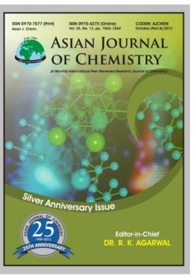
Asian Journal of Chemistry; Vol. 25, No. 15 (2013), 8737-8740

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15356



Synthesis and Characterization of Novel Alkyds Derived From Palm Oil Based Polyester Resin

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(*Received*: 20 February 2013; *Accepted*: 29 August 2013) AJC-14038

Alkyds that are formulated from an identical chemical composition will exhibit different properties and performance depending on the preparation process. In general, alkyds can be prepared from two processes, *i.e.*, alcoholysis (monoglyceride) or fatty acid. Fatty acid process is chosen in this study as the preparation process of alkyd resin. In this process, it involves a step-by-step addition of material to complete the esterification at 180-250 ºC. In addition, synthesis of alkyd can be carried out without solvent (fusion cook) or with solvent (solvent cook). Nowadays, the concern about emission of volatile organic compounds lead to reduction or elimination of solvents as base of industry materials in order to produce more environmental friendly products. In this project, three different alkyd resins namely alk-45, alk-47 and alk-65 were successfully synthesized under fatty acid process by employing without solvent technique. The prepared resins were characterized by FTIR, NMR, TGA, GPC and DSC instruments. Other physical tests such as acid number, hydroxyl number, moisture content were also performed.

Key Words: Alkyds, Alcoholysis, Fatty acid, Fusion cook, Solvent cook, Environmental friendly.

INTRODUCTION

During the past one hundred years, the industry has employed large quantities of fats and oils. The decline in fats and oils has largely been a result of the substitution of petroleum products for the vegetable oils. Alkyd resin contains a large percentage of fatty acids and has been the predominate binder used in the trade-sales and industry for over 35 years. Petroleum based product usage increased dramatically over the past decade, but it is noted that alkyd resins are still employed in large quantities. A large percentage of the trade sales market has switched to water-borne latex coatings based on petroleum-derived materials. The major reason for this is consumer convenience in clean-up, short dry times and low odor.

Vegetables oils are the modifier in an alkyd formulation, *e.g.*, palm oil, palm kernel oil, soybean oil, olive oil, colza oil, sesame oil, wood oil, castor oil, linseed oil. While, for animal oil are such as fish oil, whale oil, beef oil, mutton oil and hoof oil. Natural resins such as rosin, amber and shellac; and the synthetic ones such as phenol resin, carbon resin and melamine resin have also been used in the alkyd formulation. In addition, the naturally occurring oils consist of triglycerides, tri-esters of glycerol and fatty acids. Alkyd resins are polyfunctional oil-modified polyesters, synthesized by reaction of polybasic acid together with mono-functional acid. Kienle was the first person to introduce the term 'Alkyd' in 1927 and is derived from 'al' of alcohol and 'cid' of acid, where the later 'Kyd' employed to give the desired phonics[1-3].

Ever since alkyd resins were first introduced some 35 years ago, they have enjoyed a consistent annual growth, with current production now running well over one-half billion pounds. Today alkyds outrank all other synthetic coating resins in importance, accounting for approximately half of all resins used by the paint industry, which approaches a size of two billion dollars annually in the United States. The alkyd reaction is concerned to be the most versatile resin-forming reaction known. No other resin lends itself to greater internal variation or to more useful modification by physical or chemical blending with other polymers[4]. Alkyd resins are used extensively for synthesis of paint, adhesives, ink and varnish also various coating industries. The common problems for alkyd resins are that they are typically used in diluted form in organic and that some of the alkyd resins such as palm oil-based alkyd resin are not able to air dry due to their low iodine value[5,6].

In order to overcome these problems, the use of alkyd emulsions had been employed by emulsifying the alkyd resins in water[8] and by copolymerizing it with other monomer to enhance their properties or to interesterification with oil to produce a workable resin product[10]. Based on our literature search, there are few reports on the use of palm oil or its derivatives alone in making alkyd resin for coating adhesive application. Some of the research groups have modified palm oil-based alkyd resin with other chemicals to form the polymers with improved properties[7-9].

EXPERIMENTAL

Oleic acid and glycerol were a kind gift from Cognis Oleochemicals (M) Sdn Bhd. These materials were used as such without any purification. Phthalic anhydride (PA), fumaric acid (FA), potassium hydroxide (KOH) were chemicals of analytical grade.

