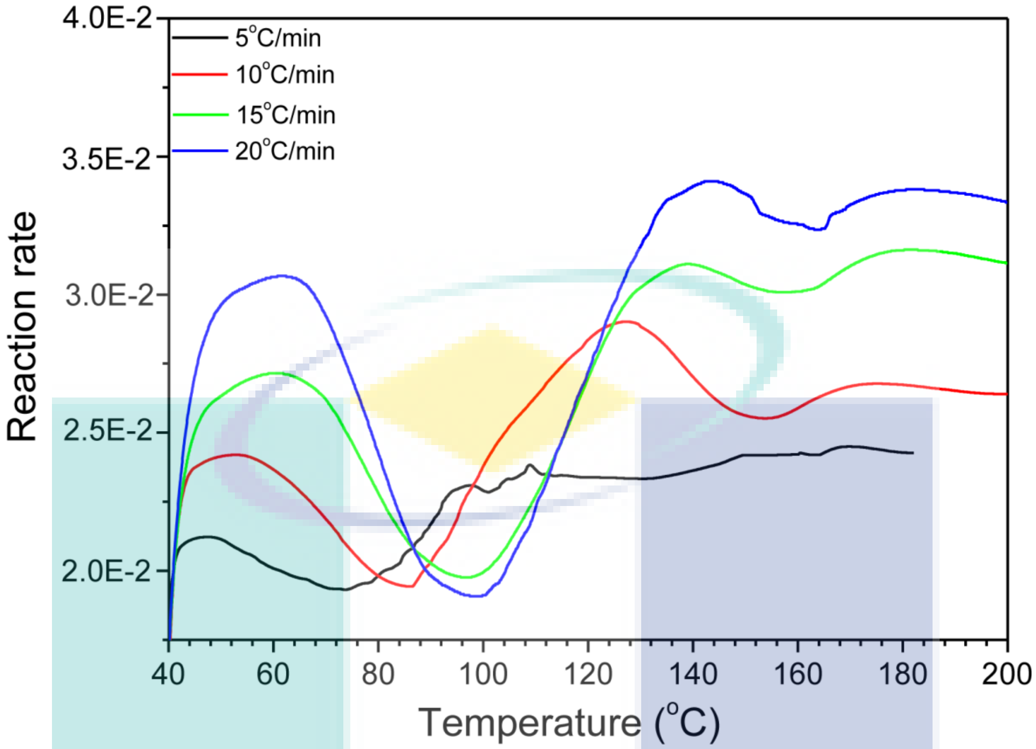


Figure 4.27: Reaction rate vs. temperature curve for the curing process of palm oil based alkyds.

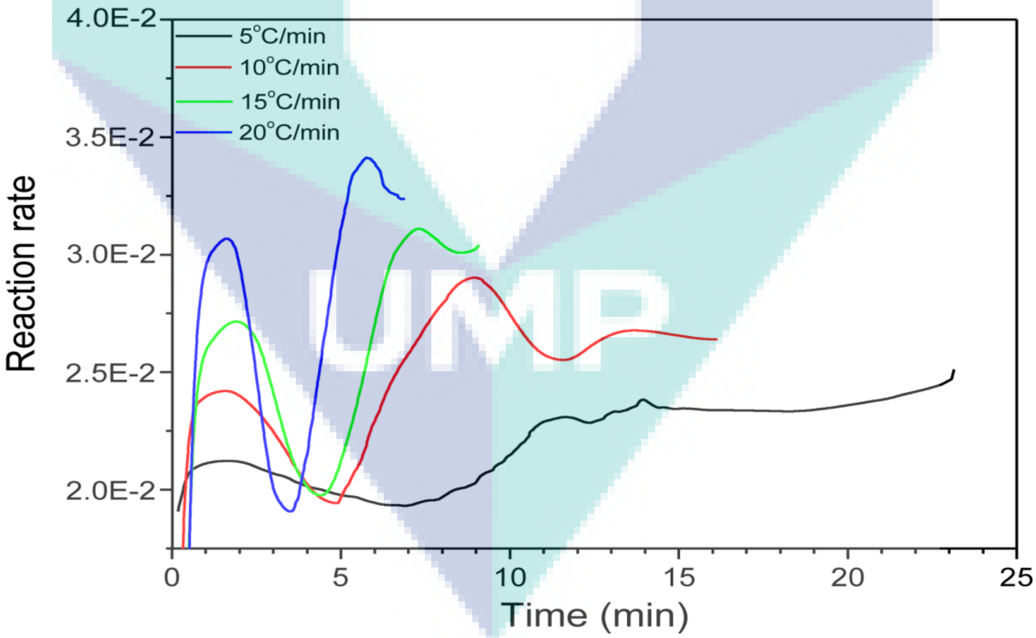


Figure 4.28: Reaction rate vs. Time plot for the curing process of palm oil based alkyds.

Table 4.14 summarizes the kinetic parameters such as activation energy Ea, the reaction order x and pre-exponential factor for each heating rate, obtained from the aforementioned equations. The kinetic parameters depend on the heating rate and the activation energy. It was found that the kinetic parameters decrease with the increasing of heating rate. When the heating rate increases, the activation energy decreases from 52.32 kJ/mol to 19.23 kJ/mol and the reaction order from 2.153 to 0.564. The pre-exponential factor was also found to be changed from 3.9834E+15 to 1.8954E+6.

Table 4.14: Kinetic parameters for different heating rates.

Heating rate, β (^{o}C/min)	Activation energy, Ea (KJ/mol)	Reaction order, x	Pre-exponential factor
5	52.32	2.153	3.9834E+15
10	44.32	1.543	3.9523E+13
15	24.54	1.123	1.5432E+7
20	19.23	0.564	1.8954E+6

4.4.4 XRD

Figure 4.29 shows XRD patterns of different films, which include intensity vs. scattering angle plot. The scattering angle, d-spacing, crystalline size and crystallinity are enlisted in Table 4.15. The scattering angle was apparent in between 2θ values of 19.36^{o} and 19.84^{o}, and this is probably due to the crystalline and amorphous region of the alkyd resin, as shown by the medium sharp peak. The peak for MA0 (100% TPA-based film) was found to be 21.43^{o} and that of MA100 showed 19.67^{o}. The crystalline size of MA0, MA50, MA75 and MA100 was found to be 12.76 to 15.5, 13.54, 13.65 and 12.76 nm, respectively. The corresponding d-spacing between the layers was found to be 4.14 4.42, 4.44 and 4.50 Å. However, the peaks in the range of 19.67 to 19.83^{o} were found to be apparent for MA50, MA75 and MA100, which was shifted to 20.43^{o} for the case of MA0. The overall crystallinity was found to be in the range of 39.85 to 45.76%.

