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FORMULATION OF HIGH-QUALITY UV-CURABLE COATING CONTAINING RENEWABLE REACTIVE DILUENTS FOR WOOD PROTECTION

(Formulasi Salutan Awetan-UV Berkualiti Tinggi yang Mengandungi Diluen Reaktif yang Boleh Diperbaharui untuk Perlindungan Kayu)

Noraini Abd Ghani[1,2,3], Emilia Abdulmalek[1,2], Rajni Hatti-Kaul[4], Azren Aida Asmawi[1,2], Mohd Basyaruddin Abdul Rahman[1,2]*

[1]*Integrated Chemical BioPhysics Research, Faculty of Science*
[2]*Department of Chemistry, Faculty of Science*
Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[3]*Department of Fundamental and Applied Sciences, Faculty of Science and Information Technology, Universiti Teknologi PETRONAS, 32610, Perak, Malaysia*
[4]*Department of Biotechnology, Center for Chemistry and Chemical Engineering, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden*

**Corresponding author: basya@upm.edu.my*

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Abstract

Fine quality coating materials for a variety of surfaces using environmentally friendly substrates are continuously in demand. A large proportion of acrylate derivatives, which are toxic and hazardous, were found in most of the coating formulations. Many efforts have been done to replace acrylate derivatives with other materials derived from renewable resources. In this work, several formulations of wood coating containing different composition of epoxy acrylate and enzymatically synthesized epoxide from soybean oil or wax esters mixture of dioleyl adipate and 1,5-pentanediol diricinoleate were prepared. The formulations were subjected to performance evaluations including gel content, pendulum hardness, and surface test. Formulation 1 containing 85% epoxy acrylate and 15% epoxidation from soybean oil exhibited the highest gel content (79.5%), pendulum hardness (61.02%) and surface resistance to different types of liquid. Increase in surface resistance was observed using a formulation containing 85% epoxy acrylate and a mixture of 1,5-pentanediol diricinoleate and dioleyl adipate (1:1, w/w; 15%). Therefore, these reduced acrylate formulations showed good potential in the development of high-quality UV-curable wood coating.

Keywords: coating, acrylate, epoxide, ester, ricinoleate

Abstrak

Bahan salutan yang berkualiti untuk pelbagai permukaan menggunakan substrat mesra alam sentiasa mendapat permintaan. Sebilangan besar derivatif akrilat, yang beracun dan berbahaya, ditemui dalam kebanyakan rumusan salutan. Pelbagai usaha telah dilakukan untuk menggantikan derivatif akrilat dengan bahan lain yang diperoleh daripada sumber yang boleh diperbaharui. Dalam kajian ini, beberapa formulasi salutan kayu yang mengandungi komposisi epoksi akrilat dan epoksida yang disintesis secara enzimatik daripada minyak kacang soya atau campuran ester lilin dioleil adipate dan 1,5-pentanediol dirisinoleate yang berbeza telah disediakan. Formulasi ini tertakluk kepada penilaian prestasi termasuk kandungan gel, kekerasan pendulum, dan ujian permukaan. Formulasi 1 yang mengandungi 85% epoksi akrilik dan 15% epoksida dari minyak kacang soya menunjukan kandungan gel (79.5%), kekerasan pendulum (61.02%) dan rintangan permukaan terhadap pelbagai jenis cecair yang tertinggi. Selain itu, peningkatan terhadap rintangan permukaan diperhatikan menggunakan formulasi yang mengandungi 85% epoksi akrilik dan campuran dioleil adipate dan 1,5-pentanediol dirisinoleate (1:1, w/w; 15%). Oleh itu, formulasi akrilat yang dikurangkan ini menunjukan potensi yang baik dalam pembangunan salutan kayu awetan-UV yang berkualiti tinggi.

