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ACRYLATED PALM OIL OLIGOMER FOR RADIATION CURING OVER PRINT VARNISH

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ABSTRACT

The purpose of this project was to determine the effects of Acrylated Epoxidized Palm Oil (EPOLA) on a radiation curing Over Print Varnish (OPV) application. The initial target was to produce an environmentally friendly resin (non-VOC) and reduce the dependence on petroleum (hydrocarbon) based products which are more toxic. Toxicity was determined via Acute Oral Toxicity (LD_{50}), OECD 423 and Acute Toxicity (Dermal), OECD 402 technique whilst the reactivity, chemical resistance and other physical properties were obtained from actual printing application test. The developed EPOLA resin was combined with acrylated monomers, photoinitiator and additives in typical OPV formulation before being chemically converted into protective glossy printed film under Ultra Violet (UV-C) light. The gloss, flexibility and adhesion effects are significantly greater than conventional OPV epoxy based coupled with further extremely low irritancy to skin.The contributions of this project are twofold. First, the toxicity of developed acrylated Palm Oil resin is certainly lower than conventional epoxy acrylates resin. Secondly, the benefits towards radiation curing OPV applications were significantly demonstrated.

Keywords: polyurethane; acrylated palm oil: Acute Oral; Acute dermal; Toxicity; Over Print Varnish (OPV)

INTRODUCTION

UV curing technology has advanced in oligomer and monomer selection. It presenting formulators with an ever growing selection to choose from for various end applications and provide the necessary properties range from flexible, resilient or hard formulations directed at wider ranges of industries. Anyhow, the drawback of limited substrates to which they would adhere, and the possibility of dermatitis when exposed to the flesh of personnel are still occurred significantly.

With this in mind, a study was designed to look at an array of Acrylated Palm Oil oligomer (resin) as a substitute to minimize the hazardous of skin irritation. Specific properties on toxicology effects were identified through Acute Oral Toxicity (LD_{50}), OECD 423 and Acute Toxicity (Dermal), OECD 402 technique which being conducted via collaboration with National University of Malaysia (Bio-compatibility lab) whilst the reactivity, chemical resistance and other physical properties were obtained from actual formulation and printing of Over Print Varnish (OPV) application.

Therefore, with those accumulative data, hopefully, the formulators and end user could retrieve the desired yield of UV curing coatings properties by using a more environmental friendly, less toxicity level and sustainable materials in their finished goods.

EXPERIMENTAL PROCEDURES

2.1 Acute Oral Toxicity Test (OECD Guideline 423)

2.1.1 Description of Test Procedure

2.1.1.1 Preparation and selection of animals

On the day before initiation, animals were weighed and the skin, fur and eyes were examined for any abnormalities. The animals were fasted overnight by removing feed from their cages but allowing continuous water supply.

2.1.1.2 Treatment and observation period

Following oral administration of test material, rats were returned to their cages and feeding was resumed after 3 hours of dosing.

Rats were observed for mortality, signs of gross toxicity and behavioral changes. Changes on the fur, and eyes were observed. Respiratory effects, tremors, convulsion, diarrhea and other effects such as walking backwards were also observed.

2.2 Acute Dermal Toxicity Test (OECD Guideline 402)

2.2.1 Description of Test Procedure

2.2.1.1 Preparation and selection of animals

On the day before initiation, animals were shaved to expose treatment sites. The skin, fur and eyes were examined for any abnormalities.

2.1.1.3 Treatment and observation period

Following dermal application of 2000 mg/kg of test material, rats were returned to their cages.

Rats were observed for mortality, signs of gross toxicity and behavioral changes. Changes on the fur, and eyes were observed. Respiratory effects, tremors, convulsion, diarrhea and other effects such as walking backwards were also observed.

