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Effect of fumaric acid on the properties of alkyd resin and palm oil blend

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Two blends of palm oil and alkyd resins were prepared. The first blend comprises 20% palm oil while the second blend comprises 30% palm oil. These blends contained quantities of fumaric acid ranging from 2g to 10g. Also, a drying agent composed of a mixture of cobalt, calcium and lead compounds was included in each blend sample. After the preparation of the samples, their physicochemical properties such as density, viscosity, drying time, acid value, peroxide value, saponification value, and dry extract were determined following standard methods. Structural properties of prepared blends were determined by proton magnetic nuclear resonance spectroscopy. In the absence of fumaric acid, the analysis showed that the blends exhibited high drying times, low viscosity and density. However, the drying times of both alkyd blends decreased with the increase in fumaric acid content and 20% palm oil is the optimum proportion for alkyd palm oil blend. The results suggest that fumaric acid can be used in alkyd resins based on non-drying oils as a blending additive in coating formulations.

Keywords : Alkyd resin; blend; palm oil; fumaric acid; physicochemical properties; drying properties.

INTRODUCTION

Modification of polymers is one of the techniques industrially used for obtaining a large range of new products [1, 2]. Chemical and/or physical modification found large application in the industries with the aim of adjusting polymer properties to the various technical applications [3, 4]. Alkyd resins are widely used in the surface coatings industry as a binder for making industrial and offshore paints [5]. They are resinous materials synthesized by the reactions of polyol, dicarboxylic acid, and triglycerides of fatty acids derived from vegetable oils [6]. In order to enhance film properties, alkyd resins are usually modified by raw materials and/or resins by chemical incorporating [7] or physical blending [8].

The trending down of petroleum resources has resulted in an increasing demand toward vegetable oils as an inexpensive and renewable source. It is estimated that about 1 million tons of vegetable oils are used in polymeric surface coatings each year [9]. In the recent 20 years palm oil production has increased, as a result of the increasing demand toward vegetable oils as an inexpensive and renewable source. Now, compared to soybean oil, palm oil takes the second place in the list of oils produced around the world and will probably overtake soybean oil in another 10–15 years [10]. Palm oil can be considered as a useful candidate to respond to the increasing oil consumption of organic coatings industry. Many studies are using palm oil as an alternative vegetable oil for alkyd synthesis [11, 12] and as an additive [13] for enhancing rheological properties of alkyd resins. The main problem for resins based on palm oil is that they are not able to air dry due to the low iodine value of palm oil. But the literature survey reveals that if vegetable oils are used in the blend for alkyd resin synthesis, the drying properties of alkyd resins could be improved [14]. Based on designed formulations, different types of alkyd resin were synthesized by using a mixture of oils.

Fumaric acid is a dicarboxylic acid with the same molecular weight as maleic acid. Nevertheless, they have different structural formulas. Maleic acid is cis-(Z)-2-butenedioic acid and fumaric acid is trans-(E)-2-butenedioic acid. Fumaric acid is an organic acid widely found in nature, in humans, animal feed and is an essential ingredient of plant life [15]. Fumaric acid has been used in food and beverage products since 1946 [16]. Research shows that it improves quality and reduces costs of many food products. In coating industries, fumaric acid contributes to the Improvement of the properties of vegetable oils [17].Through modification with fumaric acid in the synthesis of alkyd resins, changes are imported in their physicochemical properties[18]. In the present work the improvement of physicochemical properties of alkyd resin and palm oil blend through physical modification with different proportions of fumaric acid was investigated.

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EXPERIMENTAL

Materials

Palm oil was obtained from Ng. Enterprise (Ng Enterprise, Edou, Oyo District, Republic of Congo). Commercial long alkyd resin was produced by MPCROKIM, 32, Rue du Mercure Z.I, Ben Arous 2013 Ben Arous, Tunisia and it was supplied by the Congolese Enterprise of Paint (COPE). The driers used were produced by DSM Coating resin, The Netherlands. The drier is a mixture of 10% of zinc-based drier, 10% of calcium-based drier, 10% of cobalt-based drier, and 10% of lead-based drier in white spirit as solvent. All materials were used as received.