Preparation of palm oleic acid based alkyd resins: Three alkyd samples having oleic acid contents of 45, 47 and 65 % were coded as Alk-45, Alk-47 and Alk-65, respectively. These alkyds were prepared by fatty acid process using fusion cook technique (without solvent) as per the formulation given in Table-1 and were formulated according to the procedure of Patton[10]. All the ingredients were charged into a 1 L four neck round bottom glass reactor equipped with a condenser, thermometer, mechanical agitator and a Dean-Stark decanter for separating the water evolved from the reaction. The mixture was heated up to 180-200 ºC and maintained for 2 h. Water that was evolved at the side arm of condenser was collected. Heating rate was maintained until no water collected, mixture was allowed to cool down to 100 ºC. A moderate and continuous stirring rate 130-140 rpm was chosen to ensure a uniform reaction. Phthalic anhydride was added to the flask and reacted at temperature ranges from 140-180 ºC for 1-2 h and allowed to cool to 100 ºC. Fumaric acid was added and temperature was raised up to temperature range from 180-210 ºC for 3-4 h. Another amount of water was collected and heating was turned off when the acid number had reached desired value.

TABLE-1
FORMULATION OF FUSION COOKS ALKYDS

Compositions	Charge per 100 part yield			
Alkyd	Oleic acid	Glycerol	PA	FA
Alk-45	43.16	33.68	16.84	6.32
Alk-47	44.12	26.47	21.01	8.40
Alk-65	64.00	17.60	13.60	4.80

Progress of reaction during synthesis of samples, was monitored by peridiocally checking the acid number of the reaction. Acid number was checked by titration of KOH solution against alkyd sample[10].

Infrared spectroscopy (FTIR): Infrared spectra of alkyd samples were recorded on a Perkin Elmer FTIR RX1 spectrometer at room temperature, with 4 scans from 4,000-600 cm^{-1}. Background effects due to atmospheric water, carbon dioxide and other volatiles were subtracted. The source is a tungsten-halogen source.

Nuclear magnetic resonance spectroscopy (NMR): About 10 mg mL^{-1} for ^1H NMR sample was dissolved in solvent; deuterated chloroform,$CDCl_3$. The ^1H spectra for alkyds were recorded in a JOEL JNM-LA 400FT-NMR spectrometer, which operating at 400 MHz. The chemical shifts were referenced against tetramethylsilane (TMS) as 0 ppm, was used as an internal standard. The solvent peak was showed at value of 7.26 ppm for ^1H NMR.

Differential scanning calorimetry with hyper DSC: Rheometric Scientific Perkin Elmer Diamond DSC with hyper DSC was used to measure the glass transition temperature (Tg) of the alkyds. Hyper DSC means the ability to perform valid heat flow measurements while heating or cooling sample with fast linear controlled rates.

About 1-2 mg of the sample was weighed and placed into a sample pan kit along with a blank pan as a reference. Hyper DSC measurement was conducted over temperature range from -50 ºC to 100 ºC at the heating rate of 10 0C/min.

Thermogravimetric analysis (TGA): Rheometric Scientific thermal analyzer of 1000 series was employed to perform the TGA test. Basic instrumental requirements for thermogravimetry are a precision balance with a pan, a furnace capable being programmed for a linear rise of temperature with time and a recoder. A computer is used to control the instrument. This test was done to study thermal decomposition behaviors of the alkyds. About 5-10 mg of the sample was weighed and placed into the sample crucible which was located in the furnace of thermal analyzer. Test was conducted over the temperature ranging from 40-950 ºC at the 20 ºC of heating rate under the nitrogen gas atmosphere.

Gel permeation chromatography (GPC): Gel permeation chromatography was performed on WATERS equipment with refractive index detector, Waters TM 717 plus auto sampler and Waters TM 600 Controller. Tetrahydrofuran was used as the mobile phase. About 2 % (w/v) of sample solution was injected into the column at 40 ºC. The flow rate was set at 1 cm^3 min^{-1}. Polystyrene standards of various molecular weights were used to calibrate the column.

Other physical characterization: Acid number was determined by procedure adapted from ASTM D1980-87. Hydroxyl number was done according to the procedure from ASTM D4274-94, with test method B. Karl Fischer Titrator (701 KF Titrino, Metrohm) titration was used to quantify water/moisture content in polyesters. Result was tabulated in Table-2.