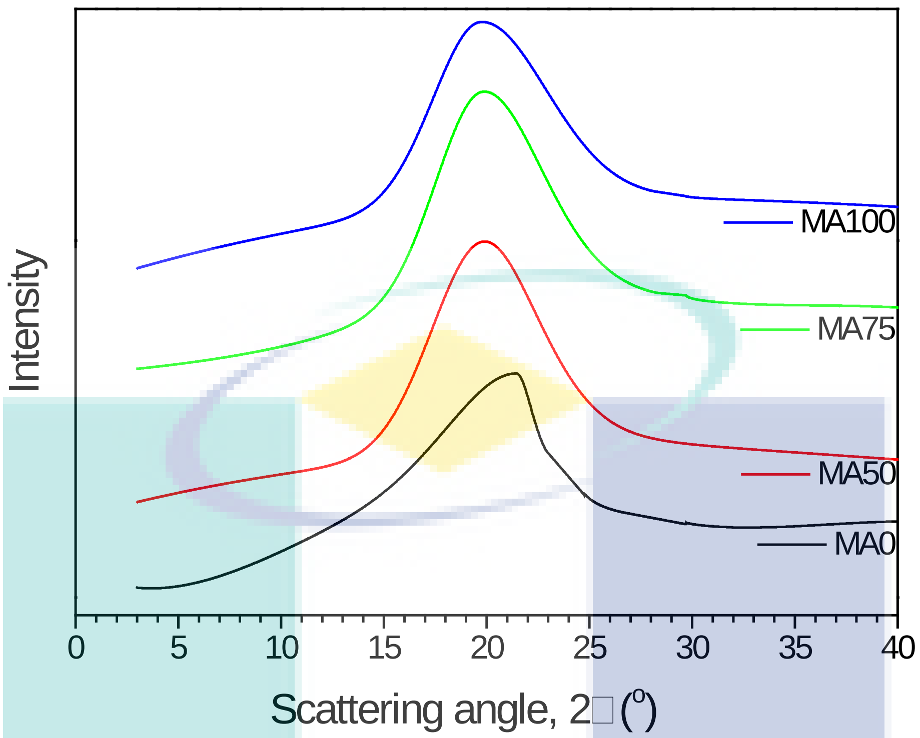


Figure 4.29: XRD profiles of different resins based on aromatic or/and aliphatic acid anhydrides.

Table 4.15: XRD parameters for different types of resins.

Resin types	Peak position (2θ)	d (Å)	Crystalline size (nm)	Crystallinity (%)
MA0	21.43	4.14	15.50	39.85
MA50	19.83	4.42	13.54	44.46
MA75	19.77	4.44	13.65	45.76
MA100	19.67	4.50	12.76	44.89

4.4.5 Surface Property

Figure 4.30 shows the contact angle images of different films prepared from different resins. The contact angle of MA0, MA50, MA75 and MA100 was found to be 90, 84.5, 95.1 and 65.1^{o}, respectively. The hydrophobicity of aromatic acid anhydride based films was found to be better than that of aliphatic anhydride based. It was found that the increase in percentage of MA into the polymeric chain made the film more hydrophobic as proved by the higher contact angle measurement. This is may be due to high degree of crosslinking and stable benzene ring in the polymeric chain (Pathan et al., 2013).

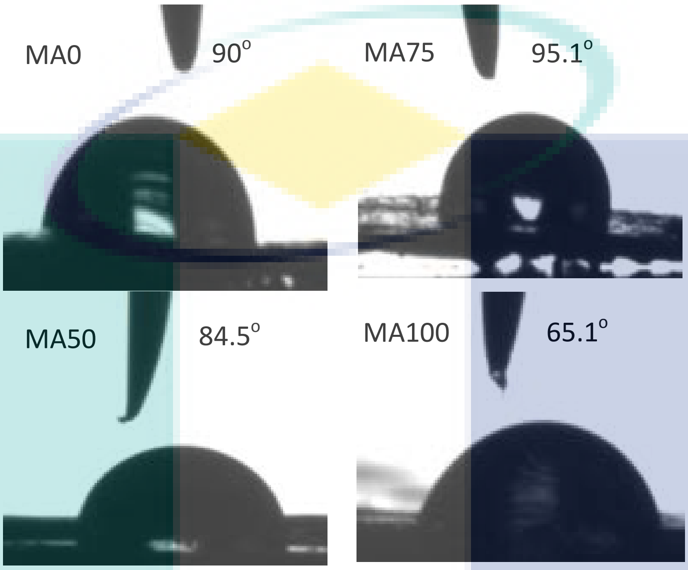


Figure 4.30: Contact angles of different films.

The gloss property of different films was measured and listed in Table 4.16. The gloss at 60° was measured and the values were found to be different due to the variation of the relative percentages of TPA and MA. Acceptable gloss was showed by the films produced from different resins viz. MA0, MA50, MA75 and MA100 of values 75, 77, 80 and 67, respectively.

The adhesion property was found to be excellent for all the resins and the maximum value was found to be 100% (Table 4.16). The better adhesion was observed due to the unsaturated nature of the acid anhydrides present in the polymeric chain. Both the acid anhydrides are unsaturated in nature; therefore, they are more susceptible for atmospheric oxygen attack which may result in increased adhesion property of the resins. Moreover the presence of polar ester groups in polymeric chains is also responsible for better adhesion property (Mahapatra et al., 2004).

Table 4.16: Gloss, gel content, swelling ratio, crosslinking density and adhesion properties of different resins.

Resin types	**Gloss (60^{o})**	**Gel content (%)**	**Swelling ratio**	**Crosslinking density x 10^4 mol cm^3**	**Adhesion (%)**
MA0	75	87	1.25	4.1	100
MA50	77	92	1.19	5.3	100
MA75	80	95	1.14	5.7	100
MA100	67	80	1.33	3.7	98

Figure 4.31 shows the surfaces of the films produced from different resins. The surfaces of the films were found to be dark and plain due to unsaturated acid anhydrides. These results are found to be similar as observed by other researcher (Bora et al., 2013). Relatively smoother surface was observed for the case of MA50 and MA75 compared to others. A few spots were apparent in MA-based film (MA100) due to unsaturated aliphatic acid anhydride. However, a rigid and smooth surface was noticed for MA0, MA50, and MA75. This is probably due to additional crosslinking density because of the unsaturation nature of TPA and MA. Rigidity, smooth surface property and dark colour of films (MA0, MA50 and MA75) are probably the reasons for higher thermal stability and low wettability compared to MA100.