Method

Preparation of alkyd and palm oil blends

Alkyd resins were mixed intimately with palm oil in a small aluminum box of 50ml using a spatula as a mixer. After near-perfect homogeneity of the mixture, it was left for two hours for letting air bubbles in the mixture to escape. Different samples with 10%, 20%, 30%, 40% and 50% palm oil were prepared. The same quantity of driers (0.2%) was mixed with each sample.

Preparation of alkyd and palm oil blends with fumaric acid

The samples with 20% and 30% palm oil were mixed in a small aluminium box of 50 ml to perfect homogeneity with 2g, 4g, 6g, 8g and 10g fumaric acid. The quantity of driers was increased (0,6%) to accelerate the drying time. The different samples obtained are presented in table 1.

Testing

Viscosity

The viscosity was measured by using a Brookfield rotary Viscometer KU-2 model DV-III according to ISO 288. It is composed of a dial with digital display and keys for the hand drive operation. The measurements were performed by using spindle n°6 posted directly on the numerical dial.

Density

The density was determined according to NF en 1097-6. The measurement was performed by using analytical scale and Pycnometer S9611826. The Pycnometer is a metal container standardized with volume of 100 cm^3. It is equipped with a bored lid of a hole to evacuate the bubbles of air and remove the excess of product.

The density was determined by the following relation:

$$D = \frac{M2 - M1}{V}; \qquad (1)$$

D: density of the product
M1: weight of the pycnometer empty
M2: weight of the Pycnometer filled with product
V: volume of the pycnometer

Dry extract

The quantity of dry extract was determined by using a cooking isotherm (123°C) according to ISO 3251. The dry extract was calculated from the difference of the plates, which were taken initially and lineally. The mean value of three results was reported as the percent non-volatile matter.

Drying time

The drying time (set-to-touch time) was determined according to ISO 9117. The measurement was performed by using a painting applicator of 150 microns. A thickness of 150µm is applied on the contrast paper and exposed for drying in free air. The drying time is measured when the film is not sticking to the touch any more.

^{1}H NMR spectra analysis

The proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on aNuclear Magnetic Resonance 500 MHz (Model: FT-NMR Avance II, Bruker 500, UltraShield) instrument after dissolving the samples in deuterated chloroform $CDCl_3$.Each sample was dissolved in $CDCl_3$, and the resulting mixture was placed into a ultra-precision NMR sample tube. The probe was at room temperature. The chemical shifts are reported in ppm, using the solvent proton signal as a standard.

Acid value

Acid value was determined according to the AOAC method and the standard 969.17 1997 by titrating the mixture with a KOH solution till a pale pink coloring. The acid value (IA) was calculated as follows:

Table 1: Blend of alkyd resin and palm oil with various proportions of fumaric acid

Alkyd /Oil	80:20						70:30					
Fumaric acid [g]	0	2	4	6	8	10	0	2	4	6	8	10
Blend designation	M_1	M_2	M_3	M_4	M_6	M_7	M_1	M_2	M_3	M_4	M_5	M_6

$$IA = \frac{V x N x\ 56{,}1}{M}; \qquad (2)$$

V: the volume of KOH (in ml) necessary to the neutralization of the free fatty acids.

N: normality of the solution of KOH

M: mass test specimen

Peroxide value

Peroxide value was determined using AOAC method and according to standard 965.33,1977 by titrating the iodine released with a thiosulfate solution.

The peroxide index (IP) was calculated as follows:

$$IP = \frac{(V-V0)\times N\times 100}{M} = \frac{(V-V0)\times N\times 100}{M} \ ; \qquad (3)$$

V: volume in ml of the thiosulfate solution used;

V0: volume in ml of the thiosulfate solution used for the white test;

N: exact normality of the thiosulfate solution;

M: mass test specimen.

Saponification value

Saponification value was determined using AOAC method and according to standard 920.160,1997 by titrating the mixture with a solution of HCl. The saponification index (IS) was calculated as follows:

$$IS = \frac{56.1\times N\times(V_0 - V)}{M}; \qquad (4)$$

V_0 : volume of HCl used for the white test;

V : volume of HCl used;

N : normality of KOH solution;

M : mass test specimen.