2.2Scoring Method

Table 1a: Gross clinical features

Fur and skin Changes	A
Eyes Changes (*Please specify*)	B
Respiratory Effect (*Please specify*)	C
Mucous membrane - Pale - Congested	D a b
Motor activity - Increased motor activity- speed of movement increased - Decreased motor activity- lethargy, does not respond to external stimuli	E a b
Tremor (Continuous repetitive twitching of skeletal muscle, usually palpable and visible)	F
Convulsion (Involuntary contraction of the voluntary muscle) - Tonic convulsion-sustained spasm with head arched backward - Clonic convulsion- short choppy spasm with head arched toward stomach - Mixed convulsions-combination of clonic and tonic	G a b c
Walking backwards and/or Ataxia-inability to coordinate bodily movement (gross wobbling)	H

Diarrhea	I
Death-self-explanatory	J

Table 1b: Severity Score of Observed Changes

Changes	Score
Normal/No changes	0
Mild	1
Moderate	2
Severe	3

2.3 Materials

2.3.1 Oligomer

2.3.1.1 EPOLA oligomer used in the present work was prepared at Nuclear Malaysia lab through acrylation of the epoxidized palm oil product (EPOP).

2.3.1.2 The molecular weights (MW) is measured by GPC (model HLC-8020), T_g is measured by Shimadzu Thermal Analyser (Model DSC-50) while the viscosity is measured by Brookfield Viscometer (Model RVTDV-IICP).

2.3.2 Over Print Varnish (OPV)

2.3.2.1 The developed EPOLA resin was combined with acrylated monomers, photoinitiator and additives in typical OPV formulation before being chemically converted into protective glossy printed film under Ultra Violet (UV-C) light. A ~5 micron layer of each of the formulations was applied onto various substrates (as shown on Figure 1) consist of non-printed graphic paper, decorative laminating paper and conventional ink printed paper via bar coater (#3). The air should be expelled out by sufficient pressure between the bar coater and the substrate. The uncured samples were then exposed under 80 W/cm UV Hg lamp. The samples were then left for 2 hours before testing.

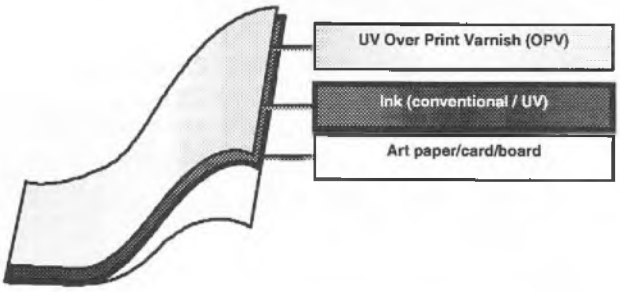

Figure 1: Application system of UV OPV

2.3.2.2 **Description of Test Procedure**

2.3.2.2.1 Reactivity: The reactivity was determined by Carbon Black/Talc test on Opacity Chart paper. The Carbon Black/ Talc test consists of applying a small amount of Carbon Black/ Talc to coating surface after UV exposure. The coating is then inverted to allow the Carbon Black/ Talc to fall away. The coating is considered cured if no talc clings to coating surface.

2.3.2.2.2 Tape adhesion: tested on the cured film after conditioning minimum 2 hours at room temperature (RT). The SEKISUI transparent tape was stuck firmly to the surface coating using reasonable pressure. The tape was then ripped off the surface and a mark was given according to the amount of coating removed. A mark of 5 indicates that all of the coating was removed. A mark of 0 indicates that none of the coating was removed.

2.3.2.2.3 Optical properties: Gloss is measured using BYK gloss meter.

2.3.2.2.4 Solvent resistance: A piece of fiber less cloth/tissue was soaked in a solvent (Acetone) and the surface coating was rubbed >100 times with 1kg load. A score was given according to the number of passes till the coatings scratch-off.

2.3.2.2.5 Flexibility: Bend the coated substrate at 90 – 180 degree. A mark of 5 indicates a white mark or cracking. A mark of 0 indicates that none of the coating was cracked.

2.3.2.2.6 Shelf-life: pass threshold whenever there is no sedimentation, gelification, phase separation or % viscosity change is less than 50% compared to initial value after storage at 60°C for 2 weeks.

$$\% \text{ viscosity change} = \frac{(Va - Vu)}{Vu} \times 100$$

*Notes: V_a = aged sample viscosity; V_u = unaged sample viscosity

2.3.2.2.7 Scratch resistance: by scuffing test (rubs the two of coated surface together for 10 passes).

RESULTS AND DISCUSSIONS

3.1 Acute Oral Toxicity Test (OECD Guideline 423)

Based on the observations and raw data generated (Table 2, Table 3 and Table 4) there was no death or remarkable loss of body weight and no adverse reaction in all groups of animals treated with 300mg/kg and 2000mg/kg body weight of test material. Gross necropsy of the brain, spleen, liver, heart, pancreas, lungs, kidneys and stomach of all animals did not show any abnormality. The single acute median lethal dose of EPOLA was greater than 2000 mg/kg of body weight when administrated once orally via gastric intubation to male and female albino rats.