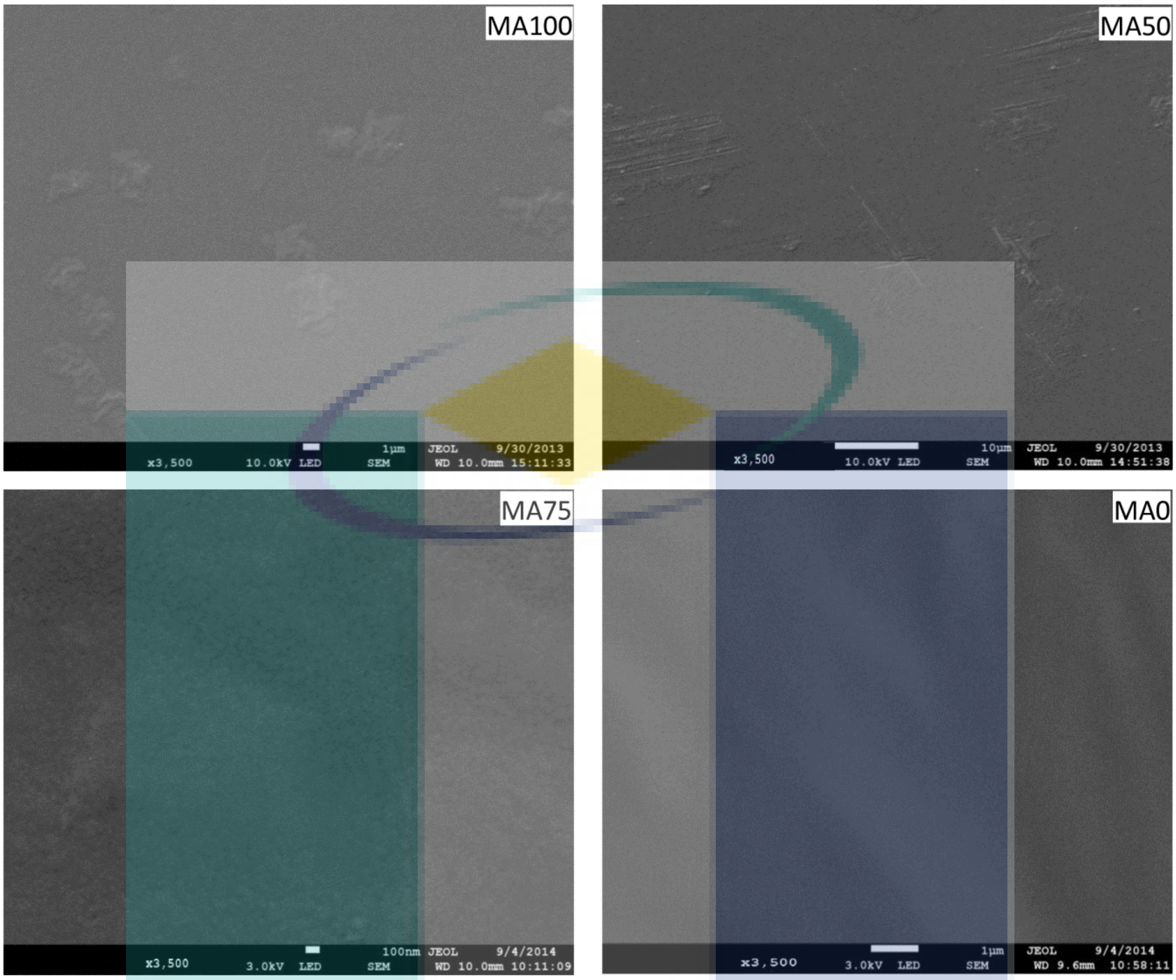


Figure 4.31: FE-SEM images of different films.

4.4.6 Crosslinking Density

The gel content of different polymeric films was measured and the data is listed in Table 4.16. The gel content was found to be higher for all the resins, indicating sufficient amount of crosslinking present in the structure of the films. However, TPA and MA-based film (MA75) showed gel content of 95%, whereas only MA (MA100) and TPA-based (MA0) film showed gel content value of 80% and 87%, respectively. The results for gel content analysis affects in a similar manner for the case of swelling ratio. The values for swelling ratios were found to be 1.25, 1.19, 1.14 and 1.33 for the case of MA0, MA50, MA75 and MA100, respectively (Table 4.16). This is the similar behaviour, commonly observed for the case of others films. The films which show higher amount of gel content should swell lower. It was found that increased amount of MA showed higher gel content due to higher crosslinking density. The crosslinking density of MA0, MA50, MA75 and MA100 was found to be 4.1 x 10^4, 5.3 x 10^4, 5.7 x 10^4 and 3.7 x 10^4 mol cm^3, respectively.

4.4.7 Solubility

Different kinds of organic solvents such as, ethanol, butanol, methanol, xylene and toluene were used to dissolve the polymeric resins. The solubility of the resins prepared from different ratios of TPA and MA were found to be different. The relative proportion of aromatic and aliphatic acid anhydrides was found to be an important factor for solubility performance. The higher proportion of TPA based resin showed shorter time in aromatic solvent like xylene and toluene. In that case, MA0 (100% TPA) and MA50 (50% TPA) took shorter time to dissolve into xylene and toluene than that of MA75 and MA100. The usual behaviour of methanol and ethanol was also observed for taking longer time to dissolve the resins. The dependency on molecular weight was observed as well.

4.4.8 Pencil Hardness

The hardness of the polymeric films was measured by pencil hardness tester and found to be different for different ratio of TPA and MA based films (Table 4.17). The analysis showed that higher percentage of aromatic acid anhydride and higher amount of crosslinking density in the polymeric film are responsible for the higher hardness of the films. MA0 (100% TPA) showed positive result for the testing of 2B, B and HB type of pencil. The similar result was observed for the case of MA75 (25% TPA and 75% MA). The rigidity of the aromatic compound and increment of crosslinking density due to MA are probably the reasons behind the results. All the films were found to be passed successfully for the testing of 2B-type of pencil. The difference was observed for B-type of pencil testing. The result showed that aromatic acid anhydride-based resins showed positive result, whereas aliphatic acid anhydride based one failed (Oldring et al., 2000; Sharma et al., 2001).