Kata kunci: salutan, akrilat, epoksida, ester, risinoleate

Introduction

A protective coating is an essential layer of material that is applied to the surface of another material, especially wood-based products, to protect it against degradation and disintegration over time [1–3]. The coating must be stabilized from yellowing, cracking, blistering, and delaminating. The commonly used conventional solvent-based curing coatings are always susceptible to environmental pollution. High amounts of volatile organic compounds (VOCs) or hazardous air pollutants (HAPs) are emitted into the atmosphere during the curing process [4]. In recent years, advances in environmental awareness, economic view, energy preservation, and products performance have prompted a change from conventional to UV radiation curing method. A high number of tightly crosslinked polymer networks can be easily formed using the method, which improves coating properties including high gel content, hardness, and surface resistance [5–7].

In UV curable coatings formulation, the use of acrylate derivatives in the coating formulations is unavoidable as it is essential for polymerization during the curing process [3, 8, 9]. However, many health issues have been reported due to its toxicity [10, 11]. Epoxides derived from vegetable oils have been prospected to lead the changes in UV-curable coatings due to their biodegradability, high abundance, low toxicity, and triglyceride structures suitable for the preparation of major constituents of UV-curable coatings [12, 13]. Demengeot et al. has discovered that the crosslinking of epoxidized linseed and rapeseed oils without reactive diluents resulted in viscous formulations that were difficult to dry. The addition of reactive diluents, on the other hand, had greatly increased the film's hardness [14]. Besides, epoxidation of soybean oil (ESBO) with hydroxyethyl methacrylated maleate precursor had significantly improved in the coating properties when compared with the commercial product [13].

Liquid wax esters are also gaining industrial interest since they are non-hazardous, biodegradable, and have excellent tribological properties [15], thus being attractive in lubricants and coating applications. They consist of long-chain fatty acids and fatty alcohols with a chain length of 12 carbons or more. Liquid wax adipate esters such as dioleyl adipate can be enzymatically synthesized in a solvent-free system which offers a green benign process and great product selectivity [16]. Dioleyl adipate, which contains two double bonds, may have a significant effect on the radiation curing because the free radical would attack the bonds for polymerization to occur. It was reported that a coated thin film of formulation containing dioleyl adipate made from renewable raw materials can produce 90% polymerization and surface resistant performance of up to 4.5 N [17].

Hence, this study aimed to evaluate and validate the usage of epoxide (ESBO) or a mixture of esters (dioleyl adipate and 1,5-pentanediol diricinoleate) produced via enzymatic reaction in replacing acrylate derivatives for wood coating formulations. The products were then undergone ultraviolet (UV) radiation curing and their hardness and chemical resistance were tested to estimate their suitability as wood coatings.

Materials and Methods

Materials

Craynor 104D80 (mixture of EB600 and glyceryl propoxylated triacrylates, 60:40) used in this study was a gift from Akzo Nobel Industrial Coatings (Malmo, Sweden) while, Darocur 1173 was a gift from Malaysia Nuclear Agency (Selangor, Malaysia). Epoxidized Soybean Oil (ESBO) was a gift from Prof. Rajni Hatti-Kaul (Lund University, Sweden). Novozyme® 435 (immobilized *Candida antarctica* lipase B on macroporous acrylic resin, 10,000 propyl laurate units/g) was purchased from Novozymes A/S (Bagvaerd, Denmark). All chemicals and solvents used in this study were analytical grade and used without any further treatments unless otherwise stated.

Enzymatic Production of Esters

Dioleyl adipate was synthesized using an optimized method from a previous study [16]. Briefly, the synthesis was prepared in a 500 ml stirred tank reactor with a working volume of 350 ml. The reactor was equipped with a flat-blade disk turbine agitator, with a temperature control system (Julabo MB-13, Germany) and sampling ports. The enzymatic synthesis of dioleyl adipate was prepared by mixing oleyl alcohol and adipic acid in the reactor at a molar ratio of 5.3:1 and catalyzed by Novozym® 435. Meanwhile, 1,5-pentanediol diricinoleate was produced by reacting ricinoleic acid and 1,5-pentanediol with a molar ratio of 3:1 in a 1 L three-neck flask for a large-scale reaction. An amount of 3% Novozyme® was used in toluene solvent. The reaction was started at 65 °C with 200 rpm under 100 mmHg vacuum pressure for 9 hours. The percentage of fatty acid conversion during the esterification was then quantitated using Equation (1). The ester formed was expressed as equivalent to the conversion of the fatty acid. In addition, both products were confirmed by Fourier transform infrared (FTIR) analysis (Perkin-Elmer, Model 1650, United States).

