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SYNTHESIS AND CHARACTERIZATION OF ACRYLATED *PARKIA BIGLOBOSA* MEDIUM OIL ALKYDS

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ABSTRACT. Acrylated *Parkia biglobosa* medium oil alkyd prepared by the reaction between an acid containing acrylic copolymer and a monoglyceride followed by the addition of polyol and dibasic acid has been investigated for improved properties. The results revealed that acid functional acrylic copolymers containing maleic anhydride as a functional co-monomer can successfully be used to modify alkyd resins yielding acrylated resins with better drying, flexibility, scratch hardness, impact resistance and chemical resistance properties. However there exist optimum levels for modification of alkyds with such copolymers beyond which certain film properties are adversely affected.

KEY WORDS: *Parkia biglobosa*, Medium oil alkyd, Acrylated resins, Alkyd resins

INTRODUCTION

Alkyd resins are used extensively as binder for making paints. Such paints are usually exposed to UV-radiation, thermal fluctuations, high humidity and especially when applied on superstructure of ships, the paint is also in addition to the above exposed to wind driven salt spray. Under these conditions, the paint shows considerable chalking, colour fading and loss of gloss within six months under the Nigerian tropical conditions. A good remedy to enhancing the durability of such paints is to improve its weather resistance through chemical modifications of alkyd resins with acrylic resins [1]. Modification of alkyd resins by acrylic monomers offers the possibility of combining the desirable application and film forming properties of the alkyd with the weathering and general resistance properties of acrylic systems.

Aigbodon and Okiemen [2] had investigated the utilization of Africa locust bean (*Parkia biglobosa)* seed oil in the preparation of alkyd resin and found that the plant seed oil is very good in preparing medium oil alkyd resin. African locust bean is of the family Fabaceae. It is a tree of 30-70 ft high. It bears fruits and the matured and ripe pods have edible pulp [3]. The seeds are processed into a local product (Iru in Yoruba) used as soup ingredient. Percentage oil in African locust bean (*Parkia biglobosa)* is approximately 27% and its fatty acid composition is palmitic (27.5%), stearic (10.5%), oleic (14.5%), linoleic (44.5%) and linolenic (3.0%) [4]. It is a non drying oil with iodine value of 94 mg iodine/g oil [4]. The modification of alkyd resins by acrylation has been extremely investigated and for a non drying oil alkyds, Solomon [5] suggested their acrylation by either condensation of a preformed addition copolymer with an alkyd or reaction between an acid containing acrylic copolymer and a monoglyceride followed by the addition of polyol and dibasic acid and then further condensation to the desired acid value and viscosity. For convenience the former method is called post acrylation and the latter monoglyceride method. Fletcher *et al.* [6] reported that difficulties due to alkyd gelation were encountered in attempts to prepare methacrylated alkyds by the reaction between an alkyd and a preformed acid containing polymer.

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In view of the above, this work aims at investigating the synthesis of acrylated *Parkia biglobosa* medium oil alkyd via a monoglyceride method. The alkyd would then be characterized and evaluated in comparison to the non-acrylated resin.

EXPERIMENTAL

Materials

Parkia biglobosa seeds were purchased from various markets in Ibadan, Akure and Ado-Ekiti, all in the South-Western part of Nigeria. The seeds were screened, washed, oven dried (103 °C) and milled in a C & N Junior laboratory mill size 5 (Christy and Norris limited Engineers Chemlsford, England).

Parkia biglobosa oil (PBO) was extracted using n-hexane in a Soxhlets apparatus and solvent removed in a rotavapour. The crude oil was refined by agitating with 18 M NaOH (1:30 g/g of alkali:powder) for 15 min. The resultant mixture was heated to 75-80 °C to break the soap stock and the neutral oil separated by centrifugation.

Acrylic monomer, n-butylmethacrylate (n-BMA), maleic anhydride (MA), phthalic anhydride (PA), benzoyl peroxide (BPO) and pentaerythritol (PE) were obtained from Merck (Darmstadt, Germany).

Methods

Preparation of addition copolymers

The copolymers in three ratios of n-BMA and MA viz, 80:20, 65:35, 50:50 (by weight) were prepared as follows: all the required maleic anhydride was added to xylene and the mixture allowed to reflux at 100 °C (solution A). The monomer mixture (n-BMA) containing the dissolved BPO was added gradually to solution A while refluxing and stirring continued over 3 h. After addition, the solution was further heated for another 2 h. The crude polymer was purified by dissolving in acetone and re-precipitating by adding methanol as non-solvent. The composition of the copolymer by weight is shown in Table 1. The composition of the copolymer obtained has been shown to reflect the composition of the component mixture [7].

Table 1. Composition of addition copolymer.