TABLE-2
CHARACTERISTICS OF FUSION COOK ALKYDS

Properties	Alk-45	Alk-47	Alk-65
Oil length	45	47	65
Acid number	8.10	18.52	16.58
Hydroxyl number	354.450	160.386	44.230
Molecular weight	1455	4380	970
Colour	Light brown	Brownish	Brownish

RESULTS AND DISCUSSION

The overlay of FTIR spectra was presented in Fig. 1. All alkyds had showed similar absorption peaks. These as expected since the alkyds were prepared from the same material and just vary in the proportion. Peak that corresponding to the OH group of the free glycerol or residual moisture is observed at 3415-3400 cm^{-1}. The hydroxyl group of the alkyds was expected to enhance the adhesion of the blends of the resin.

The C-H of the double bonds (*sp*^{2}) stretching was observed at 3006 cm^{-1}. Also, C-H stretching of (*sp*^{3}) observed at region 2900-2800 cm^{-1}. The appearance of the characteristic of strong

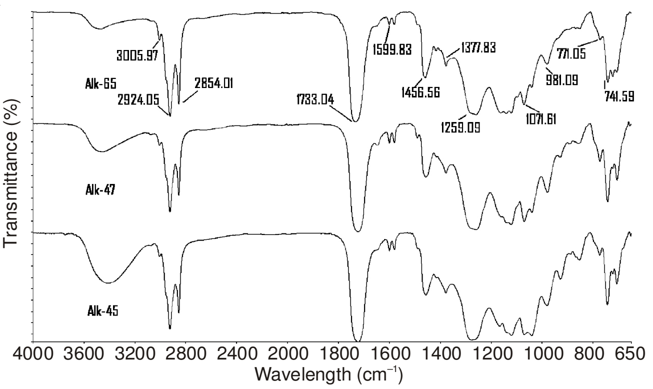

Fig. 1. FTIR spectrum of fusion cook alkyds

band of ester group of -C=O stretching at 1733 cm^{-1}. The weak absorption bands at 1599 cm^{-1} arising from C=C are due to the aromatic rings in PA. Bands were observed at 1456 cm^{-1} for C-H stretching aromatic and aliphatic. Moreover band in the aromatic region at 741-773 cm^{-1}, confirms the esterification reaction of the alkyd resins. All these characteristic absorption bands support the structure of alkyd samples formed from palm oleic acid.

The spectra of Alk-45, Alk-47 and Alk-65 showed similar chemical shifts of the major peaks since they were prepared from similar material and only the proportion is different. The overlay spectra of fusion cook alkyds were showed in Fig. 2. Generally, alkyd resin has an ester structure with fatty acids of the oils as the integral parts of its composition. From figure, the peak (a) appear at 0.80 ppm is assigned to the methyl protons primary in the chain end of the free fatty acids. The strong resonance (b) at 1.24 ppm is due to the methylene protons secondary of the fatty acids. While, the weaker resonance (c) at 1.5 ppm is assigned due to the methine proton tertiary attached to carbon rich of the fatty acids. The peak (d) at 1.90 ppm is due to the methylene proton which was found in the fatty acid chain. Peak (e) attributed due to the methylene proton adjacent to carbonyl group was appeared at 2.3 ppm.