Table 4.17: Pencil hardness of various types of cured resins.

Pencil type	MA0	MA50	MA75	MA100
2B	Pass	Pass	Pass	Pass
B	Pass	Pass	Pass	Fail
HB	Pass	Fail	Pass	Fail

4.4.9 Thermal Properties

The thermal stability and degradation profile of various cured films are presented in Figure 4.32 (weight vs. temperature curves) and Figure 4.33 (derivative weight vs. temperature curves). The weight loss due to moisture was estimated from 1 to 2% for all the films above 100^{o}C. The initiation of degradation was started at around 306^{o}C. It was found that MA75 showed the highest thermal stability among the resins. Table 4.18 shows the thermal properties of different films based on different percentages of acid anhydrides. The onset degradation temperatures were found to be 317, 302, 350 and 253^{o}C for the case of MA0, MA50, MA75 and MA100, respectively. The order of thermal stability was found to be as follows: MA75 > MA0 > MA50 > MA100. The higher thermal stability of aromatic acid anhydride based resins is probably due to the presence of aromatic moiety in the alkyd chains. The highest stability of MA75 is probably due to the higher crosslinking density established in the polymeric chains of the polyalkyds. The residues after 600^{o}C for all the samples were found to be in the range of 2-7 wt.%. From Figure 4.33, the T_{max} was found to be 374, 372, 377 and 364^{o}C. Thus the thermal stability of these resins was found to be high enough to be used for any type of high-temperature-sustained applications.

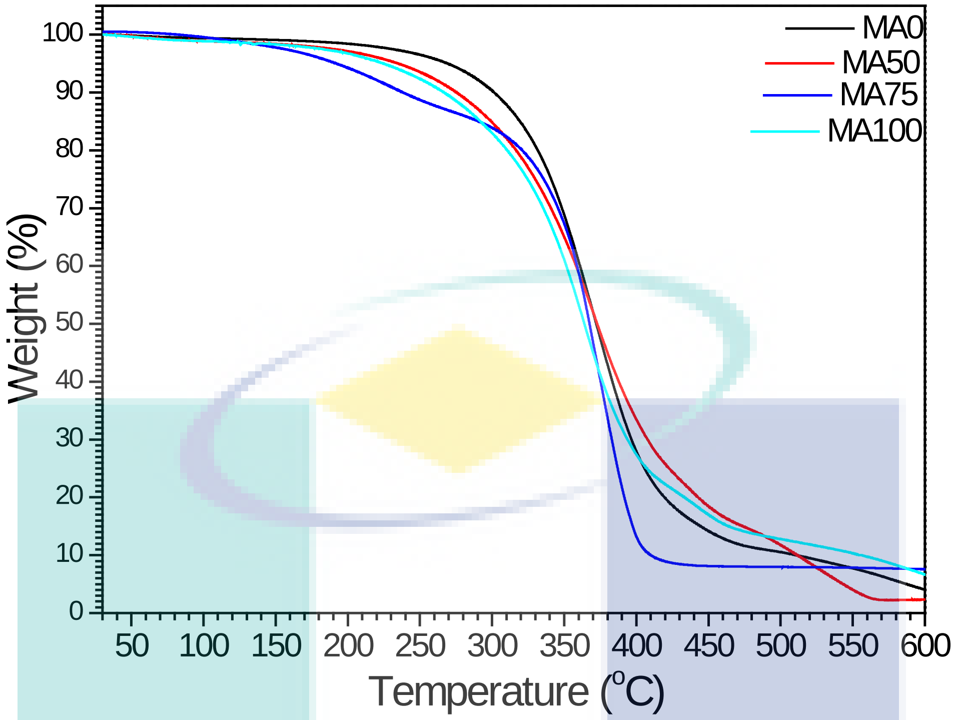


Figure 4.32: Weight vs. temperature curves of different resins.

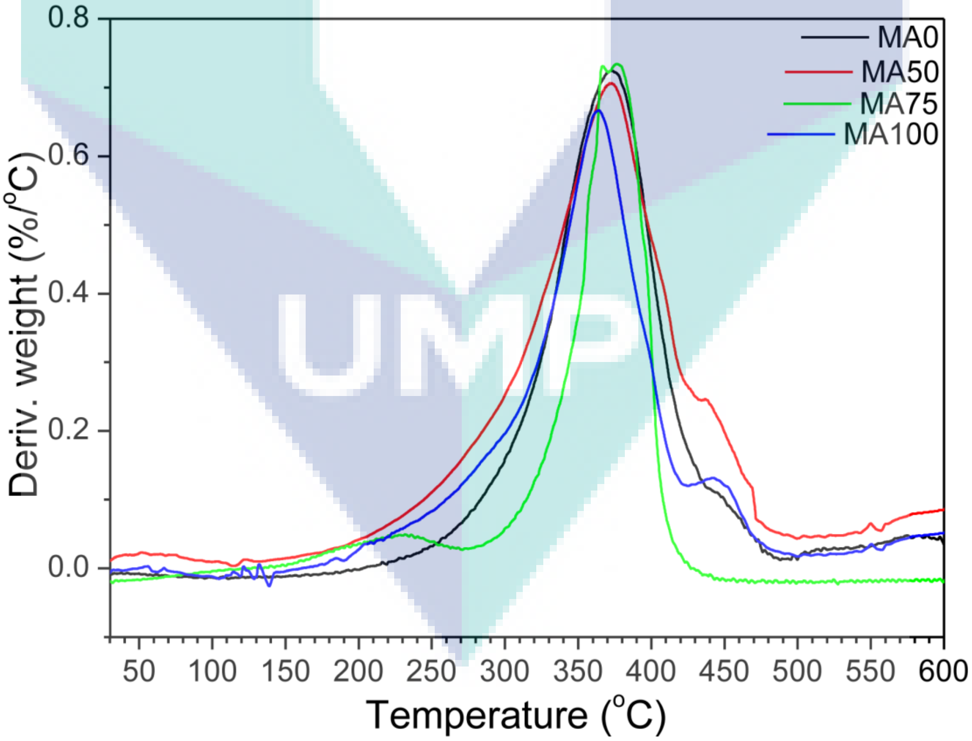


Figure 4.33: Derivative weight vs. temperature curves of different resins.