Copolymer code	n-BMA (g)	MA (g)	BPO (g)	Xylene (mL)	% MA
Copoly-20	80	20	2	50	20
Copoly-35	65	35	2	50	35
Copoly-50	50	50	2	50	50

N.B. The last digit in the copolymer code indicates the percentage of maleic anhydride in copolymer.

Preparation of methacrylated Parkia biglobosa medium oil alkyds (Acr.PBMA)

20 g of the refined *Parkia biglobosa* oil was heated to 180 °C while purging with nitrogen gas in a four necked reaction flask provided with a motorized stirrer, a Dean and Stark trap, inert gas inlet and thermometer. NaOH catalyst was added followed by 1.072 g of glycerol and 4.824 g of pentaerythritol. The temperature of the mixture was raised to 250 °C and maintained at this temperature until the product was clear when mixed with methanol (1:3 v/v) at 25 °C. The monoglyceride mixture obtained above was cooled slightly and 1.2 g of copolymer already dissolved in xylene was added. Temperature was increased to 180 °C and maintained at this

temperature for 1 h. Then the temperature was further increased to 230 °C and the reaction continued until the acid value of the mixture was less than 1.0 mg KOH/g. The mixture was then cooled to 160 °C and the remaining polyol which amounted to 0.528 g glycerol and 2.376 g of PE were added. Temperature was maintained at 160 °C for 1 h and then increased to 220 °C. Condensation reaction was allowed to continue until the acid value of the resin was approximately 10 mg KOH/g.

Fourier Transform infrared (FTIR) analysis

A film of small amount of the addition copolymer and methacrylated alkyds were separately deposited between KBr discs. IR spectra were recorded on a Fourier Transform infrared spectrometer, Jasco FT/IR-430 (Jasco corporation, Japan). The frequency and intensity of each band was obtained automatically by using the "find peak" command of the instrument software.

^{1}H NMR analysis

^{1}H NMR of the acrylic copolymer and acrylated resins dissolved in deuterated chloroform ($CDCl_3$) were recorded on the Bruker AM-400 (Bruker Instruments, Inc. Karlsruhe, Germany) Fourier Transform spectrometer operating at 100.6 MHz. The gated decoupling pulse sequence was used with the following parameters: number of scans 512, acquisition time 1.366 s, pulse width 10.3 s, free induction decay (FID) is transformed and zero filled to 300 K to give digital resolution of 0.366 Hz/point.

Evaluation of the acrylated resins

Samples of the *Parkia biglobosa* alkyd resins (PBMA) and acrylated *Parkia biglobosa* alkyd resin (Acr.PBMA) were thinned with xylene to brushable consistency. The solutions prepared were applied by brush on clean mild steel panels of 15 x 15 cm for evaluating drying time, tin panels of the size 15 x 15 cm for flexibility and adhesion, scratch hardness and impact resistance and glass panels of the size 15 x 15 cm for water, alkali and solvent resistances. All coated panels were air-dried for 48 h and their sides protected by dipping them into molten wax before carrying out the above tests. The film characteristics were determined according to Indian standard specifications IS: 101 [8] and IS: 158 [9].

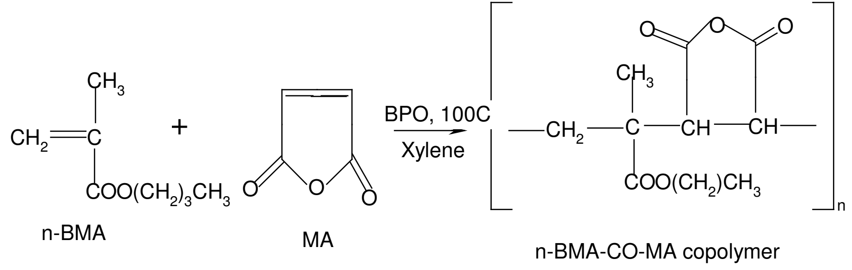
RESULTS AND DISCUSSION

The reaction schemes for the preparation of the MA-nBMA copolymer and the methacrylated alkyds are outlined below (Figure 1). The confirmation of the structures was done by the IR and NMR studies.

