

New Polyester Acrylate Resins from Palm Oil for Wood Coating Application

M. AZAM ALI,¹ T. L. OOI,¹ A. SALMIAH,¹ UMARU S. ISHIAKU,² Z. A. MOHD. ISHAK²

¹ Advanced Oleochemical Technology Centre (AOTC), Palm Oil Research Institute of Malaysia (PORIM), 43500 Bangi, Selangor, Kuala Lumpur, Malaysia

² Polymer Technology Division, School of Industrial Technology, University Science Malaysia, 11800 Penang, Malaysia

Received 14 February 2000; accepted 4 April 2000

ABSTRACT: The aim of this study is to investigate the potential use of palm oil and to prepare new UV (ultraviolet) radiation-curable acrylated polyester prepolymers, which could be used in the wood coating industry. Thus, palm oil-based acrylated polyester resins PEPP-1 (from refined, bleached, and deodorized palm oil) and PEPP-2 (from crude palm oil) were synthesized at the Advanced Oleochemical Technology Centre (AOTC) laboratory of Palm Oil Research Institute of Malaysia (PORIM). The performances of these resins with respect to their curing rate and physical-mechanical properties of cured products under UV radiation were studied. It can be concluded that newly synthesized UV radiation-curable polyester acrylated prepolymers (palm oil based), namely PEPP-1 and PEPP-2, can be used as radiation curable coating materials for wood coating applications. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2156–2163, 2001

Key words: polyester acrylate resins; palm oil; wood-coating applications

INTRODUCTION

Agricultural raw materials precede petrochemicals by millennia in nonfood applications. Vegetable oils, for instance, had been used in coating industries for many centuries before an abundant and cheap supply of mineral oil became available for a wide range of products.^{1–6} However, in the past few years, consumer's and industrial interests in environmentally friendlier coatings has been growing tremendously.

This trend has been spurred not only by the realization that the supply of fossil resources is inherently finite, but also by a growing concern

for environmental issues. Furthermore, developments in organic chemistry and fundamental knowledge on the physics and chemistry of coatings encountered some problems. This resulted in the development of coatings formulations with much improved performance that are based on renewable resources.

Radiation-curable systems are assuming increasing importance in the field of coatings in various industrial applications due to their peculiar characteristics and advantages with respect to the thermal and solvent based coatings. Over all, the most important features of this new technology can be summarized as follows: (a) solvent-free process (100% solid system, no VOC emission); (b) the curing reaction is very fast and can be controlled; (c) instant start and shut down; (d) the curing reaction takes place at room temperature; (e) lower energy consumption than thermal

Correspondence to: M. Azam. Ali.
Contract grant sponsors: Palm Oil Research Institute of Malaysia; contract grant number USM-PORIM.

Journal of Applied Polymer Science, Vol. 79, 2156–2163 (2001)
© 2001 John Wiley & Sons, Inc.

Table I Compositions (w/w) of Formulated Solution Containing Palm Oil-Based Prepolymers Incorporated with Different Reactive Diluents

Formulations	Diluents/ Monomer	RA ₁	RA ₂	RA ₃	RA ₄	CA ₁	CA ₂	CA ₃	CA ₄
PEPP-1	HDDA	50 : 46	—	—	—	—	—	—	—
	TPGDA	—	50 : 46	—	—	—	—	—	—
	TMPTA	—	—	50 : 46	—	—	—	—	—
	Eb-810	—	—	—	50 : 46	—	—	—	—
PEPP-2	HDDA	—	—	—	—	50 : 46	—	—	—
	TPGDA	—	—	—	—	—	50 : 46	—	—
	TMPTA	—	—	—	—	—	—	50 : 46	—
	Eb-810	—	—	—	—	—	—	—	50 : 46
PI	D1173	3	3	3	3	3	3	3	
CA	NMDEA	1	1	1	1	1	1	1	
Viscosity (cPs)	@25°C	62.8	73.3	101.6	111.4	68.2	77.8	122.6	154.1

PEPP-1 = palm oil prepolymer (from refined bleached and deodorized (RBD) palm oil); PEPP-2 = palm oil prepolymer (from crude palm oil (CPO)); Eb-810 = Ebecryl 810; PI = photoinitiator; D1173 = Darocure 1173; CA = curing agent; NMDEA = *n*-methyldiethanolamine.

curing; (f) high production line with minimum working space, i.e., highly efficient; (g) heat-sensitive substrates can be coated without degradation (electronics field); and (h) environmental friendly process technology (called “green technology”).