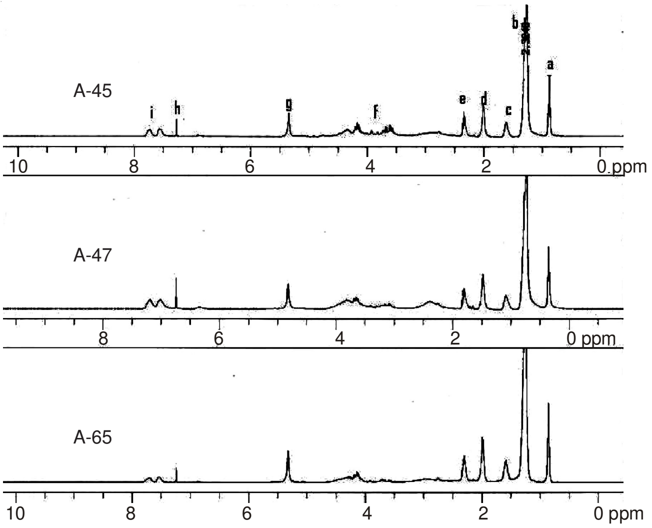

Fig. 2. NMR spectrum of fusion cook alkyds

While, both methylene and methine protons on the glycerol unit that attached to the oxygen of an ester group and fumaric acid are deshielded to form a broad peak (f) at the lower field range between at 3.5-4.5 ppm. Besides that, the peak (g) which appears at 5.3 ppm is attributed to the vinylic proton of the unsaturated fatty acids. The peak (h) which appears at 7.2 ppm is attributed to the $CHCl_3$ in the $CDCl_3$ solvent. On the other hand, the last two peaks (i) appear at 7.54 and 7.72 ppm, respectively represents the vinylic protons of aromatic ring of phthalate anhydride.

From the DSC curve (Fig. 3), Alk -65 had a Tg of -33.87 ºC, Alk-47, Tg of -18.29 ºC, while Alk-45 had a Tg of -15.28 ºC. Between the fusion cook alkyds, Alk-65 had more fatty acid side chain in the polymer linkages as we can see from the synthesis formulation. This makes the structure less compact. Thus less energy required as compared to Alk-45 and Alk-47 which more heat energy required to break the rigid state at room temperature.

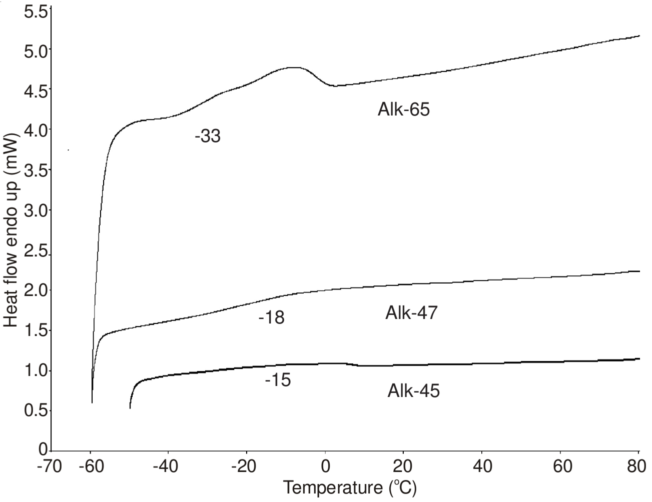

Fig. 3. Overlay of DSC curve of fusion cook alkyds

The overlay curve of TGA thermogrammes for the fusion cook alkyds was shown in Fig. 4. Thermogravimetric analysis was used to study the thermal stability of alkyds. From the study, there were three distinct stages of thermal degradation was occurred at temperature above 160 ºC. The first thermal degradation was noted at 10 wt % of Alk-45, Alk-47 and Alk-65 which started at 160 ºC and reached the maximum between 306.15-332.16 ºC with the weight loss between 5.923-8.748 %. The second weight loss was between 86.25-92.07 % which started at temperature 332.16 ºC and reached the maximum between 447.31-461.86 ºC. Meanwhile, the third thermal degradation was started at 461.86 ºC and reached the maximum between 601.19-824.54 ºC. The weight loss was occurred between 1.770-4.320 %.

The result shows that the degradation of higher molecular weight polymer was occurred at higher temperature, whereas the lower weight polymer the degradation occurred at lower temperature. From these thermograms, it can be seen that Alk-47 has a relatively higher thermal stability, followed by Alk-45 and Alk-65. Generally, high molecular weight polymer would facilitate rapid drying during coating process while lower molecular weight fraction would act as plasticizer.

The GPC chromatogram for fusion cook alkyds is presented in Figs. 5-7. The M_w and M_n of the Alk-47 were 14792

