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Investigating the optimum unsaturated fatty acid content and oil length for auto-oxidative drying of palm-stearin-based alkyd resin

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ABSTRACT

The pendant chain of the Palm Kernel Stearin (PKS) was modified by blending it with measured ratio of rubber seed oil (RSO), followed by dehydration of the oil blend with the aim of increasing the degree of unsaturation in the oil chain. The modified dehydrated palm kernel stearin oil blend with ratio of 80:20, 75:25,70:30 and 65:35 by wt/wt% of PKS to RSO, respectively, were used to synthesized four different medium oil length alkyds, labelled as Alkyd A, Alkyd B, Alkyd C and Alkyd D, respectively, using a two stage alcoholysis-polyesterification method. The film properties of the synthesized alkyds were determined by carrying out the physico-chemico-mechanical properties and drying test of the Alky A to Alkyd D. The aim was to get the optimum ratio of PKS to RSO which will give the best and suitable result as regards to the total PKS content of the oil blend. The alkyd resin synthesized with 70:30 (by wt/wt%) of PKS to RSO (alkyd C) yields the best result with respect to the three other oil blend series. Also, the effect of oil length variation were investigated, which leads to the production of two additional alkyd resin labelled as Alkyd C_s and Alkyd C_L with the same oil blend ratio with respect to alkyd C but with short and long oil length respectively as regards to the fatty acid composition of the resin. From the results obtained, the film of Alkyd C_S gave the best mechanical properties whereas the film of Alkyd C_L has a good chemical resistance and drying properties as compared to Alkyd C and Alkyd C₅, respectively. Overall, it can be concluded that for palm kernel stearin which is a saturated fatty acid to be utilized in the synthesis of a molecule of an auto-oxidative drying alkyd, approximately two – third of the total oil content must be blended with an unsaturated fatty acid (one unsaturation per molecule).

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1. Introduction

Lately, the use of edible oil in the synthesis of alkyd resin is increasing day by day, and this poses a great danger in the availability of such oil in the food sector. The high costs, the environmental impact, and the decrease in fossil resources are the main reasons behind attracting a great deal of attention of the research community towards searching for alternative raw materials in different industrial fields. So, with the increase in world demand for oil and the challenges to expand the existing oil supply for human consumption and industrial utilization [1], there is need to utilized less expensive and non-edible product (oil) in the synthesis of the alkyd resin in order to meet up with the competitive environment of the coating industries. One of such product which can be utilized in the synthesis of surface coating, generally, to yield a desirable

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http://dx.doi.org/10.1016/j.porgcoat.2016.07.019 0300-9440/© 2016 Elsevier B.V. All rights reserved. result both in terms of cost, renewability, biodegradability and nonedibility is palm kernel stearin (PKS)

Alkyd resins have been defined as the product of polycondensation reaction between a polybasic and polyhydric alcohol, modified with a monobasic acid or its anhydrides and drying oil with suitable catalyst at controlled temperature [2]. They are used in the formulation of paints, varnishes, lacquers and other finishes. Alkyd resin have become an indispensable raw material due its extensive usage for decorative and protective purposes. They are of enormous importance in the building industry where they are used for interior and exterior architectectural finishes [3].

Oil Palm (*Elaeis guineensis*) is native to Africa and remains a source of the most abundant and widely used plant oils in the world, grown in mass in tropic countries. Palm oil and palm kernel oil are edible plant oil derived from fruit of the trees. It differ from its major competitors (soybean, sunflower seed and rape seed) in that it is obtained from perennial tree crop and drought impact are less severe in comparison to oil seed crops. Palm stearins are more solid fractions of palm and palm kernel oils. It has not been commercially utilized and almost a non-useful product in most part of the world.

