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Novel approach to enhance film properties of environmentally friendly UV-curable alkyd coating using epoxidised natural rubber

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ABSTRACT

Environmental friendly coatings have gained popularity and importance owing to the implementation of various environmental legislations to curb the emission of air pollutants. The present work deals with the conversion of non-self drying palm stearin alkyd into UV curable coating, followed by enhancement of the film properties of the coating using epoxidised natural rubber (ENR). Alkyd was synthesised using palm stearin as the source of fatty acids and it was rendered UV-curable by increasing the level of unsaturation through incorporation of fumaric acid. The alkyd was characterised via ^{1}H NMR and FTIR before it was formulated into coating mixture, with methyl methacrylate (MMA) as reactive diluent and benzophenone as UV photoinitiator. Another two sets of coating mixtures, AlkE25 and AlkE50, were prepared using fumarised alkyd incorporated with ENR25 and ENR50, respectively. The incorporation was achieved through the reaction involving epoxide group of ENR and —COOH group of alkyd. AlkE25 and AlkE50 coatings have better film properties than the control coating (formulated without ENR) attributed to the increase in the crosslink density that results from the introduction of ENR into the coating formulation.

1. Introduction

Rising concern over environmental pollution and global warming has led to a dramatic change in lifestyle, with more consumers shifting to eco-friendly products, while manufacturers and scientists continuously develop green technologies. The coating industry is not excluded from the green evolution as there has been a rapid change of direction in the industry starting from 1965 [1]. Significant adjustment after this time has included efforts to reduce the emission of volatile organic compounds (VOCs) originating from the wide usage of organic solvents in the industry. Excessive VOCs in the atmosphere have been proven to have detrimental effects on the environment and to human health [2–5]. Consequently, many formulators and chemists in the field have developed coatings that are free from hazardous pollutants.

UV-curable coating is environmentally friendly as it is formulated to be free from VOCs or hazardous air pollutants (HAPs) [6]. In addition, usage of sustainable raw materials such as palm stearin and glycerol in the development of UV-curable alkyd coating is an added feature to the environmentally friendly aspect of the product. Besides being green, UV-curable coatings are also known to exhibit superior properties and have many economical advantages compared to conventional thermal curable coatings [7]. Generally, UV-cured coatings have high durability, high scratch and chemical resistance, and exceptional abrasion resistance, attributed to the high crosslink density achieved during radiation curing [8]. A qualitative comparison with respect to production of UV curable coatings and conventional thermal curable coatings is summarised in Table 1 [9]. As shown in the table, a typical thermal curable coating consists of approximate 30–80% of organic solvent which could appear as major air pollutants. Other advantages of production using UV curable coating include lower energy consumption, lower cost and higher production rate.

Palm stearin which is used to prepare the alkyd in this work is the solid fraction of palm oil and it is an example of a non-drying oil with ≤35% of unsaturated fatty acids. The general free fatty acid composition of palm stearin is listed in Table 2. Resin with a high level of unsaturation is crucial to ensure good curability and performance of a coating [10]. Poor drying ability of unmodified palm stearin alkyd, attributed to the limited amount of —CH=CH— in the alkyd chain is shown in our earlier work [11], and also from the work of Teo and Gan [12,13]. The problem related to low unsaturation in palm stearin alkyd could however be overcome by incorporating unsaturated diacids into the alkyd chain, making palm stearin a feasible raw material in alkyd syntheses for surface coating applications. Palm stearin could be viewed as a by-product from palm olein production and is consistently traded at a lower price compared to palm olein or palm oil [14]. This makes palm stearin an economical raw material in alkyd resin production.

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Table 1
Qualitative comparison between production using UV curable coating and conventional thermal curable coating.

Properties	UV curable coating	Conventional thermal curable coating
Environmental friendly	The coatings are free from solvent	On average there are 30–80% of organic solvent
Energy consumption	Low (average 0.046 MJ/m^2)	High (average 0.5–1.1 MJ/m^2)
Production rate	Very fast owing to rapid curing time	Slow
Cost	Low	High

Table 2
General composition of palm stearin [15].

Fatty acid	Structure	%
Lauric	$CH_3(CH_2)_{10}COOH$	0.2
Myristic	$CH_3(CH_2)_{12}COOH$	1.4
Palmitic	$CH_3(CH_2)_{14}COOH$	59.0
Palmitoleic	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	0.5
Stearic	$CH_3(CH_2)_{16}COOH$	4.8
Oleic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	27.4
Linoleic	$CH_3(CH_2)_4CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_7COOH$	7.0
α-Linolenic	$CH_3CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_7COOH$	0.3
Arachidic	$CH_3(CH_2)_{18}COOH$	0.5

Table 3
Specifications of ENR25 and ENR50.