IR

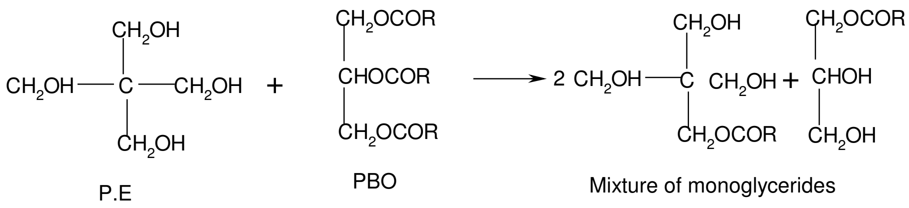
The IR of Acr.PBMA showed two strong bands at 1781 and 1727 cm^{-1} which are characteristic of carbonyls of anhydrides. The lower frequency was more intense than the higher frequency thereby confirming the presence of cyclic anhydride and therefore supports the structure of acrylic copolymer suggested in the reaction scheme. The IR of the Acr.PBMA showed a strong band at 3438 cm^{-1} which can be attributed to the free hydroxyl group present in the resin. Free hydroxyl groups are expected to be present since the resin was synthesized with stoichiometric excess of hydroxyl compound. Bands were observed at 3008-2854 cm^{-1} for C-H stretching aromatic and aliphatic, 1752 cm^{-1} for C=O ester, 1598 and 1580 cm^{-1} for C=C aromatic, 1465 cm^{-1} for C-H bending, 1285 and 1138 cm^{-1} for C-O-C stretching of ester. All these bands support the structure of acrylated alkyd suggested in the reaction scheme.

Preparation of copolymer



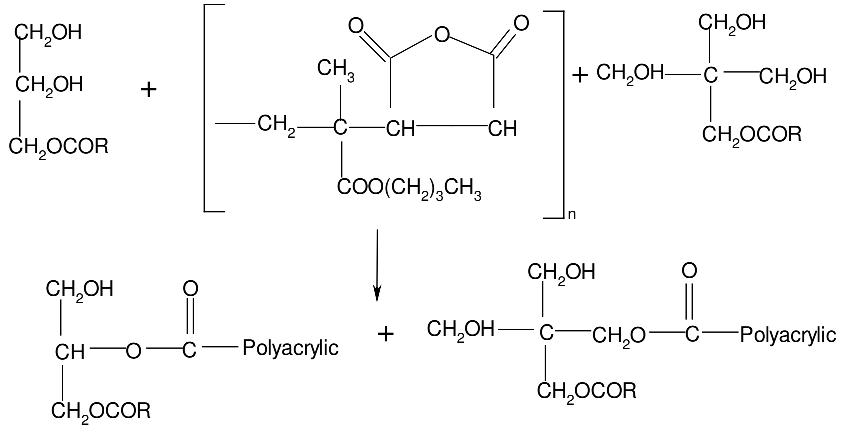
Preparation of acrylated alkyd

Step 1



The monoglycerides can then be further reacted with acrylic copolymer to yield the resin as follows:

Step 2



Step 3

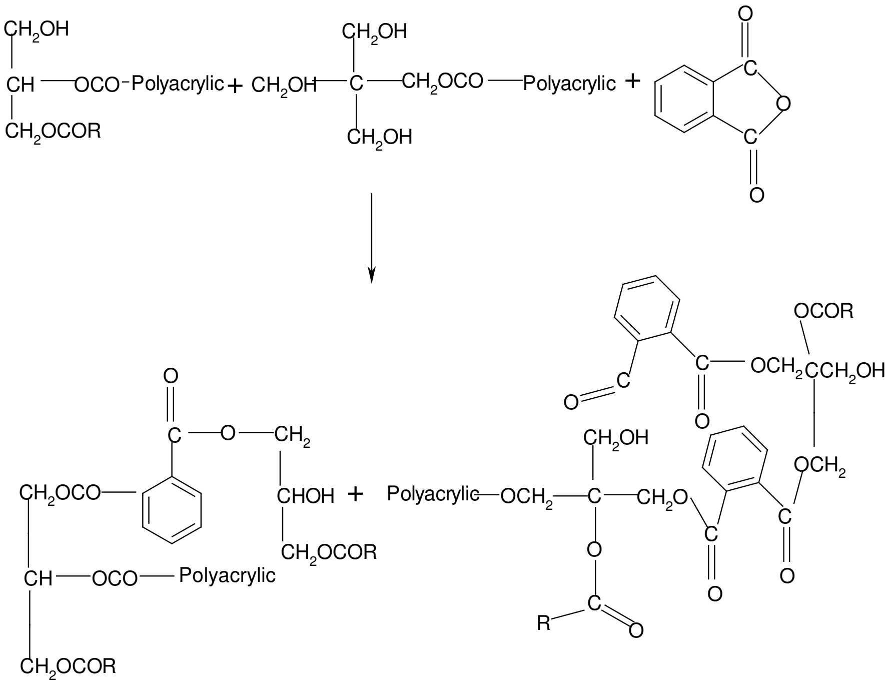


Figure 1. Reaction schemes for synthesis of acrylic copolymer and methacrylated *Parkia biglobosa* alkyd resin.

NMR

The ^1H NMR spectral data of MA-nBMA and Acr.PBMA are given in Table 2.

Table 2. The ^1H NMR spectral data of MA-nBMA and Acr.PBMA.