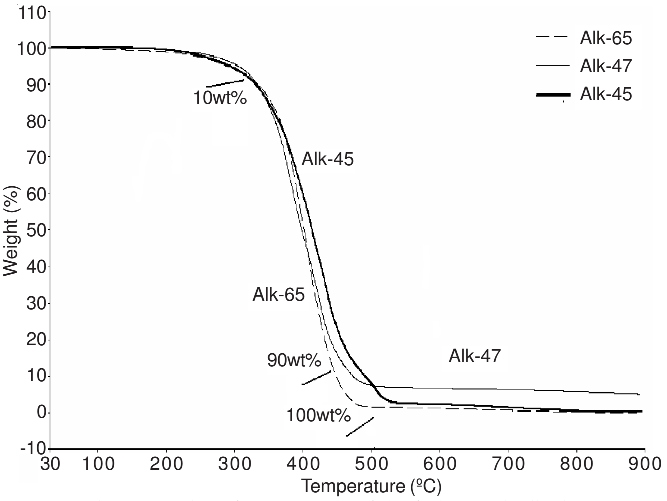

Fig. 4. Overlay of TGA curves of the fusion cook alkyds

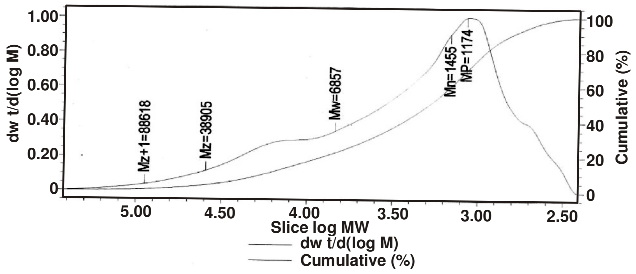

Fig. 5. GPC chromatogram for the Alk-45

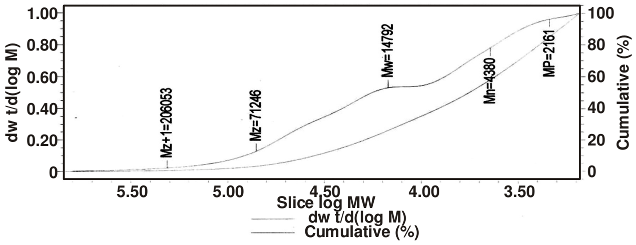

Fig. 6. GPC chromatogram for the Alk-47

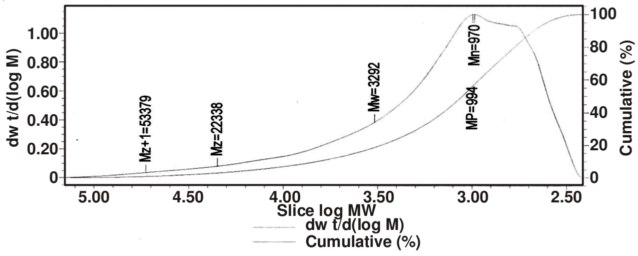

Fig. 7. GPC chromatogram for the Alk-65

and 4380, respectively, whereas their polydispersity index (PDI) is 3.37686. Polydispersity index (PDI), is a division of M_w by M_n and it is a measurement of the distribution of molecular weight in polymer sample. It indicates the distribution of an individual molecular weight in a batch of polymers. Generally, short oil length alkyd resulted high molecular weight polymer since the molecules are more compact, rigid and which had less fatty acid side chain in the polymer linkages. However, for this analysis the medium oil length alkyd had higher molecular weight than short oil length alkyd. This is might due to the formulation of Alk-47 which had more phthalic anhydride and fumaric acid ratio in the synthesis and makes structure more compact and rigid. Thus, the molecular weight for that particular alkyd was higher than the other[11-15].

Conclusion

Palm oleic acid based alkyds,a plant based and environmentally friendly alkyds, were successfully synthesized by using the one step fatty acid process and employing fusion cook (without solvent) technique. The novel alkyds was name as Alk-45, Alk47 and Alk-65. From the GPC result, showed that Alk-47 sample, having relatively the highest molecular weight and consequently highest viscosity follow by Alk-45 and Alk-65. Other characterization test showed the unique and different criteria of each single alkyd. Even though they were prepared from same material, however the formulation and oil length are different. Thus, thermal stability, the glass transition temperature (T_g) and other properties were different. For further application, palm oleic acid based alkyds investigated as non drying alkyds are recommended to be modified either by blending or copolymerization with other fast drying to reduce production cost, provide crosslinking, good glosss, flexibility and to produce a workable application of this resin such coating, adhesives, ink, *etc*.

ACKNOWLEDGEMENTS

The authors thank IPPP of University Malaya, Malaysia for financial support (PS251/2009A) and Ministry of Science and Technology, Malaysia (MOSTI) for National Science Fellowship (NSF).

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