$$\text{Percentage of conversion (\%)} = \frac{V_{\text{control}} - V_{\text{sample}}}{V_{\text{control}}} \times 100\% \qquad (1)$$

where, $V_{control}$ is a volume of 0.1 M KOH needed to titrate the control, and V_{sample} is a volume of 0.1 M KOH needed to titrate the sample.

Formulation of wood coating

Oligomer (epoxy acrylate) and reactive diluents (ESBO and esters) were mixed in different proportions with continuous stirring to obtain a homogenous mixture for reduced acrylate wood coating formulations as summarized in Table 1. Formulations 1-8 were mixed with a 6% photoinitiator (Daracour1173) and applied onto paper plates of desired sizes using a bar coater with 150 µm thickness. The coated samples were irradiated using a UV curing conveyor system which is available at Akzo Nobel Surface Coatings, Malmö, Sweden. Even though formulations were aimed as wood surface coating, paper plates have been used as a standard to undergo further analysis after radiation. The formulation mixture was applied on a paper to determine the maximum curing rate by passing through a UV oven equipped with a 120 W/cm^2 mercury lamp. Performances of Formulations 1-8 on pendulum hardness, surface test and physical observation were evaluated according to the standard requirements.

Table 1. Epoxide and esters composition in reduced acrylate wood coating formulations

Formulation	Composition (%, w/w)			
	Epoxy Acrylate	Epoxidation Soybean Oil	1,5-Pentanediol Diricinoleate	Dioleyl Adipate
1	85	15	-	-
2	85	-	7.5	7.5
3	75	25	-	-
4	75	-	12.5	12.5
5	65	35	-	-
6	65	-	17.5	17.5
7	55	45	-	-
8	55	-	22.5	22.5

Gel content

Gel content was determined by measuring the weight loss of the sample after extraction using acetone for 10 hours at 60 °C [17]. Cured films for different UV radiation exposure were peeled off from the glass tile and weighed to obtain the initial weight. Then, the films were extracted using a Soxhlet extractor to remove unreacted materials inside the coating film. Finally, all cured films were dried in a vacuum and weighed to estimate the gel content. Higher gel content means more crosslinking took place. The amount of gel content was calculated using Equation (2).

Pendulum hardness

Two pendulum hardness methods including Köenig and Persoz can be used to measure the hardness of a coating. A Köenig pendulum hardness tester (Byk, Switzerland) was employed to monitor the surface hardness of the cured film during UV curing, where oscillation was counted between 6° and 3°[18]. After UV exposure, the pendulum hardness of the UV cured film surface was measured with respect to the pendulum oscillation time. The result is expressed as percentage hardness and calculated using Equation (3).

Surface resistance

Assessment of the surface resistance including mar and chemical resistance was evaluated according to EN 12720 (European Standard EN 12720: 1997 Furniture-Assessment of surface resistance to cold liquid) and was performed using Akzo Nobel Industrial Coatings, Malmö, Sweden. The high-speed mar tester was utilized to simulate the effect of fingernail mar at a computed velocity range from 0.3 m/s to 3.4 m/s in a consistent manner by controlling the speed and normal impact force across a coating surface as described by Anderson et al. [19]. The chemical resistance test was then conducted by exposing the cured film to different types of liquids including alcohol (1 hour), coffee (1 hour), water (24 hours), and grease (24 hours). Briefly, a filter paper was immersed in a liquid and was placed on the test surface and later was covered by an inverted glass basin. After a specified period, the paper was removed, and the surface was washed and dried. The surface was then examined for possible damages such as discoloration, changes in gloss or color, and blistering [4].