The DSC thermograms of the films are illustrated in Figure 4.34. From the graph, the melting temperature of the cured resins can be observed. The thermosetting resins showed a broad region close to the melting point. The melting temperature found maximum, 360°C, for the case of MA0, whereas MA50, MA75 and MA100 showed that of 366, 375 and 334°C, respectively. The higher melting point of MA0, MA50 and MA75 is due to the presence of stable aromatic ring in the backbone chain of the polymer. The highest melting temperature for MA75 is probably due to the additional crosslinking density.

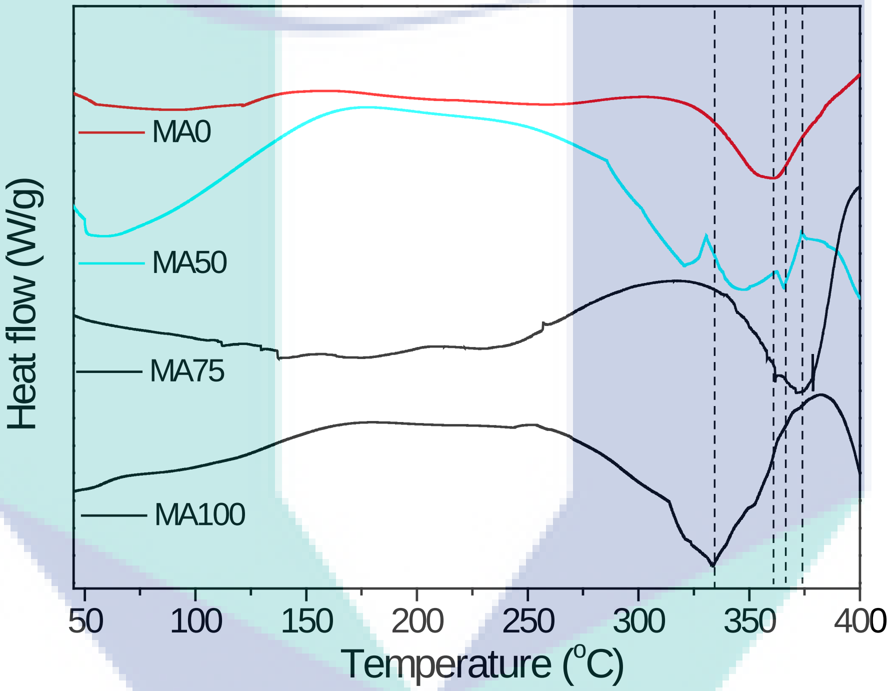


Figure 4.34: DSC thermograms of the cured films.

Table 4.18: Thermal properties of different resins.

	T_{onset} (°C)	T_{max} (°C)	Residue (%)	T_m (°C)
MA0	317	374	4	360
MA50	302	372	7	366
MA75	350	377	2	375

MA100	353	364	6	334

4.4.10 Chemical Resistivity

The chemical resistivity of various cured films is presented in Table 4.19. It was observed that all kinds of films were unaffected and highly resistant to distilled water, aqueous sodium chloride and hydrochloric acid during the immersion period. The variation of the property was found only for sodium hydroxide solution. Among the resins, MA50, MA75 and MA100 showed poor resistivity to alkali solution due to their hydrolysable aliphatic ester group (Sharma et al., 2001), but aromatic acid anhydride based resins viz. MA0 showed comparatively fair resistivity to the same solution. The better property of the aromatic acid anhydride based resins may be due to the presence of stable aromatic ring in the polyalkyd chains. The similar observation was found in previous study (Dutta et al., 2004; Sharma et al., 2001).

Table 4.19: Chemical resistivity of the cured resins.

Solution	MA0	MA50	MA75	MA100
Distilled water	Excellent	Excellent	Excellent	Excellent
5%HCl (aq.)	Excellent	Excellent	Excellent	Excellent
5%NaOH (aq.)	Fair	Poor	Poor	Poor
5%NaCl (aq.)	Excellent	Excellent	Excellent	Excellent

CHAPTER FIVE

CONCLUSION AND RECOMENDATIONS

5.1 CONCLUSION

Palm oil was used to prepare polyalkyds through alcoholysis and esterification process. The crude oil was subjected for dehydration process to increase the unsaturation. It was found that the usage of H_2SO_4 improves the unsaturation of oil as maximum as 165%. After performing a preliminary screening of the reaction parameters, the esterification process was optimized through RSM. Result analyses revealed very high desirability of 0.985 through RSM analyses. Moreover, 91.5% fractional conversion was achieved actually, which is close to the predicted value. The optimum reaction conditions were used to formulate different types of polyalkyds by using different acid anhydrides, viz., SA, MA, PA, TPA and CDA. The properties of the resins were found to be dependent on the types of acid anhydrides. Among the resins, the TPA-based resin was found to be the best in terms of different resinous properties. The density and viscosity of the resin were found to be the highest for the case of TPA-based resin, whereas the drying time was observed to be the minimum (4 h 32 min). The wettability of the films was found to be affected due to the variation of the acid anhydrides. The properties like thermal stability, surface morphology, adhesion and solubility were also found to be altered due to the types of acid anhydrides. The aromatic acid anhydride based films were found to more stable thermally compared to aliphatic acid anhydrides based films. Additionally, rigid surfaces were observed for the case of aromatic acid anhydride based films, whereas relatively smooth surfaces were observed for unsaturated acid anhydrides based films. For solubility analyses, it was found that the aromatic solvent shows faster behaviour in dissolving aromatic acid anhydride based films, whereas aliphatic solvent are good for aliphatic acid anhydride based films. The chemical resistivity and pencil hardness was found to be best for those, whose crosslinking density was found to be higher. Moreover, presence of aromatic ring was found to be an additional support showing higher pencil hardness.

The effects of the different ratios of aromatic and aliphatic acid anhydride content were analysed on the properties of resins and films. The higher amount of crosslinking density of MA75 was confirmed by the higher gel content. The wettability was also affected by a similar manner and found to be reduced the maximum for the case of MA75.

Resin prepared with 25 % TPA and 75 % MA (MA75) showed shorter drying time (3 h 50 min). The chemical resistivity, adhesion property and surface morphology of the MA75 was found to be superior compared to the other formulations. In curing kinetics analyses, the degree of conversion and curing rate in against of temperature and time were used to understand the curing kinetics of palm oil based polyalkyds. It was found that the higher temperature is needed to achieve same amount of conversion for the higher heating rate. It was also found that the amount of heat produced per unit of mass is independent of the heating rate.

