Development of UV Curable Overprint Varnishes (OPV) Formulation from Epoxidized Palm Olein Acrylated (EPOLA)

Pembangunan Formulasi bagi Overprint Varnishes Sinar Ultra Lembanyung Termatang dari Epoksi Minyak Sawit Terkarilat

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ABSTRACT

The synthesis procedure of Epoxidized Palm Olein Acrylated (EPOLA) has been established by Radiation Curing and Synthesis Group. The quality control test such as acid value, oxirane oxygen content and Fourier-Transform Infra Red (FTIR) were done to monitor the synthesis process. The completion of synthesis process was observed via FTIR with the presence of hydroxyl (-OH) absorption between 3440-3480 cm^{-1} and an absorption of acrylate groups at 819 cm^{-1}**.** The EPOLA was then coated on glass plate and irradiated with UV light. It was found that EPOLA is curable under exposure of UV light and has potential in the application of Overprint Varnishes (OPV). Several formulations have been developed which basically consist of oligomer, monomer, photoinitiator EPOLA and additives. The formulations were then coated on black and white paper and irradiated under UV light. The speed of the conveyer was set at 5m/min and 20 m/min during irradiation and the number of passes for the coated substrate to be cured is recorded. The physical characterization such as adhesion and curing rate were observed compared with desirable finished products.

Keyword: Epoxidized Palm Olein Acrylated (EPOLA), Curable, Overprint Varnishes (OPV), oxirane oxygen content and UV light

ABSTRAK

Prosedur bagi sintesis Epoksi Minyak Sawit Terakrilat (EPOLA) telah dibangunkan oleh Kumpulan Sintesis dan Pematangan Sinaran. Ujian kawalan kualiti seperti nilai asid, kandungan oksigen oziren dan Fourier-Transform Infra Red (FTIR) telah dilakukan untuk memantau proses sintesis. Proses sintesis telah tamat dikenalpasti menggunakan FTIR dengan kehadiran puncak hydroxyl (-OH) antara 3440-3480 cm^{-1} dan kehilangan kumpulan akrilat pada 819 cm^{-1}. EPOLA kemudiannya disalut pada permukaan kacadan disinarkan di bawah sinar ultra lembayung. Didapati bahawa EPOLA ini adalah termatang di bawah dedahan sinaran ultra lembayung dan berpotensi untuk digunakan bagi aplikasi Lapisan Atas Percetakan (OPV). Beberapa formulasi telah dibangunkan yang secara amnya terdiri dari oligomer, monomer, pemula foto EPOLA dan bahan penambah. Formulasi yang dihasilkan kemudiaanya disalut di atas permukaan kertas hitam dan putih dan disinarkan di bawah sinaran ultralembanyung. Kelajuan conveyer diset pada 5 m/min dan 20 m/min semasa substrat disinarkan dan bilangan laluan substart yang telah disalut untuk termatang direkodkan. Sifat fizikal seperti lekatan dan kadar pematangan filem diperhatikan dan dibandingkan dengan hasil akhir produk yang dikehendaki.

Kata kunci : Epoksi Minyak Sawit Terakrilat (EPOLA), termatang, Overprint Varnishes (OPV), kandungan oksigen oziren dan sinaran ultra lembayung

1.0 Introduction

Vegetable oils based coating (such as soy, palm, linseed and sunflower oils) have captured the consumer and industrial interests especially towards the development of eco-friendly materials. Vegetable oils are non-toxic, domestically abundant, non-volatile and biodegradable resource that are capable to reduce the dependency on volatile organic compound which indirectly contribute to low cost of raw materials and green technology (Salimon *et al*., 2012).

The outstanding feature of natural vegetable oils is due to their triacylglycerols of the fatty acids which contain suitable functionalities on the backbone such as double bonds, epoxies, hydroxyls, esters and others that can further undergo several chemical reactions and producing low molecular weight of polymeric materials for various applications (Alam et al., 2014). Natural vegetable oils have tendency to form films when react with atmospheric oxygen to form polymeric materials with crosslinked structured which depends upon their unsaturated portion; number of carbon-carbon double bonds, conjugation and the geometrical arrangement of the substituents of the double bond. (Lu and Larrock, 2009).