Table 2: Mean Value of Clinical signs observed after EPOLA administration.

Group/ Dosage	Animal number	Sex	Observation-Post Dosing (for A – J criteria)									
			0.5h	1hr	2hrs	4hrs	1d	2d	4d	6d	1wk	2wk
1 (300mg/kg)	rt244A, rt246A, rt247A	F	0	0	0	0	0	0	0	0	0	0
2 (300mg/kg)	rt251A, rt252A, rt253A	F	0	0	0	0	0	0	0	0	0	0
3 (2000mg/kg)	rt254A, rt255A, rt256A	F	0	0	0	0	0	0	0	0	0	0
4 (2000mg/kg)	rt245A, rt263A, rt264A	F	0	0	0	0	0	0	0	0	0	0

F: Female

Table 3: Mean value of Animal body weight and dosage following EPOLA administration

Group	Animal number	Sex	Body weight (g)			Dose (ml)
			Day 1 (Initial)	Day 7	Days 2/14 *	
1	rt244A, rt246A, rt247A	F	171.91	194.58	186.35	1.72
2	rt251A, rt252A, rt253A	F	195.03	-	193.82	1.95
3	rt254A, rt255A, rt256A	F	207.87	221.56	238.86	2.07
4	rt245A, rt263A, rt264A	F	176.07	-	183.93	1.76

*Day 2 refers to body weight for dose groups 2 and 4; *Day 14 refers to body weight for dose groups 1 and 3

Table 4: Organ weight (gram) as a percentage of body weight of test animals

Group	Animal number	Sex	Organ Weight (g) against Percent of Animal Body weight (%)															
			Brain		Spleen		Liver		Heart		Pancreas		Lungs		Kidneys		Stomach	
1	rt244A	F	1.54	0.70	0.46	0.21	9.28	4.22	0.83	0.38	0.52	0.24	1.8	0.82	1.74	0.79	1.59	0.72
	rt246A	F	1.56	1.15	0.2	0.15	4.82	3.56	0.55	0.41	0.35	0.26	1.3	0.96	1.28	0.95	1.08	0.80
	rt247A	F	1.78	0.87	0.43	0.21	8.71	4.27	0.79	0.39	0.89	0.44	1.48	0.73	1.62	0.79	1.62	0.79
2	rt251A	F	1.84	0.91	0.42	0.21	9.53	4.73	0.7	0.35	0.48	0.24	1.97	0.98	1.84	0.91	1.38	0.69
	rt252A	F	1.72	0.91	0.31	0.16	8.02	4.22	0.78	0.41	0.47	0.25	1.57	0.83	1.73	0.91	1.37	0.72
	rt253A	F	1.70	0.89	0.33	0.17	5.50	2.89	0.76	0.40	0.48	0.25	1.35	0.71	1.41	0.74	1.32	0.69
3	rt254A	F	1.88	0.80	0.43	0.18	10.5	4.49	0.72	0.31	0.72	0.31	1.74	0.74	1.62	0.69	1.86	0.79
	rt255A	F	1.63	0.65	0.41	0.16	8.79	3.51	0.84	0.34	0.66	0.26	1.64	0.66	1.65	0.66	1.80	0.72
	rt256A	F	1.80	0.78	0.47	0.20	9.96	4.29	0.80	0.34	0.94	0.40	2.01	0.87	1.73	0.75	1.98	0.85
4	rt245A	F	1.57	0.96	0.40	0.24	6.70	4.08	0.75	0.46	0.58	0.35	1.75	1.07	1.50	0.91	1.32	0.80
	rt263A	F	1.67	0.83	0.40	0.20	8.63	4.29	0.76	0.38	0.66	0.33	1.47	0.73	1.63	0.81	1.56	0.78
	rt264A	F	1.70	0.91	0.38	0.20	6.88	3.69	0.57	0.31	0.67	0.36	1.31	0.70	1.25	0.67	1.24	0.66
Mean			**1.70**	**0.86**	**0.39**	**0.19**	**8.11**	**4.02**	**0.74**	**0.37**	**0.62**	**0.31**	**1.62**	**0.82**	**1.58**	**0.80**	**1.51**	**0.75**