The development of new radiation-curable materials for applications such as wood and plastic coatings, printing ink, digital video disk (DVD) printing, pressure-sensitive adhesive (PSA), electronic industries, etc., are most important research areas.^{7–9} Most of the radiation-curable resins in the market are commercially derived from petrochemical-based raw materials,¹⁰ and vegetable oil-based products such as soya bean oil, tung oil, and linseed oils for such resins are few.¹¹

Some scientists¹² tried to synthesize epoxy palm oil acrylated resins (EPOLA/EPOMA) from palm oil products, but their synthesized resins showed poorer curing properties in radiation-curable coating applications due to limited unsaturation in the fatty acid chain of palm oil molecules. The presence of unsaturation in the fatty acids chain is important for the production of acceptable-performance radiation-curable resins.¹³ The paucity of unsaturation in palm oil fatty acid has technically paved the way for the production of acrylated resins. However, this article deals with palm oil-based polyester acrylate resins that were synthesized from palm oil-based products.^{14,15} Palm oil-based products were developed by modifying higher functionality in the palm oil chain system.^{16,17}

The main aim of this article is to explore and to present evidence of the possibility of radiation (UV)-curable wood coating applications using palm oil-based resins.

EXPERIMENTAL

Two types of polyester acrylate prepolymers, PEPP-1 and PEPP-2, were used in the present study. Both prepolymers were synthesized through the acrylation process at the Advanced Oleochemical Technology Center (AOTC) laboratory of the Palm Oil Research Institute of Malaysia (PORIM).^{14,15} Other oligomers, monomers namely Ebecryl 810 (polyester tetra acrylate), TPGDA (tripropylene glycol diacrylate, Mol. Wt. 300, $T_g = 90^\circ\text{C}$), HDDA (1,6-hexanediol diacrylate, Mol. Wt. 226), and TMPTA (trimethylol propane triacrylate, Mol. Wt. 296, $T_g = 250^\circ\text{C}$), were procured from Sharikat Bumi Science (UCB, Union Carbide Belgium agent). Darocure 1173, a photoinitiator, was obtained from Ciba-Specialty Chemicals (Singapore). *N*-Methyldiethanol amine (NMDEA) was procured from Merck, Germany, and used as the curing agent.

Eight formulations were developed using palm oil-based prepolymers PEPP-1 and PEPP-2 incorporated with different reactive diluents (monomers) (shown in Table I). The formulated solution was coated on a clean glass plate ($5 \times 3 \times 0.3$ cm), and cured under UV lamp (2 kW; type of lamp: MC200; UV range: 180–450 nm) using IST-UV-

Minicure (U-200-M-1-Tr, Germany). The coated plate was irradiated by up to 12 passes under a UV lamp at a conveyor speed of 4 m/min to achieve maximum crosslinking and gel formation. The current supply was 8 A, of which energy given per pass was approximately 0.18 J/cm^2 . The relative degree of cure was measured by qualitative simple tests, for example, odor, tackiness, and finger marking.

Various hardness properties of the UV-cured polymeric films such as pendulum hardness (measured by a pendulum hardness tester, Model BYK Labotron, Germany), universal hardness (measured using Sheen Universal hardness tester), etc., were adopted. The cured film was peeled off and used for gel fraction determination. A known weight of cured film was wrapped up in a finely meshed stainless steel net, and extracted in hot acetone for 24 h in a soxhlet extractor. The residues in the steel basket were dried under vacuum to a constant weight. The gel fraction of the UV-cured film was then determined by the following equation:

$$\% \text{ Gel fraction} = \frac{W_f}{W_o} \times 100$$

where, W_f is the weight after extraction and W_o is the weight before extraction.

The gel obtained above was soaked in acetone at room temperature for 24 h. The surface of the swollen gel was dried between two filter papers and pressed for 30 s between two glass plates ($5 \times 5 \times 0.3 \text{ cm}$). The weight of the swollen gel divided by the weight of the gel (before soaking) gives the swelling ratio of the gel

$$\text{Swelling ratio} = \frac{W_{sg}}{W_g}$$

where W_{sg} is the weight of the swollen gel (after soaking in acetone), and W_g is the weight of the gel (before soaking).

A fresh portion of the cured film was also used to determine tensile properties such as tensile strength and elongation at break using an INSTRON tester (1 kN, IBM computer compatible, Model 4301, UK).

After characterization of the film properties, the formulated solutions were applied on wood substrate (Hevea rubber wood; size: $15 \times 10 \times 0.5 \text{ cm}$; moisture content: 5–6%) and coated using a bar coater (RDS # 20). Simultaneously, the coated materials were then cured by UV radiation.