Epoxidised Palm Olein Acrylated (EPOLA) has been synthesized via acrylation process on epoxidised palm olein product (EPOP) by Radiation Curing and Synthesis Group in Nuclear Malaysia. One of the promising application of EPOLA is as coating material on printed pages or known as overprint varnishes (OPV). The purpose of applying OPV is for gloss enhancement; stain resistance; edge fusion resistance; burnish or scuff resistance; and resistance to discoloration from absorption of impurities in the environment. This application is widely used in printing industries for magazine and food packaging. Basically, there are three types of OPVs; water based, oil based and radiation curable that widely use in ink and printing industry for magazine and food packaging. UV-curing provides many advantages such as instant drying, broad formulating range, low energy consumption and low space and capital requirement for curing equipment (Wang *et al*., 2008)

In this paper, EPOLA was synthesized using 25L reactor. The formulation of overprint varnishes were prepared with addition of EPOLA and coated on paper. The physical properties of the formulation were evaluated.

2.0 Experimental

2.1 Materials

All chemicals were used as received. The epoxidised palm olein product (EPOP) and acrylic acid was purchased from Intermed Sdn. Bhd. Both were used for producing of EPOLA. Chlorobenzene and acetone were purchased from Merck. Crystal violet and phenol red/bromothymol blue were the indicator used for oxirane oxygen content and acid value test respectively. Urethane acrylate (EB 210) was used as oligomer while Trimethylolpropane Triacrylate (TMPTA), Tripropylene Glycol Diacrylate (TPGDA), Hexane Diacrylate (Additol HDDA), dipropylene Glycol Diacrylate (DPGDA) and Pentaerythritol Diacrylate (PETIA) were used as reactive diluents in the formulations. Benzophenon act as the photoinitiator to start the polymerization when exposed under ultraviolet lamp. EB P115 is an additive that works as synergy with benzophenon.

2.2 Synthesis of EPOLA

The EPOLA was produced in 25 L synthesis reactor unit. For this system, about 18 kg of EPOP was mixed with 3.6 kg of acrylic acid in the synthesis reactor. The reactor was then heated up to 110-120 °C and the mixture was stirred until the reaction was completed. The progress of the reaction was monitored and characterized by the standard method (Mohd Nor *et al*., 1990, 1992).

2.3 Standard Methods and Characterization of EPOLA

EPOLA has been characterized for oxirane oxygen content (ASTMD-1652-97) and acid value (ASTM D-1639-96). The viscosity was determined at 25 ºC using the Brookfield viscometer. The FTIR spectrum was recorded using Perkin Elmer, Japan. Gel Permeation Chromatography (Agilent, United Kingdom) was used to determine the molecular weight of the oligomer.

2.4 Coating Composition and Testing

The mixtures of oligomer and reactive diluents which consists of the total resin were prepared as shown on Table 1.The photoinitiator, additives and EPOLA were added to mixture in parts per hundreds of the total resin unit, phr. The mixtures were stirred using electrical stirrer (Caframo,Canada) at 800 rpm until it reach the homogeneous state.

Table 1: Formulation of overprint varnishes*

Material	**F1**	**F2**	**F3**	**F4**	**F5**
EB 210	50	50	50	50	50
TMPTA	25	25	25	25	25
TPGDA	25	25	-	-	-
HDDA	-	-	25	-	-
DPGDA	-	-	-	25	10
PETIA	-	-	-	-	15
Benzophenon	5	5	5	5	5
EB P115	-	1	1	1	1
EPOLA	5	5	5	5	5

*parts per hundreds of total resin, phr

2.4.1 Curing Test

The formulations were then coated paper using 10 m of rolled steel panel and exposed under UV lamp. The speed of the conveyer was set at 5m/min and 20 m/min for each sample. The number of passes of the film to cure were recorded.

2.4.2 Adhesion Test

This test is conducted according to the standard of ASTM D3359. An adhesive tape (3M) was placed on the center of the intersection of the coating cuts and then removed rapidly. The cut area was then inspected for removal of coating from the substrate or previous coating and rated.