$$\text{Gel Content (\%)} = \frac{\text{Weight after extraction}}{\text{Initial Weight}} \times 100\% \tag{2}$$

$$\text{Pendulum Hardness (\%)} = \frac{\text{No. of oscillation for sample}}{\text{No. of oscillation for standard glass}} \times 100\% \tag{3}$$

Results and Discussion

Enzymatic production of esters

Direct enzymatic esterification of oleyl alcohol and adipic acid using the previously optimized method [16] was found to produce 95% conversion of dioleyl adipate in the reactor. The presence of ester was confirmed by the FTIR analysis. The FTIR analysis of dioleyl adipate was found to be similar as reported by Chaibakhsh et al. [16], where the absorption bands of C=O and C-O were observed in the region 1690-1794 cm^{-1} and 1162-1263 cm^{-1}, respectively. In addition, ricinoleic ester had also been enzymatically prepared using lipase to evade the problems of discoloration, odor, and high energy costs which usually occurred in high-temperature chemical processes [13,14]. Approximately 87% conversion of 1,5-pentanediol diricinoleate was successfully achieved after 9 hours of reaction. Figure 1 shows that ricinoleate ester had a higher absorption band at wavenumber 1733 cm^{-1} as compared to ricinoleic acid due to the transmittance percentage of C=O (carboxyl and ester group). A similar finding was reported by Ghoshray et al. on the enzymatic synthesis of ricinoleate ester with long-chain fatty alcohol by Lipozyme TM [22].

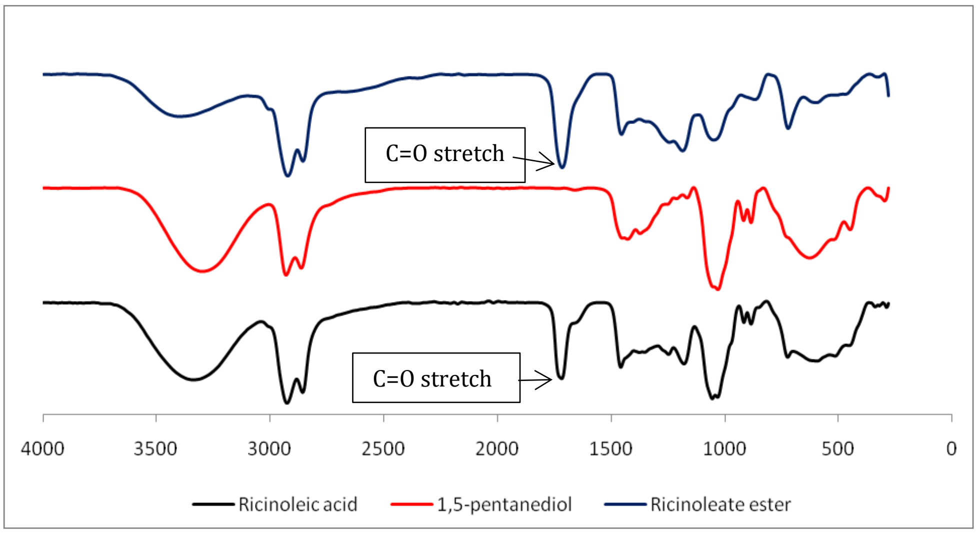

Figure 1. Infrared spectrum for ricinoleic acid, 1,5-pentanediol, and ricinoleate ester after enzymatic reaction using Novozyme® in toluene at 65 °C and 200 rpm stirring rate under 100 mmHg vacuum pressures for 9 hours.