Property	ENR25	ENR50
Epoxidation level (%)	25 ± 2	50 ± 2
Epoxy equivalent weight ($\times 10^{-3}$ mol g^{-1})	3.57	6.58
Density (kg m^{-3})	0.97	1.02
T_g (°C)	−47	−24
M_n ($\times 10^5$ g mol^{-1})	9.9	9.9

Alkyd resin is a form of condensation polymer derived from reaction of polyacids with polyols, with fatty acids comprising a major part of its composition. It has been widely used as coatings in many fields owing to its excellent film forming ability, ease of pigmentation and ability to blend well with additives to form coatings with a wide range of characteristics for various applications [16]. Besides, alkyd is very versatile as it can be easily modified with other materials, for example with rosins, styrene, phenolic resins, or silicones, to produce end products with desired characteristics [17]. In this work, ENR was incorporated into fumarised alkyd chains via the ring opening reaction of the epoxide group from ENR by the —COOH of alkyd. The —OOC—CH=CH—COO— in the alkyd chain, together with the —C=C— from the incorporated ENR are expected to participate in crosslinking reaction during UV curing to produce an even greater network of polymer chains. Some properties of the coatings have improved as a result of the integration.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) was obtained from Sigma Aldrich and it was treated with 1.5% w/v of NaOH aqueous solution to remove inhibitors, and subsequently dried over activated molecular sieves prior to usage. All other chemicals and materials were used without further treatment. ENR50 and ENR25 were a kind gift from Rubber Research Institute of Malaysia (RRIM). Specifications of ENR25 and ENR50 are given in Table 3. Refined, bleached, and deodorised palm stearin, and glycerol 99.5% were kind gifts from Emery Oleochemical Malaysia Sendirian Berhad. Phthalic anhydride (PA) was obtained from D.C. Chemical Korea, fumaric acid (FA) and benzophenone 99% were obtained from Sigma Aldrich, and $Ca(OH)_2$ was obtained from HmbG Chemicals.

Table 4
Composition of alkyd coatings (9 phr of benzophenone was added as UV photoinitiator to each coating mixture).

Alkyd coating	wt.%				Ratio of —COOH/ epoxide
	Alkyd	MMA	ENR 25	ENR 50	
Alk0	60	40	–	–	–
AlkE25	60	38	2	–	3.08
AlkE50	60	38	–	2	1.63

2.2. Methods

2.2.1. Synthesis and characterisation of alkyd

Alkyd synthesis begins with alcoholysis of 304.4 g of palm stearin with 167.1 g of glycerol, and 0.24 g of $Ca(OH)_2$ served as the catalyst. The mixture was gradually heated to 230 °C and held constant for 2 h before conducting solubility test on the products in ethanol to confirm the completion of the process. Subsequently, temperature of the reaction mixture was reduced to 150 °C and mixture of diacids consisting of 153.9 g of PA and 80.1 g of FA was added into the system to allow polycondensation to take place. The temperature was then gradually increased back to 220 °C and held constant until the acid number of the mixture reached 20 mg KOH/g resin (<10% of the initials). The time needed for the acid number to drop from 267 mg KOH/g (initial acid number) to 20 mg KOH/g resin was approximately 6 h. The purpose of stopping the reaction around 90% conversion is to reserve the unreacted —COOH in the alkyd to participate in the subsequent reaction with ENR during the preparation of the coating mixture. Besides, the presence of high amount of reactive —OOC—CH=CH—COO— from incorporated FA increases the risk of premature gelation at prolonged heating at high temperature. The plausible synthesis route of the alkyd is shown in Fig. 1.

The alkyd produced was characterised via FTIR and ^{1}H NMR. In FTIR analysis, alkyd was applied on KBr cell and scanned on Perkin Elmer FTIR (RX-1) from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. ^{1}H NMR analysis was conducted on JEOL JNMGSX 270 NMR and the sample was dissolved in deuterated chloroform with TMS to lock the signal at 0 ppm.

2.2.2. Preparation of coating mixtures

A total of 3 coating mixtures (Alk0, AlkE25 and AlkE50) were prepared at ambient temperature, with Alk0 which was formulated without ENR serving as a control. Alk0 was obtained by mixing alkyd and MMA directly, while AlkE25 and AlkE50 were prepared by mixing alkyd with ENR25 solution (5% w/w ENR25 in MMA) and ENR50 solution (5% w/w ENR50 in MMA), respectively. The blending of alkyd in ENR solution was carried out for 24 h at ambient temperature. The coating compositions are shown in Table 4. In each of the coating mixtures, 9 parts per hundred parts resins (phr) of benzophenone was added as UV photoinitiator.

2.2.3. Coating preparations and film properties

The homogeneous coating mixtures were applied on mild steel panels and irradiated under UV light for 240 s. The steel panels had been cleaned with toluene to remove any stains or grease on the surface of the panels prior to usage. The source of UV light was from a 400 W lamp emitting 225 mW/cm^2 of UV radiation (λ = 365 nm). Film adhesion of the coating was measured using crosshatch adhesion tape test method according to ASTM D3359. Thermal analyses on the coatings were conducted using differential