3.0 Results and Discussion

3.1 Synthesis of EPOLA

Basically, EPOLA was synthesized via the acrylation reaction of the EPOP. The chemical reaction was started by the ring opening of the oxirane oxygen group in the EPOP and at the same time the acrylate group reacted and attached to the opened epoxide ring. The chemical reaction of synthesis of EPOLA is shown in Figure 1.

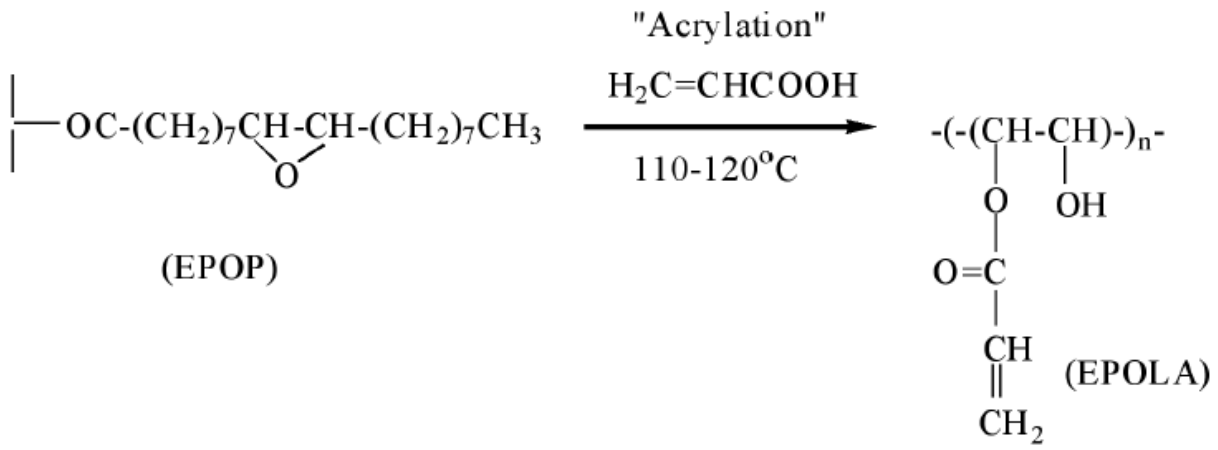

Figure 1: Chemical reaction of synthesizing EPOLA (Tajau *et al*., 2013)

3.2 Characterization and standard method of EPOLA

As for oxirane oxygen content acid value, the FTIR spectra, the tests were conducted for every four hours to monitor the chemical reaction. It was found that the oxirane oxygen content and acid value were gradually decreased during the reaction and almost constant when the complete reaction was reached at 34 hours.

The complete synthesis of EPOLA was further confirmed via FTIR spectra with the presence of hydroxyl (-OH) absorption between 3440-3480 cm^{-1} and an absorption of acrylate groups at 819 cm^{-1} which strongly indicate the product was an EPOLA (Tajau *et al*., 2013). Figure 2 shows the FTIR spectra of EPOP (0 hours) and EPOLA (after 34 hours of reaction).