Formulation of Wood Coating

Many researchers have reported on the development of UV-curable coating formulations. However, only a few studies on the production of high-quality UV-curable wood coatings with reduced epoxy acrylate using liquid wax esters as reactive diluents have been done. In this study, different percentages (15-45%) of epoxide (ESBO) or ester (mixture of dioleyl adipate and pentanediol ricinoleate) were used in the formulation. As shown in Table 2, the physical appearance of Formulation 1 and Formulation 2 showed a clear and transparent coating, which was similar to the commercial product containing high epoxy concentration. However, further reducing the epoxy concentration will lead to a transparent and opaque appearance on the glass plate.

Table 2. The physical appearance of coating formulations cured by UV light

Formulation	**Amount of Epoxy Acrylate (%)**	**Physical Appearance After Radiation**
Epoxidation of soybean oil		
1	85	Cured, transparent
3	75	Cured, translucent
5	65	Not cured
7	55	Not cured
Mixture of 1,5-pentanediol diricinoleate and dioleyl adipate (1:1, w/w)		
2	85	Cured, transparent
4	75	Cured, opaque
6	65	Cured, opaque
8	55	Cured, opaque

Gel content

Gel content estimation is an important property of any coating as it directly measures the degree of crosslinking, which decides the final properties of the coating [23]. Since the first pass under the ultraviolet light, the photoinitiators will break and produce active radicals. The radicals will then attack the unsaturated double bond of ESBO and wax esters in the formulation and start the crosslinking process. More crosslinking occurs if the process is repeated, resulting in a higher percentage of gel content. As shown in Figure 2, more than 69% of gel contents were found in Formulations 1-4, representing a well cross-linking behavior amongst the various constituents present in different formulations. It was found that as the proportion of epoxy acrylates in the formulations decreased, the gel content values of the film were found to gradually decrease. Formulation 1, which contained ESBO with a high oxirane number and the highest vinyl group from acrylates, had the highest gel content value (79.53%). It is known that oxirane and vinyl groups have a branching effect and can yield more crosslinking in the cured film as compared to double bonds and a hydroxyl group.

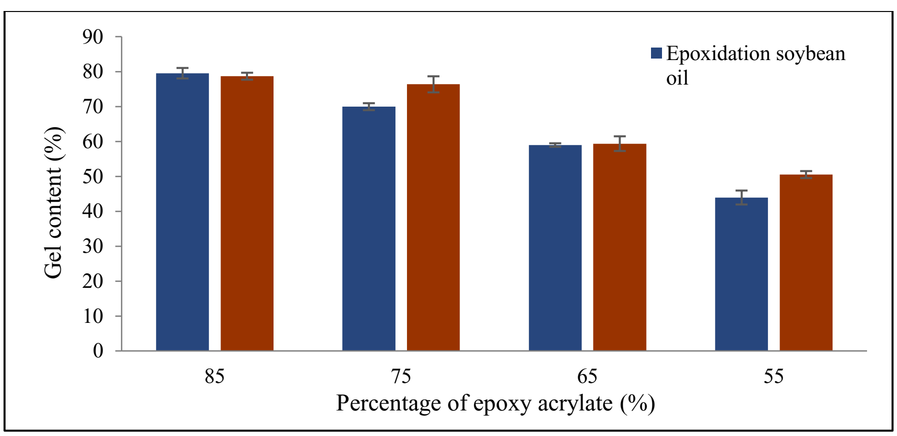

Figure 2. The effect of reduced-epoxy acrylate formulations containing epoxidation soybean oil (ESBO) and a mixture of 1,5-pentanediol diricinoleate and dioleyl adipate (1:1, w/w) on the gel content of coating cured by UV light

Pendulum hardness

One of the most important parameters to ensure scratch resistance in coating formulation is the pendulum hardness. Formulations 1-4 successfully dried in a single exposure to UV curing. Meanwhile, Formulations 5-8 required more UV exposure of up to six passes to completely dry. The formulation was then applied onto glass to test the pendulum hardness. The level of hardness varies depending on the final application, but a pendulum hardness of 40% can be considered as a minimum in many applications. The hardness of coating was found to increase in parallel with the number of passes under UV-light until maximum exposure was reached, at which the point of hardness value remained constant. The hardness percentage of Formulations 1-8 after being exposed to the UV-light until completely dry is shown in Table 3.