Different percentages of MWCNTs viz., 0.5, 1.0 and 1.5 wt.% were loaded in the polyalkyd resins to improve the film properties. Based on the tensile property, the best loading was selected and 1.0 wt.% was found to be suitable loading percentage. The TS of MWCNTs-loaded (1.0 wt.%) film was found to be improved by 140% compared to without MWCNT-based film. The improvement in TS (by 50%) was observed for the case of in-situ reacted film. The degradation temperature was found to be increased by 8^{o}C for in-situ condition at same percentages of loading. The d-spacing and crystallinity was found to be affected by in-situ condition at similar percentages of MWCNTs loading. Thus the properties of palm oil based polyalkyds can be improved by the incorporation of MWCNTs.

5.2 RECOMENDATIONS FOR FUTURE WORK

Chemical modification of fatty acids with functional groups that could facilitate subsequent polymerization has the potential to gain importance in the production of thermosetting materials. There is also enormous scope to modify vegetable oils in order to make monomers for the production of polymeric materials. Some of the vegetable oil-based polymeric materials display conventional, industrially useful characteristics as well as unique properties. However, although complete replacement of petrochemical materials by bio-based chemicals may be desirable, but a gradual evolution of materials science to incorporate increasing percentages of these bio-based chemicals is more realistic in order to produce polymers with equivalent properties. This should not exclude the development of new materials that benefit from the unique structures that can be derived from modified lipids. Overall, it is to be hoped that the production of plant oils to produce materials will complement rather than compete with current agricultural practices to produce food oils.

The polymeric resins prepared in this study are thermosetting polyesters, which can be used for nano composites preparation for different purposes. There are different kinds of nano particles like silver, aluminium, nano clay, etc. available to be incorporated into the polymeric resins. There are several properties like anti-microbial, corrosion resistant, and water-resistant which can be brought in the composites by the inclusion of these nano particles.

The alkyd resin prepared from the palm oil can be used for the preparation of high flexible and high strength film by using of different kind fillers or coupling agents. The produced films can be assessed for packaging, wrapping and laminating performances.

The biodegradability of the vegetable oil based polymers is an important consideration. It can be assessed in normal or/and accelerated weathering condition. The ultra-violate radiation can be used for extreme condition of weathering to evaluate performances at realistic condition. The weight loss, biodegradability and other changes should be measured after a certain period of time. By this assessment, initiative can be taken further to improve the longevity or to enhance the biodegradability of the product according to the users' choice.

Different kinds of copolymers can be prepared by the using of various kinds of monomers such as, poly amides, poly acrylic, polyurethane, etc. To bring in some new properties in the resulted copolymers, copolymerization with different and compatible monomer is effective. Sometimes, blending with synthetic polymers is also found to be motivational to get high-efficient materials. Particularly, the drying time, mechanical properties and thermal stability can be improved by blending with commercial monomer-based polymers. Monomers having high per branched structure and suitable cross linkers can be used to increase the stiffness and crosslinking density of the polymers. There are different types of polyesters which earlier discussed in the literature review such as, high solid content polyesters, liquid crystal polyesters and water-borne polyesters. These different types can be prepared from palm oil by following the stated methods.

By following the method and technique used in his research, other non-drying or semi-drying oil can be used to formulate different kinds of potential polyesters. The formulated resins can be trial product for commercial or pilot plant manufacturing system as a midway to large scale production. Cost and process feasibility analysis can be done prior to commercial production of these bio-based resins. The successful utilization of these bio based resins can open a new window for economic benefit in one hand and environmental sustainability on the other to the country and the world as well.

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APPENDIX A

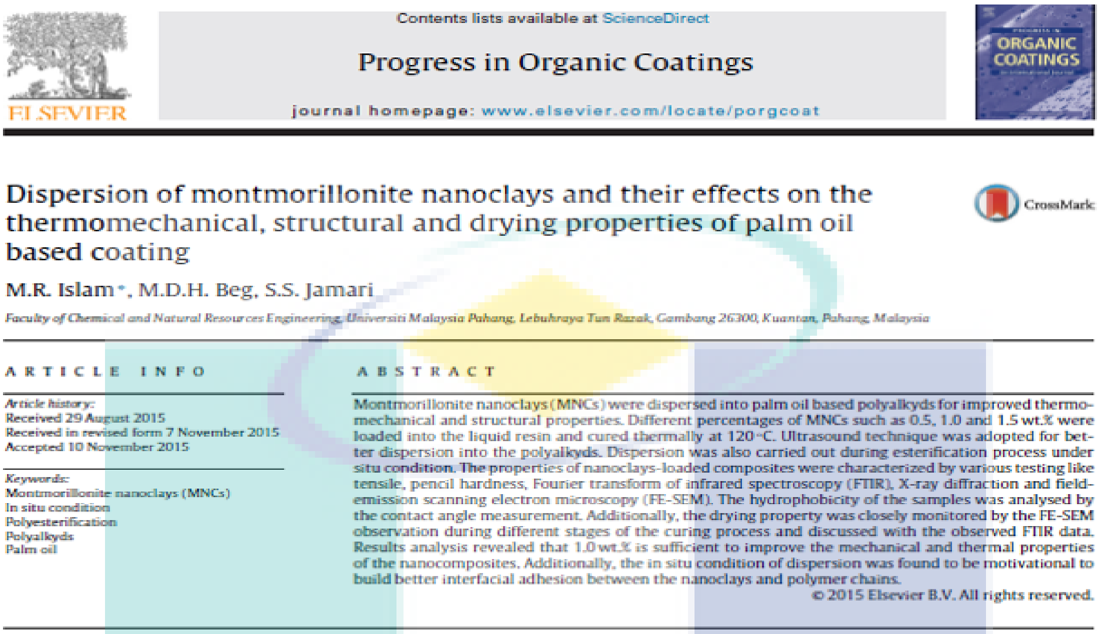
LIST OF PUBLICATIONS

Journal articles

1. M.R. Islam, M.D.H. Beg, S.S. Jamari. Dispersion of montmorillonite nanoclays and their effects on thethermomechanical, structural and drying properties of palm oil based coating, Progress in Organic Coatings, 2016, 91, 17–24
2. M. R. Islam, M.D.H. Beg and S. S. Jamari. Development of Vegetable Oil-Based Polymers. Journal of Applied Polymer Science, September 2014, Vol 131, Issue 18, Pages 40,787- 40,799.
3. M. R. Islam, M. D. H. Beg and S. S. Jamari. Alkyd resin from non-drying oil, Procedia Engineering, 2014, 90, 78-88.
4. M. R. Islam, M. D. H. Beg and S. S. Jamari. Characterization of palm oil based alkyds for surface coating applications, Journal of Materials Science and Engineering A, 2014, 9, 266-274.
5. M. R. Islam, M. D. H. Beg and S. S. Jamari. Study the effects of five different types of acid anhydrides and incorporation of montmorilonite nanoclays on thermosetting resins, Polymer Bulletin, DOI 10.1007/s00289-015-1450-0.
6. M. R. Islam, M.D.H. Beg and S. S. Jamari, The Effects of Increasing Unsaturation in Palm Oil and Incorporation of Carbon Nanotubes on Resinous Properties, International Journal of Chemical, Nuclear, Materials and Metallurgical Engineering, 2015, 9(3), 475-480.