The fatty acid composition of palm kernel stearin is approximately 60% saturated and 40% unsaturated fatty acid. The main unsaturated fatty acids compositions of palm kernel stearin are 33% oleic and 7% linoleic acid [4]. Therefore, palm kernel stearin is classified as saturated fatty acid due to its very low degree of unsaturation and alkyd resins, which are based on palm kernel stearin alone, cannot be air-dried [5]. In order to air dry, palm kernel stearin based alkyd resin, an unsaturated C-C bonds must be introduced into the main or pendent chains of the alkyd resin. Azimi et al. [5.6] investigated the effect of conventional and nano zinc pigments and modification with ketone on air drying properties of palm stearin based alkyd resin paints. They reported that palm stearin can be utilized in the synthesis of alkyd resin. Uzoh et al. [7] synthesized palm oil based air drying alkyd resin. The palm oil which is a saturated fatty was neutralized and dehydrated, followed by functional group modification with phthalic anhydride via polyesterification at 250 °C. Subsequently, the drying schedule of prepared resin were improved with the addition of cobalt. In another study [8], jatropha curcas Linnaeus oil alkyd drying properties were improved through green chemistry. Thermal stability, hardness and drying time of palm oil based alkyd has been improved by increasing the unsaturation and incorporation of carbon nanotubes [9].

In this research, attempt was made to synthesize an autooxidative drying alkyd resin by introducing unsaturation to the structure of palm kernel stearin. A new recipe was developed to increase the degree of unsaturation in the palm kernel stearin chain by modification with different ratios of rubber seed oil. The effects of the modification with RSO and the optimum oil length were investigated.

2. Experimental

2.1. Materials

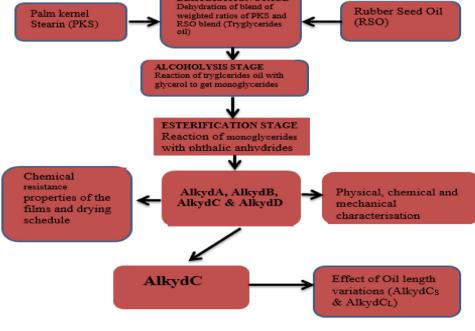
The palm kernel stearin was collected from the Upglobal Agro oil mill, Isiakpu village Nise, Anambra State. The refined rubber seed oil was purchased from the Rubber Research Institute of Nigeria, Iyanomon, Benin city, and was used without further purification. The analytical grade phthalic anhydrides, maleic anhydride, glycerol, Calcium oxide, Sodium bisulphate (NaHSO₄) and xylene were obtained from Eddy chemical shop in Onitsha, and were used without further purification.

2.2. Instruments and methods

The fatty acid profile the oil were determined with a Thermo Finnigan Trace GC/Trace DSQ/A1300, (E.I Quadropole) equipped with a SGE-BPX5 MS fused silica capillary column (film thickness $0.25\,\mu m)$ for GC-MS detection, and an electron ionization system with ionization energy of 700 eV was used. Carrier gas was helium at a flow rate of 10 mL/min. injector and MS transfer line temperatures were set at 220 °C and 290 °C respectively. The oven temperature was programmed from 50°C to 150°C at 3°C/min, then held isothermal for 100 min, and raised to 250 °C at 10 °C/min. Diluted samples (1/100, v/v, in methylene chloride) of 1.00 µL were injected manually in the slitless mode. The identification of the individual components was based on the comparison of their relative retention times with those of authentic samples on SGE-BPX5 capillary column, and by matching their mass spectral of peaks with those obtained from authentic samples and/or the Wiley 7 N and TRLIB libraries spectra and published data. The chemical compositions of the oils and their alkyds were also confirmed by SHIMADZU FTIR-84008. Viscosity was determined by Brookfield viscometer, RVT Model (#Spindle 3, RPM 20). The physico-chemical properties of the oil were determined by standard methods (ASTM, 1973). The flow scheme for palm stearin modified alkyd resin is depicted in Fig. 1.

2.3. Dehydration of modified palm kernel stearin

80 g of palm kernel stearin was blended with the 20 g of rubber seed oil and labelled as oil A. The mixture were charged into a reactor with 2% of sulphuric acid in the presence of 2% pumice for the dehydration process. It was heated to 260–298 °C at constant reaction time of 20 mins in an inert atmosphere of nitrogen. The water generated from the reaction was collected through a



DEHYDRATION STAGE

Fig. 1. Flow chart of palm-strearin-based alkyd resin.

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