From the results obtained, it can be noticed that a higher percentage of reactive diluents including both epoxide and mixed esters in the coating formulation reduced stiffness. Besides, the hardness of Formulations 5 and Formulation 7 could not be measured due to the large amount of ESBO used and the formulations were difficult to dry completely. Formulations 1-3 meets the minimum hardness requirement, which is more than 40%. However, Formulation 1 and Formulation 3 containing 15% and 25% ESBO, respectively, showed greater hardness than Formulation 2 containing a mixture of 15% of pentanediol diricinoleate and dioleyl adipate. This is possibly due to the presence of oxirane ring and more double bonds in ESBO than diricinoleate and dioleyl adipate, which only having two double bonds for crosslinking [23].

Table 3. The percentage of pendulum hardness of coatings cured by UV light

Formulation	Amount of Epoxy Acrylate (%)	Pendulum Hardness (%)
Epoxidation of soybean oil		
1	85	61.02
3	75	44.63
5	65	Not applicable
7	55	Not applicable
Mixture of 1,5-pentanediol diricinoleate and dioleyl adipate (1:1, w/w)		
2	85	43.50
4	75	32.77
6	65	14.69
8	55	9.04

Surface resistance

The ability of a good drying and high-quality formulation was evaluated by fingernail mar and chemical resistance tests as tabulated in Table 4. The coating must endure marring stress and exposure to a wide range of chemicals with various acidity and basicity without staining and losing gloss. The results showed that both mar and chemical resistance performances were reduced as the amount of epoxy acrylate was decreased. No fingernail marring was produced in a formulation containing more than 75% epoxy acrylate. Therefore, only Formulations 1-4 were chosen for further evaluation in the chemical resistance test. The test was simulated by exposing the cured film to different types of liquids including alcohol, coffee, water, and grease. Formulation 2 exhibited excellent resistance towards all the tested liquids after being exposed for up to 24 hours. However, limited exposure to alcohol was observed in Formulation 1 as a slight variation in gloss was noticed after the exposure.

Therefore, formulation containing 85% epoxy acrylate and 15% mixture of pentanediol diricinoleate and dioleyl adipate was able to provide the best coating characteristics and possessed a potential for industrial application.

Table 4. The performance of formulations as wood coatings in mar and chemical resistance

Formulation (+ 6% Photoinitiator)	**Fingernail Mar Resistance**	**Chemical Resistance**			
		Alcohol	**Coffee**	**Water**	**Grease**
1	No fingernail marring	L	R	R	R
2	No fingernail marring	R	R	R	R
3	No fingernail marring	NR	R	R	R
4	No fingernail marring	NR	NR	NR	NR
5	Fingernail marring	NA	NA	NA	NA
6	Fingernail marring	NA	NA	NA	NA
7	Fingernail marring	NA	NA	NA	NA
8	Fingernail marring	NA	NA	NA	NA

R: recommended; L: limited exposure; NR: not recommended, NA: not available

Conclusion

This work proposed up to 15% reduction of epoxy acrylate by replacing it with enzymatically synthesized epoxide from soybean oil (ESBO) or wax esters mixture of dioleyl adipate and 1,5-pentanediol diricinoleate (1:1, w/w) to produce high-quality and transparent coating formulations. The reduced acrylate formulations were found to perform well in terms of pendulum hardness test and surface resistance. Moreover, the effect of irradiation doses on the gel content of coated film cured by UV light could reach almost 80%. Therefore, the enzymatically synthesized renewable monomers including ESBO and wax esters could be used as a potential reactive diluent in UV-curable wood coating to reduce the proportion of highly toxic acrylate products.

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