MA-nBMA		Acr.PBMA	
Chemical shift (δ)	Assignment	Chemical shift (δ)	Assignment
0.92	(-CH_3)	0.88	-CH_3
1.339	(-CH_3-C-CO)	1.285	-CH_2
1.401	(-CH_2-C)	2.299	CH_2-CO-C
1.612	(-CH_3-C=C)	2.765	C=C-CH_2-C=C (fatty acid chain in Acr.PBMA)
2.309	(C=C (CH_3)-CO	3.577	-CH-CO-O-CO-C (anhydride in Acr.PBMA)
3.183 and 3.280	Maleic anhydride protons	4.105	-CH_2-OCO-
4.083	-C-CH_2-OCOR	4.348	-CH-O-CO-
7.303 and 7.065	Chloroform	5.341	-CH=CH- (fatty acid chain in Acr.PBMA)
		7.288 and 7.086	Chloroform
		7.714 and 7.532	Aromatic protons

Film properties

Drying time

The steel panel used for evaluating the drying time of the resins was kept in vertical position after application of the resins. The results as presented in Table 3 reveal that drying time of the acrylated alkyds is lower than that of the unacrylated alkyds. Acrylic monomers are known to increase the molecular weight [10], and with increase in molecular weight, fewer crosslinks are required to form coherent film [11], or to reach the drying stage [12]. The results further reveal that the drying time of the acrylated alkyds decreases with increase in maleic anhydride content. With increase in maleic anhydride, the transition temperature T_g of the copolymer increases [13], which in turn increase the T_g of the acrylated alkyd. Increase in T_g of the resin leads to decrease in drying time [14].

Flexibility and adhesion

This was determined by bending the coated panel through 180^o in 1/4" and 1/8" mandrels. All the samples passed the test. The maleic anhydride on the copolymer backbone promotes adhesion [13]. Generally in acrylates, flexibility has been shown to increase as the chain length of the side group increased and the flexibility of n-butylmethacrylate > ethyl methacrylate > methylmethacrylate [15]. The good flexibility of the various Acr.PBMA is therefore understandable.

Scratch hardness

The scratch hardness was estimated by estimating pencil hardness of the films as described by Paul [15]. The hardness was expressed in terms of the designation of the hardest pencil that failed to scratch the film. The results also presented in Table 3 indicated that the scratch hardness of films of acrylated alkyd increased with increase in maleic anhydride content up to a certain limit, beyond which a reduction in scratch hardness was observed. The limitation imposed by the maleic anhydride may be due to the fact that increase in maleic anhydride leads to increase in the brittleness of the film which in turn decreases the hardness of the film.

Impact resistance

This was tested by a tubular impact tester in which a weight of 1 kg of hemispherical shape was dropped from a height of 25 inches on to the coated side of the panels. The results as presented in Table 3 followed the same trend for scratch hardness. Impact resistance test was passed up to 20% MA loading of the acrylic copolymer, but further increase in the maleic anhydride loading caused a decrease in impact resistance. This can be attributed to increase in glass transition temperature of the resin. As the maleic anhydride content of the acrylic copolymer increases, the T_g increases and the film becomes more brittle.

Chemical resistance

Table 4 shows that the acid and alkali resistance of the acrylated alkyds are better than the unmodified alkyds. Patel *et al.* [7] had made similar observations for acrylated rubber seed oil. They attributed the improved acid and alkali resistance to inclusion of acrylic polymer which are known to give better alkali and acid resistances [12]. Our results further reveal that the alkali and acid resistance decreased with increase in maleic anhydride content. This might be due to decrease in acrylic monomer proportion in the copolymer composition. The acrylated resins showed better resistance towards xylene and water.

Table 3. Film properties of various acrylated *Parkia biglobosa* oil medium alkyds.

Properties	Acr.PBMA 20*	Acr.PBMA 35*	Acr.PBMA 50*	PBMA 0*
Drying time (surface dry) (h) (hard dry) (h)	2.35 26	2.05 20	1.30 12	non-drying non-drying
Flexibility and adhesion (1/8" mandrel)	P	P	P	P
Impact resistance (1 kg load)	P	F	F	P
Scratch hardness (pencil brand)	2H	4B	6B	2B

*Numbers in the resins code indicate the percentage of maleic anhydride in the copolymer. P - pass, F - fail.

Table 4. Water, alkali, acid and solvent resistance of various Acr.PBMA.

Solvent resistance	Acr.PBMA 20*	Acr.PBMA 35*	Acr.PBMA 50*	PBMA 0*
Water resistance	a	b	d	b, f
Xylene resistance	a	d	f	f
NaOH (2%) resistance	b	d	c, d	g, h
HCl (2%) resistance	d	d	f	c, f

*Numbers in the resins code indicate the percentage of maleic anhydride in the copolymer.
a – not affected, b – loss of gloss, c – slight loss of adhesion, d – slight blistering, e – slight swelling, f – swelling and blistering, g – partially ruptured, h – partially removed.

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