Conference articles

1. M. R. Islam, M. D. H. Beg and S. S. Jamari. Alkyd resin from non-drying oil, International Conference on Mechanical Engineering 2013, 20-21 June, 2014, BUET, Dhaka, Bangladesh.
2. M. R. Islam, M. D. H. Beg and S. S. Jamari. Bio polymer matrix for the preparation of composites, Australian Composite Conference 2014, 7-9 April 2014, Newcastle, New South Wales, Australia.
3. M. R. Islam, M.D.H. Beg and S. S. Jamari. Characterization of Bio-based alkyd resin. International Conference on Chemical Engineering and Industrial Biotechnology (ICCEIB 2013), 27th – 29th August 2013, Kuantan, Pahang, Malaysia.
4. M. R. Islam, M.D.H. Beg and S. S. Jamari, Study the effects of increasing unsaturation in palm oil and incorporation of carbon nanotubes on resinous properties, World academy of science, engineering and technology, MIAMI, United States, March 9 -10, 2015.



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Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Dispersion of montmorillonite nanoclays and their effects on the thermomechanical, structural and drying properties of palm oil based coating

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ABSTRACT

Montmorillonite nanoclays (MNCs) were dispersed into palm oil based polyalkyds for improved thermo-mechanical and structural properties. Different percentages of MNCs such as 0.5, 1.0 and 1.5 wt.% were loaded into the liquid resin and cured thermally at 120 °C. Ultrasound technique was adopted for better dispersion into the polyalkyds. Dispersion was also carried out during esterification process under situ condition. The properties of nanoclays-loaded composites were characterized by various testing like tensile, pencil hardness, Fourier transform of infrared spectroscopy (FTIR), X-ray diffraction and field-emission scanning electron microscopy (FE-SEM). The hydrophobicity of the samples was analysed by the contact angle measurement. Additionally, the drying property was closely monitored by the FE-SEM observation during different stages of the curing process and discussed with the observed FTIR data. Results analysis revealed that 1.0 wt.% is sufficient to improve the mechanical and thermal properties of the nanocomposites. Additionally, the in situ condition of dispersion was found to be motivational to build better interfacial adhesion between the nanoclays and polymer chains.

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REVIEW

Development of Vegetable-Oil-Based Polymers

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ABSTRACT: The utilization of renewable resources for the preparation of new materials is an alternative option for reducing the high demand of fossil feedstocks. Vegetable oils are potential bioresources that are renewable and abundantly available. Triglyceride-based vegetable oils, such as soybean, jatropha, linseed, sunflower, palm, castor, nahar seed, and canola oil, are being considered as precursors in the production of polymers. In this article, we attempt to summarize advancements in processes and technologies for the synthesis of polymers from various kinds of vegetable oils. The advantages and disadvantages of these biobased polymers with respect to traditional monomer-based ones are also highlighted. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40787.

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Alkyd Based Resin from Non-Drying Oil

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Abstract

Palm oil-based alkyd resins were synthesized by alcoholoysis and esterification reactions. Calcium oxide was used as a catalyst for the alcoholysis reaction between palm oil and glycerin. Esterification process was carried out by using phthalic anhydride and maleic anhydride. Physico-chemical properties of the resins such as density, viscosity, acid value, iodine value, saponification value, specific gravity, and moisture content were measured following ASTM and standard methods. The structural confirmation and hydrogen density of the prepared resins were determined by Fourier transform infrared and proton nuclear magnetic resonance spectroscopy, respectively. Molecular weight of the resins was determined by using gel permeation chromatography. The curing process involved heating at 140°C, without using any organic solvent in the presence of methyl ethyl ketone peroxide and cobalt-napthenate. ASTM methods were followed to measure the gloss, hardness and chemical resistivity of the resins. Temperature behaviors were observed by differential scanning calorimetry and thermogravimetric analysis. Produced resins were found thermally stable (up to 300°C). The variations of the properties were noticed due to the types of anhydrides in terms of molecular weight, thermal and chemical resistivity of the resins, although the other properties were found close to each other. Overall, the reported properties are found suitable for the materials to be used for surface coating applications.

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Characterizations of Palm Oil-Based Alkyds for Surface Coating Applications

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Abstract: Alkyd resin was synthesized from palm oil using alcoholysis and esterification reaction. Alcoholysis was carried out between oil and glycerol in the presence of calcium oxide. In esterification process, phthalic anhydride was used to prepare the resin. Various physicochemical properties of the resins such as free fatty acid content, saponification value, iodine value, density, viscosity, specific gravity, non-volatile material content, drying time, *etc.* were measured by following standard methods. Fourier transform of infrared spectroscopy, proton nuclear magnetic resonance and gel permeation chromatography technique was also used for the characterization of the resins. Polymeric films were prepared from the resins by thermal curing process and subjected for pencil hardness, gloss and chemical resistivity testing. In addition, thermogravimetric analysis and differential scanning calorimetry was performed to evaluate the decomposition and melting properties. The prepared polymeric films showed high temperature-stability with excellent chemical resistivity and moderate gloss. The properties of these bioresins were found to be potential for surface coating applications.

Key words: Palm oil, alkyd, bioresin, alcoholysis, esterification.