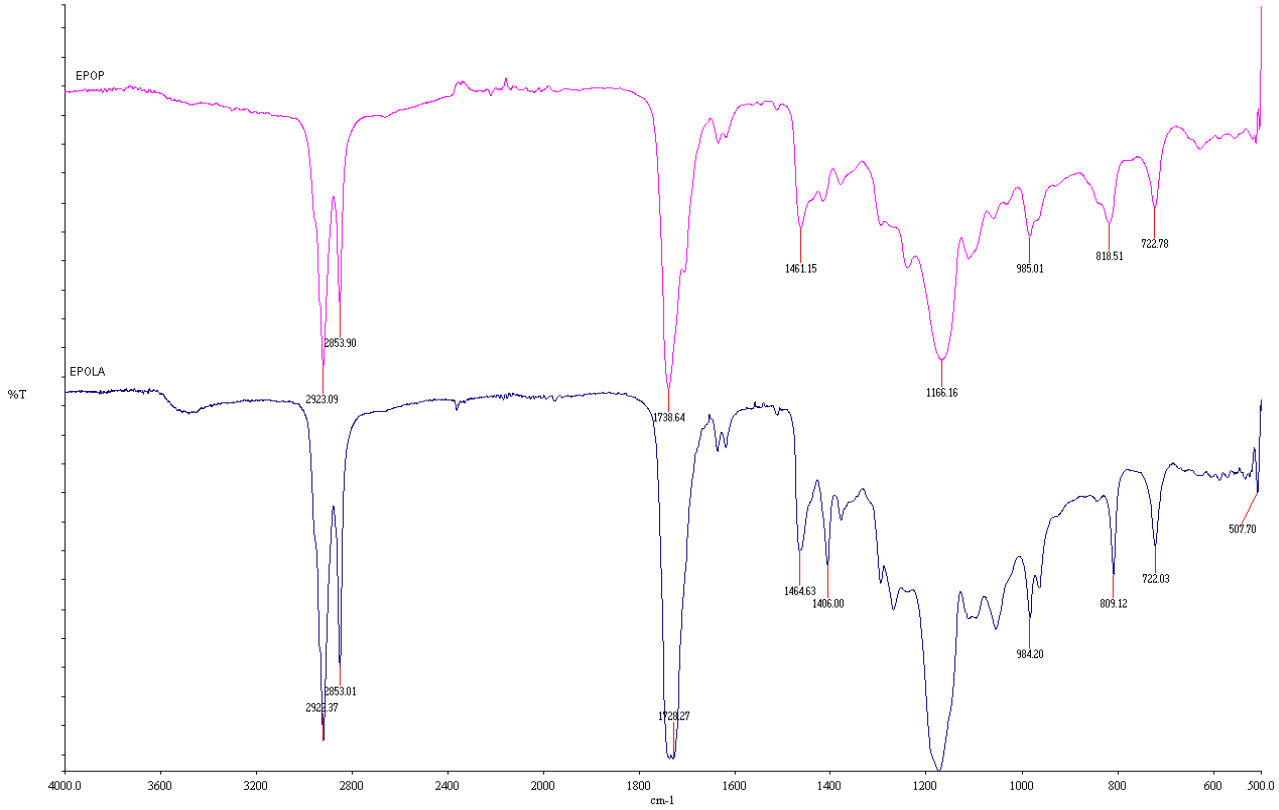

Figure 2: FTIR spectra of EPOP and EPOLA

The EPOLA was then mixed with benzophenon, coated on glass plate and exposed under UV lamp The film was peeled off and test under FTIR. It was found that the of epoxy group at peak of 809 cm^{-1} was diminished. Thus, its proved that EPOLA is UV curable resin. Figure 3 shows the comparison of FTIR spectra between EPOLA and cured EPOLA.