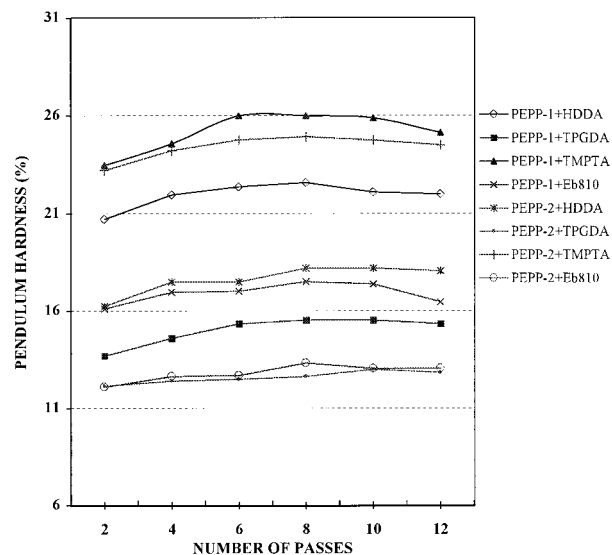


Figure 1 Pendulum hardness (PH%) of UV-cured polymeric films against number of passes under UV radiation with respect to different reactive diluents.

Gloss (60 and 20°) of the coated materials cured under UV radiation was measured in accordance with ASTM D523-80. Adhesion testing was conducted based on the ASTM D3359-83 test method. Crosscut adhesion was measured based on ASTM D-3359. Scratch (macro) was determined in accordance with ASTM D 5178, and abrasion (weight loss %) was performed according to ASTM D 985-6-81. Solvent and chemical tests of coated wood substrate were checked in accordance with ASTM D 3023-81.

RESULTS AND DISCUSSION

Four different reactive diluents were used in this study to find their suitability in the preparation of polymeric films and determine their potential for application as UV-curable surface coatings on wood substrate. Vegetable oil-based new UV-curable polyester acrylate prepolymers, PEPP-1 and PEPP-2 (palm oil based), were used in the presence of a photoinitiator (Darocure 1173) and a curing agent (NMDEA) as additives. It was necessary to determine the appropriate formulation and UV doses (number of passes).

Figure 1 represents the pendulum hardness of UV-cured films prepared with different reactive diluents and cured by UV radiation using different numbers of passes. In all cases, the hardness increases with UV radiation up to eight passes,

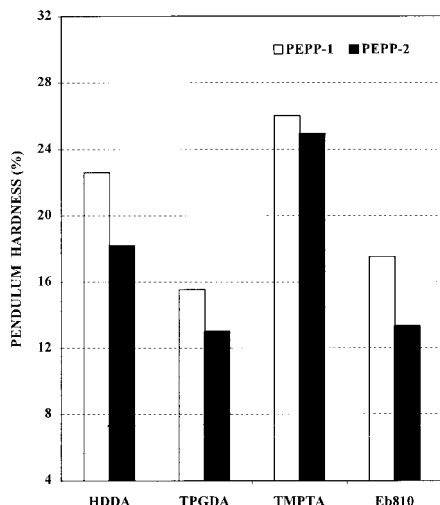


Figure 2 Pendulum hardness (%) of UV-cured polymeric films from palm oil-based resins PEPP-1 and PEPP-2 with different reactive diluents under UV radiation.

then it decreases. The reduction in the hardness as observed after eight passes may be attributed to the fact that the cured polymer is degraded at higher radiation doses. The highest pendulum hardness obtained by using TMPTA containing formulation for both PEPP-1 and PEPP-2 systems (RA₃ and CA₃) are about 26 and 25%, respectively, at eight passes under UV radiation. This suggests that higher acrylated functionality containing TMPTA diluent resulted in higher crosslinking density and, consequently, led to a higher amount of gel in the cured films. It is also interesting to note that TMPTA is a tri-functional monomer and, as such, has the ability to produce crosslinking in three directions through its branch-like molecular structure. HDDA, on the other hand, yielded the second highest pendulum hardness of 22% for RA₁ and 18% for CA₁, respectively, because the HDDA contained di-functional acrylate groups. The lower pendulum hardness of TPGDA (di-functional diluent) containing formulation (RA₂ and CA₂) may be associated with its higher molecular weight compared to HDDA. It has been reported that the crosslinking density depends upon molecular weight and the shape of reactive diluents: the lower molecular weight and simple molecular geometry of the reactive diluents tend to have a higher degree of crosslinking.^{18–20} The HDDA molecule, being of lower molecular weight and having smaller structural geometry, should be favorable for making a free radical moiety compared to the TPGDA molecule.