RESULTS AND DISCUSSION

Effect of fumaric acidon the drying time of the blends film

Figure 1 shows the change in drying time (set-to-touch time) with the increase in the content of fumaric acid in the blend. The drying time decreases with the increase in fumaric acid content.

The decrease in the drying time at 30% palm oil is moderate up to 10g fumaric acid content, and this decrease is clearly observed at 20%. However, the values of drying time at 30% palm oil are higher than those at 20% palm oil. Alkyd resin film dries by an autooxidation process [19], due to intake of oxygen from the atmosphere. Mechanistic studies of autooxidation revealed that the drying process of coatings based on alkyd resin is due to the presence of unsaturated bonds in the vegetable oil and results in lower drying times.

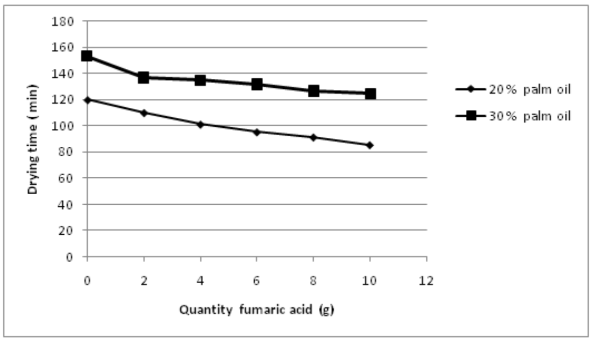

Fig.1. Drying time of alkyd resin and palm oil blend with the quantity of fumaric acid

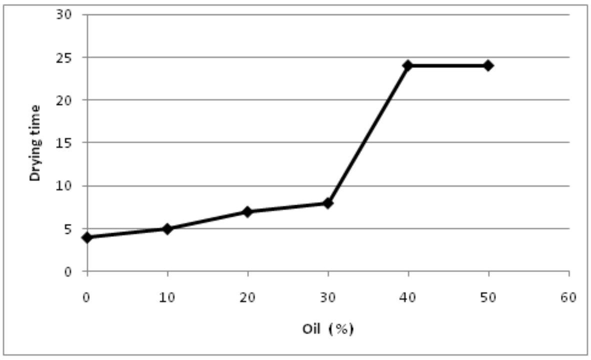

Fig. 2. Drying time of alkyd resin with the quantity of oil

Palm oil is known as a non drying oil. Its blending with alkyd resin has shown an increment of drying time (figure 2). As it is shown in figure 1, for all blends, set-to-touch (surface drying) drying time decreases on increasing the proportion of fumaric acid in the blend. This happens because of the presence of unsaturated bonds in fumaric acid which contribute to the reduction of drying times.The highest reduction of drying times in the presence of fumaric acid is for the blend with 20% palm oil content. Based on this result, it can be concluded that 20% palm oil is the optimum proportion for alkyd palm oil blend. Undoubtedly,in the presence of a more effective drying system, the oxygen activation is further accelerated and results in a shorter drying time.

Effect of fumaric acid on the dry extract of the blends film

Figure 3 shows the change of dry extract with the increase in the content of fumaric acid in the blend. The dry extract increases with the increase in fumaric acid content. The increase of dry extract is higher at 30% than at 20% palm oil content. The non-volatile material content found is 81%for the higher and 0 % for the lower, indicating a relatively solid portion of blend.

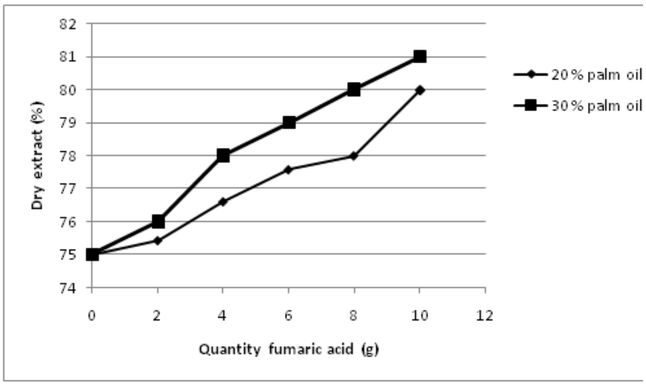

Fig. 3. Dry extract of alkyd and palm oil blend with the quantity of fumaric acid.