Percentage of organ weight: $\frac{\text{Organ weight X 100}}{\text{Body weight}}$

3.2 Acute Dermal Toxicity Test (OECD Guideline 402)

Based on the raw data generated (Table 5, Table 6 and Table 7) there was no death or remarkable loss of body weight and no adverse reaction in all groups of animals treated with 2000mg/kg body weight of test material. Gross necropsy of the brain, spleen, liver, heart, pancreas, lungs, kidneys and stomach of all animals did not show any abnormality signs. The single acute median lethal dose of EPOLA was greater than 2000 mg/kg of body weight when applied to the skin of male and female albino rats.

Table 5: Mean Value of Clinical signs observed after EPOLA administration.

Group/ Dosage	Animal number	Sex	Observation-Post Dosing (for A – J criteria)									
			0.5h	1hr	2hrs	4hrs	1d	2d	4d	6d	1wk	2wk
1	rt267A,rt268A, rt269A,rt270A, rt271A	M	0	0	0	0	0	0	0	0	0	0

2	rt282A,rt283A, rt284A,rt285A, rt286A	F	0	0	0	0	0	0	0	0	0	0
CONTROL	rT277A,rt278A, rt279A,rt292A, rt293A	M/M/ M/F/F	0	0	0	0	0	0	0	0	0	0

Table 6: Mean value of Animal body weight and dosage following EPOLA administration

Group	Animal number	Body weight (g)			Dose (ml)
		Day 1 (Initial)	Day 7	Days 14 (End)	
1 (MALE)	rt267A, rt268A, rt269A, rt270A, rt271A	**315.39**	**339.55**	**362.57**	0.65
2 (FEMALE)	rt282A, rt283A, rt284A, rt285A, rt286A	**242.61**	**242.11**	**242.01**	0.5
Mean		**279**	**290.83**	**302.29**	0.57
CONTROL	rt277A,rt278A, rt279A,rt292A, rt293A	**295.47**	**309.70**	**319.94**	0.54

*Note: Group 1 and 2 were treated with EPOLA while Control Group treated with normal saline

Table 7: Organ weight (gram) as a percentage of body weight of test animals

Group	Animal number	Sex	Organ Weight (g) against Percent of Animal Body weight (%)															
			Brain		Spleen		Liver		Heart		Pancreas		Lungs		Kidneys		Stomach	
1	rt267A, rt268A, rt269A, rt270A, rt271A	M	1.92	0.53	0.65	0.18	16.61	4.59	1.14	0.31	0.86	0.23	2.07	0.57	2.45	0.68	2.18	0.60
2	rt282A, rt283A, rt284A, rt285A, rt286A	F	1.75	0.73	0.42	0.17	9.02	3.73	0.87	0.36	0.77	0.32	1.90	0.79	1.54	0.64	1.59	0.66
Mean			**1.84**	**0.63**	**0.53**	**0.18**	**12.82**	**4.16**	**1.00**	**0.34**	**0.82**	**0.28**	**1.98**	**0.68**	**2.00**	**0.66**	**1.88**	**0.63**
CONTROL	rt277A, rt278A, rt279A, rt292A, rt293A	M/ M/ M/ F/ F	**1.88**	**0.60**	**0.58**	**0.18**	**14.07**	**4.36**	**0.96**	**0.31**	**0.88**	**0.29**	**1.96**	**0.62**	**2.17**	**0.68**	**1.96**	**0.62**

3.3 Physical properties of the EPOLA

Basic physical properties are as shown below:

Table 8: Physical data of EPOLA

Product	Molecular Weight (MW)	Viscosity (cps @ 25°C)	Acid Value (AV)	Tg (°C)
EPOLA	2200-3500	800 -1200	20 - 30	< 5

3.4 Physical properties of the EPOLA based OPV

The reactivity of the printed UV cured Over Print Varnish (OPV) based on EPOLA is comparable to the conventional epoxy acrylate OPV (CEA OPV) as shown below:

Table 9: Reactivity @ Hg lamp @80W/cm @ 25 m/min

Sample	finger print (thumb squeeze)		Carbon Black/ Talc test		Scuffing test (10 cycles)	
	Initial	After 24 hrs	Initial	After 24 hrs	Initial	After 24 hrs
EPOLA based OPV	0	0	0	0	0	0
CEA OPV	0	0	0	0	0	0

*Notes: 0 – Excellent with no marks; 5 – worst

Extra advantage on adhesion especially onto printed and decorative papers were demonstrated by EPOLA based OPV as figured:

Table 10: Adhesion test on various paper substrates

Sample	Opacity chart		Non-printed graphic paper		Printed graphic paper		Decorative laminating paper	
	Initial	24 hrs	Initial	24 hrs	Initial	24 hrs	Initial	24 hrs
EPOLA based OPV	0	0	0	0	0	0	0	0
CEA OPV	0	0	0	0	4	2	2	0

*Notes: 0 – Excellent with no peeled-off; 5 – worst as the coating completely peeled-off

The optical properties of the EPOLA based OPV appears to be better than conventional OPV. The gloss values are significantly higher at various angles:

Table 11: Optical properties

Sample	Optical properties (Gloss value)		
	20°	60°	85°
EPOLA based OPV	46.8	89.7	98.5
CEA OPV	20.6	68.3	74.9

The solvent resistance and scratch resistance of both OPV's are comparable:

Table 12: Chemical and scratch resistance properties

Sample	Acetone	Ethyl acetate	IPA	*Scratch resistance
EPOLA based OPV	>100	>100	>100	0
CEA OPV	>100	>100	>100	0

*Notes: 0 – Excellent with no marks; 5 – Cracking with white mark

Though it has a good reactivity, the developed EPOLA based OPV also demonstrated an excellent 'flexibility' behavior compared to conventional OPV:

Table 13: Bending test

Sample	90°		180°	
	Initial	24 hrs	Initial	24 hrs
EPOLA based OPV	0	0	0	0
CEA OPV	2	0	5	3

*Notes: 0 – Excellent with no marks; 5 – Cracking with white mark

Both EPOLA oligomer and EPOLA based OPV demonstrated a very good stability:

Table 14: Stability test (storage at 60°C)

Sample	Viscosity at 25°C (cps)		
	Initial	14 days	%VC
EPOLA	824	960	16.5
EPOLA based OPV	560	612	9.3

CONCLUSIONS

This report has provided technical data which will enable the formulator to have an option on oligomer selection especially with lower toxicity requirement by without sacrificing the physical and aesthetic feelings (reactivity, adhesion, flexibility/toughness, chemical resistance and optical properties).

The single acute median lethal dose of EPOLA was greater than 2000 mg/kg of body weight when administrated once orally and to the skin of rats. Therefore, the test material (EPOLA) is considered 'NON-TOXIC' under the condition of this study.

By having this, the dermatitis effect which commonly triggered chaotic on production site is can be vitally treated with an extra harmonized toxicless and odorless EPOLA oligomer.

ACKNOWLEDGMENTS

Ward, I.M., *Mechanical Properties of Solid Polymers*, 2nd Edition, Wiley Interscience, NY, 1983, pp.172-174.

Homer, D.C.E., Radiation Curing In Europe, *Proceedings RadTech Asia'99*, Kuala Lumpur, Malaysia, August 24-26, 1999, pp. 15-24.

Lawson, K., The Status of UV/EB Curable products In North America-1998-1999, *Proceedings RadTech Asia'99*, Kuala Lumpur, Malaysia, August 24-46, 1999, pp. 1-14.

Mohd. Hilmi Mahmood, Zahid Abdullah, Hajar Mohd. Nor, Roslan Ismail and Khairul Zaman Hj. Mohd. Dahlan, Development of PSA From Radiation Curable Palm Oil Acrylate Resin, *Proceedings RadTech Asia'97*, Yokohama, Japan, November 4-7, 1997, pp. 576-585.

Temin, S. C., Pressure Sensitive Adhesives For Tapes and Labels, *Handbook of Adhesives*, 3rd. Edition, Ed. Skeist, I., Van Nostrand Reinhold, NY, 1990, pages 641-663.

Zahariah Ismail, Salmiah Ahmad and Greentech Engineering Sdn. Bhd., Palm Based Anionic Surfactants, *PORIM TT No. 48*, June 1997.