Eb810 (formulations RA₄ and CA₄) produced greater pendulum hardness compared to TPGDA (Fig.2). This may be attributed to the existence of tetra-functional acrylate groups in Eb 810, which obviously have the ability to form more crosslinks. However, the pendulum hardness of Eb810 is relatively lower than that of TMPTA and HDDA due to its long chain molecular arrangement. The long chain structural arrangement should create unfavorable crosslinking with PEPP-1 and PEPP-2 prepolymers system due to steric hindrance. Thus, the trend for pendulum hardness values is TMPTA > HDDA > Eb810 > TPGDA.

The films cured with eight passes under the UV lamp were peeled off from the glass plate and used for gel content determination through the hot acetone extraction method. The profile of gel content against different diluents used in the formulations (Fig. 3) also indicates that maximum gel contents of 92 and 88% were obtained for the PEPP-1+TMPTA system (RA₃) and the PEPP-2 + TMPTA system (CA₃), respectively.

The highest gel was obtained by using diluent TMPTA, followed by HDDA, Eb810, and the lowest gel, TPGDA, for both PEPP-1 and PEPP-2 prepolymer systems.

When swelling ratio is plotted against different reactive diluents (Fig. 4), it can be seen that the lowest swelling was recorded at the highest gel content of TMPTA + PEPP-1 and TMPTA + PEPP-2 resin systems. This suggests that these films can swell less than the fully crosslinked films.

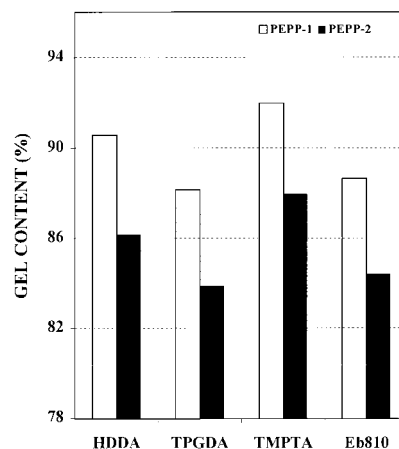


Figure 3 Gel content (%) of UV-cured polymeric films of palm oil-based resins PEPP-1 and PEPP-2 with different reactive diluents under UV radiation.

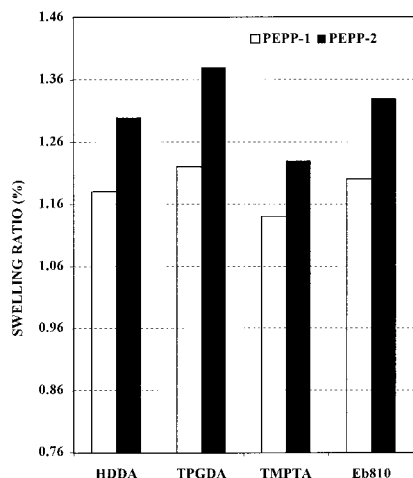


Figure 4 Swelling ratio (%) of UV-cured polymeric films produced from palm oil-based resins PEPP-1 and PEPP-2 with different reactive diluents under UV radiation.

The trend of swelling ratio is $TPGDA > Eb810 > HDDA > TMPTA$ for both PEPP-1 and PEPP-2 resin systems. This means the films with less crosslinking density will acquire the property of absorbing more solvent. So, it can be inferred that crosslinking density is directly related to gel fraction and universally related to swelling properties of UV cured polymeric films.

Tensile strength (TS) of the UV-cured polymeric film is plotted against different reactive diluents containing formulation of PEPP-1 and PEPP-2 resin systems (Fig. 5). The highest TS is obtained with film prepared by the PEPP-1 + HDDA (50 : 46 : 3 : 1) system (formulation RA₁), although TMPTA containing formulations produce the highest hardness (Fig. 2). It is known that film hardness represents the crosslinking density at the surface of the cured polymeric films, whereas tensile strength is achieved through the overall crosslinking network within the polymer film. Moreover, the augmentation of the prepolymers, PEPP-1 and PEPP-2, backbone chain through the normal chain (by HDDA) network yields a mechanically stronger film than that obtained with TMPTA. TMPTA reinforces crosslinking in the films through its three functional acrylated branches, which yields mechanically brittle films.