Characterization of palm oil and alkyd blends

Different parameters of palm oil and alkyd resin were measured and the results obtained are shown in Table 2.The density and viscosity of the alkyd was found to be 0.95 and 5000cps, respectively. The density of oil was found to be 0.89 implying freedom from any heavy metals.

Figure 2 shows the ^{1}H NMR spectrum of palm oil. The peaks at δ=0.85–0.90 ppm are characteristic for the proton of a terminal methyl group. The protons of all internal -CH_2 groups present in the fatty acids were confirmed by the peaks atδ= 1.60 ppm. Peaks at δ= 2.0 and δ= 2.75 ppm are characteristic for allylic and double allylic proton. The α-proton of ester group is found at δ=2.30 ppm. The -CH_2- protons of glycerol are found at δ=4.1–4.3 ppm and the protons for -CH of glycerol and unsaturated carbons appeared at δ= 5.33–5.35 ppm.

Table 2*:* Physico-chemical data of alkyd resin and palm oil

Parameters / Samples	Density	Gloss (60°) [%]	IA [Mg KOH/g]	IP [mgeqO_2/Kg]	IS [mgKoH/g]	Viscosity [cps]
Palm oil	0,89	-	7,29	3,29	121,2	-
Alkyd resin	0,95	86	1,68	0,28	19,63	5000