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ORIGINAL PAPER

The effects of five different types of acid anhydrides and incorporation of montmorillonite nanoclays on thermosetting resins

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Saidatul Shima Binti Jamari[1]

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Abstract Five different types of acid anhydrides such as succinic anhydride (SA), maleic anhydride (MA), phthalic anhydride (PA), 3,4,5,6-tetrahydrophthalic anhydride (TPA) and *cis*-1,2-cyclohexanedicarboxylic anhydride (CDA) were used to prepare various polyalkyd resins from palm oil by following alcoholysis and esterification reaction. Palm oil was subjected to dehydration process using concentrated sulphuric acid prior to alcoholysis to improve the unsaturation in the fatty acid chains. Various physicochemical properties of the resins such as acid value, iodine value, yield, density, specific gravity, molecular weight, non-volatile material content, drying time, colour, solubility, etc., were tested by using standard methods. The resins were cured by using methyl ethyl ketone peroxide (MEKP), styrene and cobalt naphthenate at 120 °C. To enhance the thermal, structural and other resinous properties, 0.5 wt% of montmorillonite nanoclays (MNCs) was dispersed in TPA-based resin. The cured films were tested for X-ray diffraction, surface morphology, tensile properties, pencil hardness, gloss, gel content, swelling ratio, adhesion, thermogravimetric analysis, and chemical resistivity. In addition, hydrophobicity of the cured films was observed by contact angle measurement. A comparison was drawn among the resins as well as the films prepared from different acid anhydrides. Analysis revealed that TPA-based resin/film shows improved characteristics among the others due to high degree of crosslinking. On the other hand, incorporation of MNCs into the polyalkyds led to higher thermal properties, acceptable pencil hardness and reduced wettability, which may suit this film to be applied for high-performance surface coating applications.

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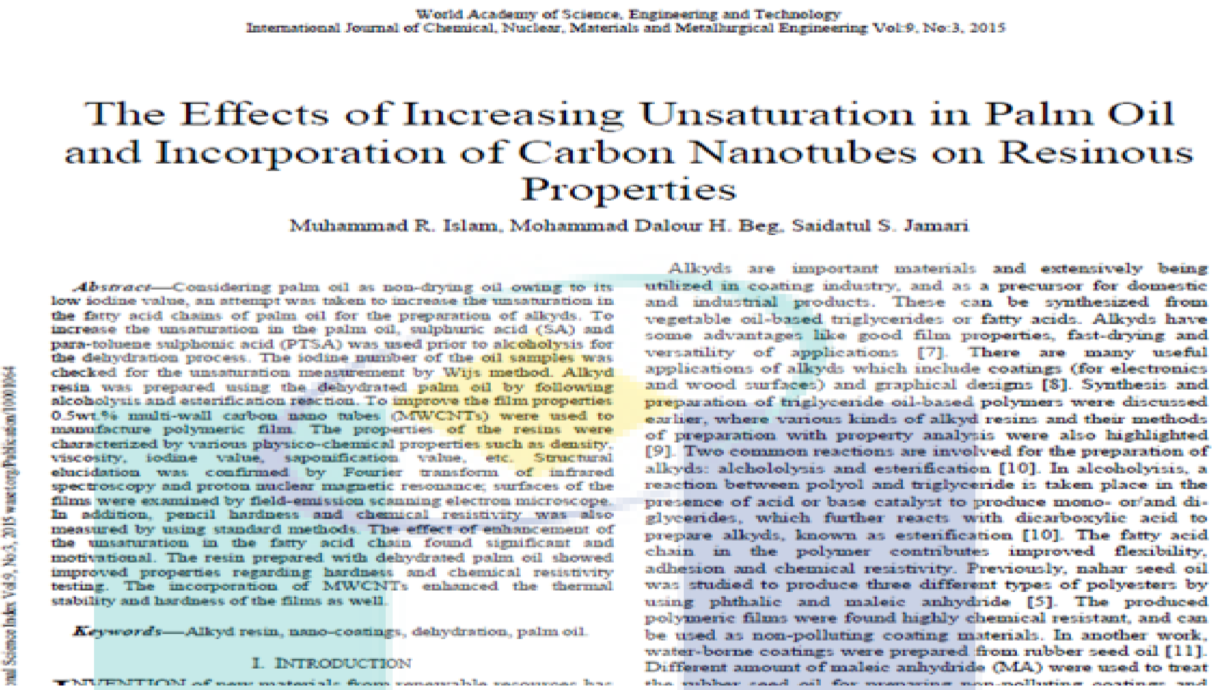

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The Effects of Increasing Unsaturation in Palm Oil and Incorporation of Carbon Nanotubes on Resinous Properties

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Abstract**—**Considering palm oil as non-drying oil owing to its low iodine value, an attempt was taken to increase the unsaturation in the fatty acid chains of palm oil for the preparation of alkyds. To increase the unsaturation in the palm oil, sulphuric acid (SA) and para-toluene sulphonic acid (PTSA) was used prior to alcoholysis for the dehydration process. The iodine number of the oil samples was checked for the unsaturation measurement by Wijs method. Alkyd resin was prepared using the dehydrated palm oil by following alcoholysis and esterification reaction. To improve the film properties 0.5wt.% multi-wall carbon nano tubes (MWCNTs) were used to manufacture polymeric film. The properties of the resins were characterized by various physico-chemical properties such as density, viscosity, iodine value, saponification value, etc. Structural elucidation was confirmed by Fourier transform of infrared spectroscopy and proton nuclear magnetic resonance; surfaces of the films were examined by field-emission scanning electron microscope. In addition, pencil hardness and chemical resistivity was also measured by using standard methods. The effect of enhancement of the unsaturation in the fatty acid chain found significant and motivational. The resin prepared with dehydrated palm oil showed improved properties regarding hardness and chemical resistivity testing. The incorporation of MWCNTs enhanced the thermal stability and hardness of the films as well.

Keywords**—**Alkyd resin, nano-coatings, dehydration, palm oil.

I. INTRODUCTION

Alkyds are important materials and extensively being utilized in coating industry, and as a precursor for domestic and industrial products. These can be synthesized from vegetable oil-based triglycerides or fatty acids. Alkyds have some advantages like good film properties, fast-drying and versatility of applications [7]. There are many useful applications of alkyds which include coatings (for electronics and wood surfaces) and graphical designs [8]. Synthesis and preparation of triglyceride oil-based polymers were discussed earlier, where various kinds of alkyd resins and their methods of preparation with property analysis were also highlighted [9]. Two common reactions are involved for the preparation of alkyds: alchololysis and esterification [10]. In alcoholyisis, a reaction between polyol and triglyceride is taken place in the presence of acid or base catalyst to produce mono- or/and di-glycerides, which further reacts with dicarboxylic acid to prepare alkyds, known as esterification [10]. The fatty acid chain in the polymer contributes improved flexibility, adhesion and chemical resistivity. Previously, nahar seed oil was studied to produce three different types of polyesters by using phthalic and maleic anhydride [5]. The produced polymeric films were found highly chemical resistant, and can be used as non-polluting coating materials. In another work, water-borne coatings were prepared from rubber seed oil [11]. Different amount of maleic anhydride (MA) were used to treat

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