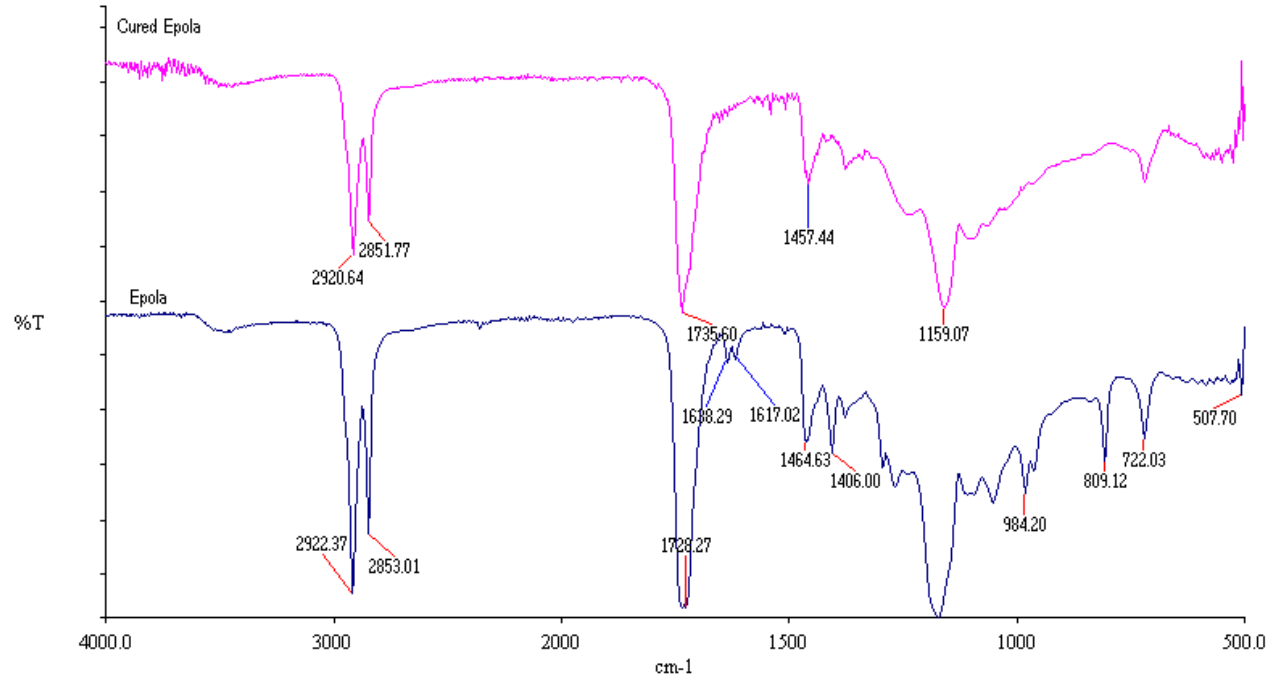

Figure 3: FTIR spectra of EPOLA and cured EPOLA

The viscosity and molecular weight of the EPOLA was the determined at 34 hours. Table 2 shows the final properties of synthesized EPOLA.

Table 2: Characteristics of EPOLA after undergo 34 hours of chemical reaction

Properties	EPOLA
Oxirane oxygen content (%)	0.18
Acid number (mg KOH/g)	47.78
Viscosity (cPs)	600
Molucular Weight (g/mole)	2000

3.3 Coating and testing

Table 3: The coating properties of the OPV formulations

Formulation	**Curing**		**Adhesion test**		**Observation**
	5 m/min	**20 m/min**	**5 m/min**	**20 m/min**	
F1	2 passes	6 passes	Fail	Fail	Smooth and glossy surface
F2	2 passes	4 passes	Pass	Pass	Smooth and glossy surface
F3	3 passes	6 passes	Pass	Pass	Smooth and glossy surface
F4	2 passes	4 passes	Pass	Pass	Smooth and glossy surface
F5	1 passes	3 passes	Pass	Pass	Smooth and glossy surface

From Table 3, it was found that the F1 failed for adhesion test for both curing at 5m/min and 20 m/min respectively. This performance for adhesion test was then improved when the additive of EB P115 is added in F2. EB P115 is a copolymerizable amine or photoactivator which acts as hydrogen donor and provides rapid UV cure response in air by mitigating the effect of oxygen inhibition on coating surface (Habib and Bajpai, 2011).

Addition of HDDA as reactive diluents results in slower curing rate; 3 passes and 6 passes for both conveyer speed of 5 m/min and 20 m/min. Meanwhile, for F4, the film cured at 2 passes at 5 m/min and 4 passes for 20 m/min. Addition of multifunctional reactive site monomer, PETIA in F5 do improves the curing rate; 1 pass for 5 m/min and 3 passes for 20 m/min. For F3, F4 and F5, all of them shows good adhesion.

4.0 Conclusion

The palm oil based resin, EPOLA has potential to be used in overprint varnishes to replace the dependency on petrochemical based and posses good properties for adhesion and glossiness. More study need to be conducted to improve the curing rate. Besides that, since EPOLA is a UV curable resin, it might have good potential in application of other radiation curable products such pressure sensitive adhesive.

5.0 References

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