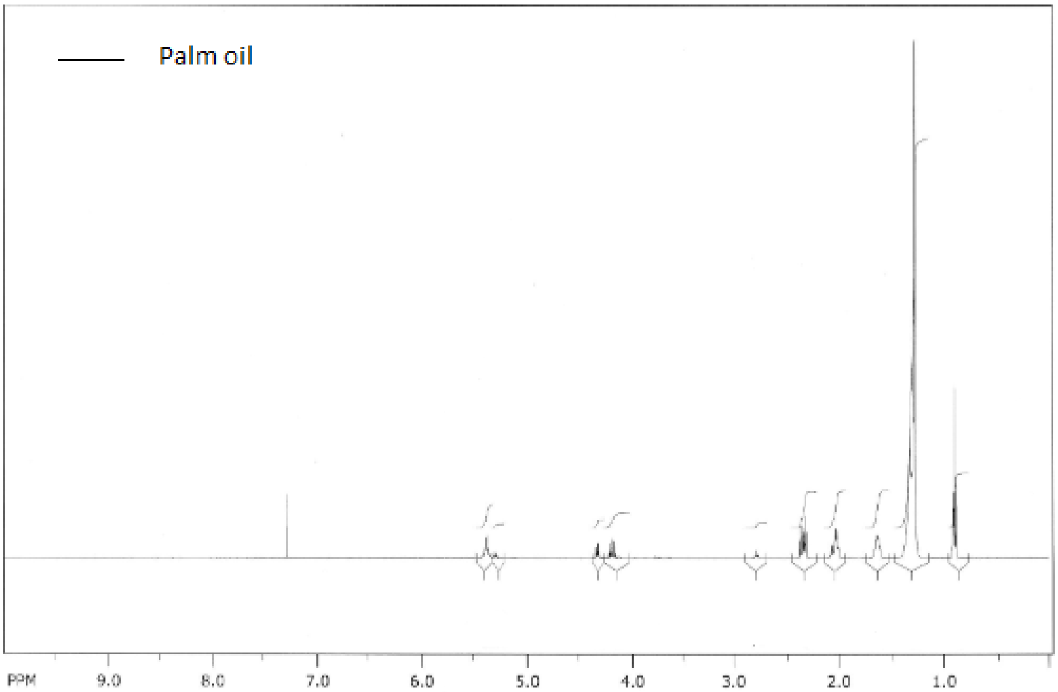

Fig .4.^{1}HNMR spectrum of palm oil

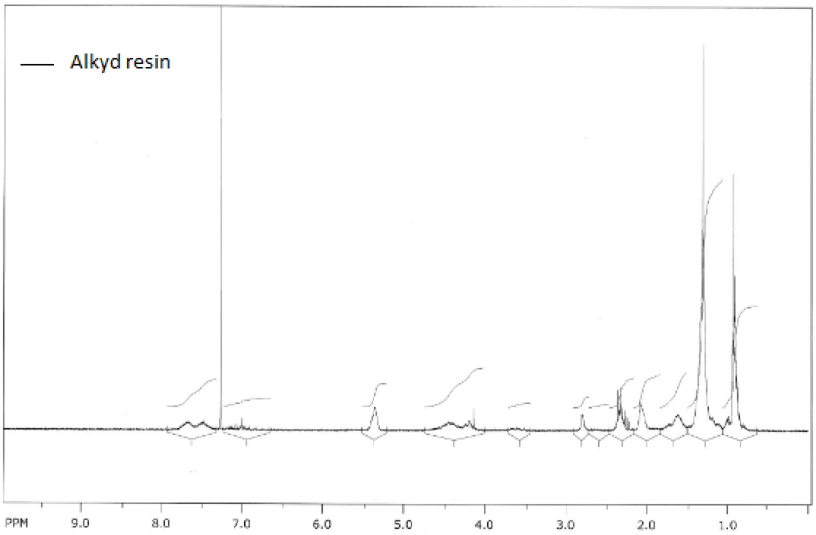

Fig.5.[1]HNMR spectrum of alkyd resin

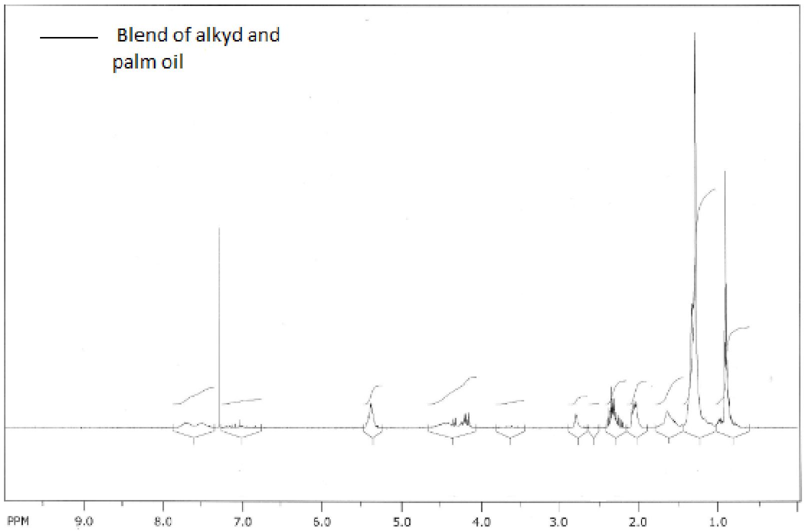

Fig. 6.[1]HNMR spectrum of alkyd and palm oil

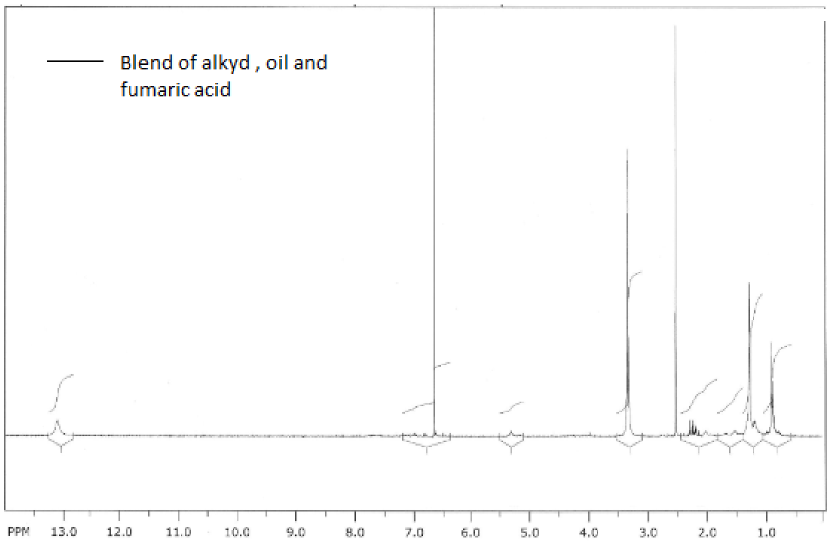

Fig. 7.[1]HNMR spectrum of a blend of alkyd, oil and fumaric acid

The information on the proton density of different alkyd samples and their blends is depicted in Figures 4, 5, 6 and 7 by ^{1}H NMR spectra.

The high-field region of the proton spectra (δ= 0–3.5) contains mainly methylene and methyl peaks from fatty acid protons. The proton for terminal methyl groups of fatty acids was confirmed by the peak at around ∂ = 0.87.

Peaks next to that in the range ofδ= 1.25 to 3.5 are due to protons of all -CH_2 present in the chain.

The middle region of the proton spectra (δ= 3.5–6.0) contains peaks from the vinyl protons of the fatty acids (FA) incorporated in the alkyd resins and from protons of neighboring hydroxyl or ester groups [20], and thus peaks appearing at 4.2 to 4.4 can be probably attributed to the methylene protons of the glycerol molecule and those at 5.25to 5.4 - to unsaturated carbons.

The low-field region 6.5– 8.0 contains aromatic protons originating from phthalic (PHT) and ester fragments of the polyesters.The peak appeared at 6.75 to 6.85 ppm is characteristic for the -CH present in the glycerol molecule. The proton of the aromatic ring is related to the peak at δ=7.5– 8.

The vinyl protons of fumaric acid appear mainly at δ= 6.53 [21]. From figure 7 at δ = 6.5 to 6.56, this peak is due to protons of CH= present in fumaric acid. The peak at δ = 13 can be probably attributed to the proton present in the COOH group of fumaric acid molecule.

CONCLUSIONS

The results obtained in the present work showed the easy blending of various proportions of fumaric acid with alkyd resin and palm oil. Such blending can be made for improving the generally long drying time of alkyd based palm oil. Two types of ratios of alkyd/ palm oil are reported. Blends of palm oil with long alkyd resin and palm oil were prepared and their physicochemical properties were studied. It was shown that palm oil contributed to the increase in drying time of long alkyd resin. Results indicated that 80/20 (w/w) is the optimal blend of alkyd and palm oil providing significant improvements in drying time by varying fumaric acid proportion and its incorporation in the alkyd palm oil blend.^{1}HNMR technique was used for understanding the improvements in the properties of coating film due to the presence of fumaric acid in the blend.

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ВЛИЯНИЕ НА ФУМАРОВАТА КИСЕЛИНА ВЪРХУ СВОЙСТВАТА НА СМЕСИ НА АЛКИДНА СМОЛА И ПАЛМОВО МАСЛО,

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(Резюме)

Изследвани са две смеси от палмово масло и алкидни смоли. Първата смес съдържа 20%, а втората - 30% палмово масло. Тези смеси съдържат количества фумарова киселина в границите от 2 до 10 грама. Освен това към всяка проба се добавят съхнещи агенти, съдържащи смеси от съединения на кобалта, калция и оловото. След приготвяне на пробите се определят техните физико-химични показатели, като плътност, вискозитет, време за изсъхване, киселинно число, пероксидно число, число на осапунване по стандартни методи. Структурите на приготвените проби се определят чрез протонна ЯМР-спектроскопия. В отсъствие на фумарова киселина пробите имат по-дълго време за изсъхване, по-малки вискозитет и плътност. Времето за изсъхване на двете алкилови смеси намалява с увеличаването на съдържанието на фумарова киселина, а съдържанието на 20% палмово масло е оптимално за сместа. Резултатите показват, че фумаровата киселина може да се използва в алкидни смоли на базата на не-съхливи масла като добавка за покриващи смеси.