Tensile strengths of TPGDA (formulation RA₂ and CA₂) and Eb810 (formulation RA₄ and CA₄) films are lower compared to those of HDDA (formulations RA₁ and CA₁) and TMPTA (formulations RA₃ and CA₃). This trend can be related to

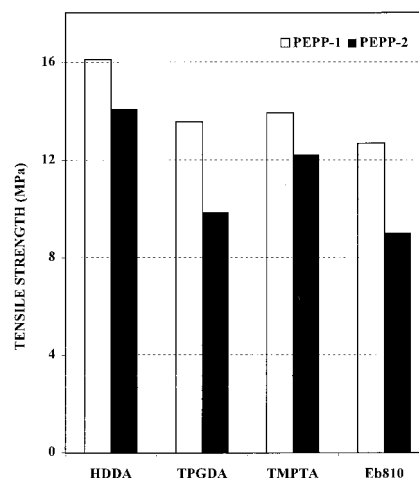


Figure 5 Tensile strength (TS) of UV-cured polymeric films of palm oil-based resins PEPP-1 and PEPP-2 with different reactive diluents under UV radiation.

crosslinking density, which was highlighted earlier. On the other hand, films with TPGDA have slightly higher TS compared to the Eb810. This is due to the geometrical and molecular configuration of Eb810 molecule. Based on molecular configuration and geometry of Eb810, free radical polymerization may hinder crosslinking, coupled with the steric hindrance of prepolymers (PEPP-1 and PEPP-2).

Elasticity and plasticity are two characteristic properties of a polymeric film. Formulations are developed to match the expected application of the film. Film elongations at the break (E_b) are shown in Figure 6. The lowest elongation was

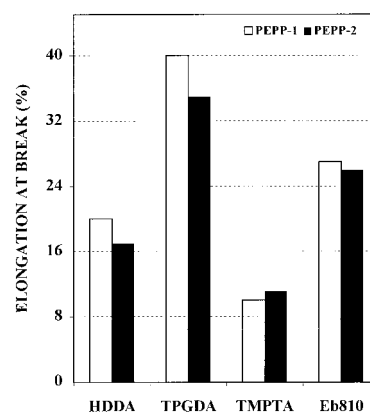


Figure 6 Elongation at break (% E_b) of UV-cured polymeric films of palm oil-based resins PEPP-1 and PEPP-2 with different reactive diluents under UV radiation.

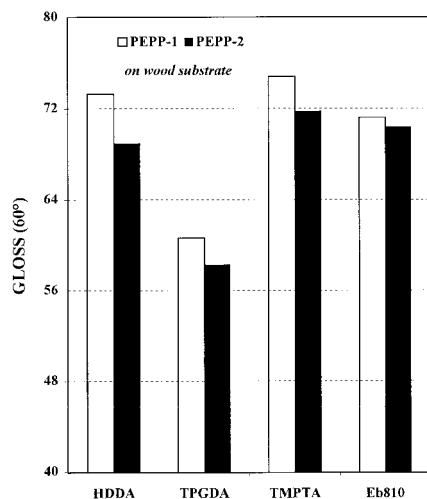


Figure 7 Gloss (60°) of UV-cured films coated on wood substrate under UV radiation.

displayed by the tri-functional acrylate containing diluent TMPTA (formulation RA₃ and CA₃). In the contrast, TPGDA containing formulations (RA₂ and CA₂) registered the highest E_b value, followed by formulation containing diluents Eb810 and HDDA. These values are in contrast to the tensile strength (TS) values (Fig. 5) reported earlier. This is because the tri-functional diluent (monomer) has the tendency to produce brittle plastic films (due to higher crosslinking density) compared to di-functional diluents, which produce elastic polymer films.

Application on Wood Coating

The full curing of the coated wood substrates (rubber wood) occurred with four passes under a UV lamp without any difficulties. This is in contrast to the case of polymeric film formations, where eight passes were required to get full curing and optimize characteristic properties.

The gloss of the coated materials cured under UV radiation was measured at two angles (60° and 20°). The results are represented by bar columns in Figures 7 and 8. In Figure 7 (at 60°), the highest gloss was achieved in the presence of the TMPTA diluent containing formulations (RA₃ and CA₃), i.e., about 74.8 and 71.8%, followed by the HDDA and Eb810 diluent containing formulations, and the lowest gloss was observed for the TPGDA (formulations RA₂ and CA₂), i.e., about 60.6 and 58.3%, respectively.

Similarly, from Figure 8, it can be seen that maximum gloss was observed for reactive diluent TMPTA containing formulations followed by

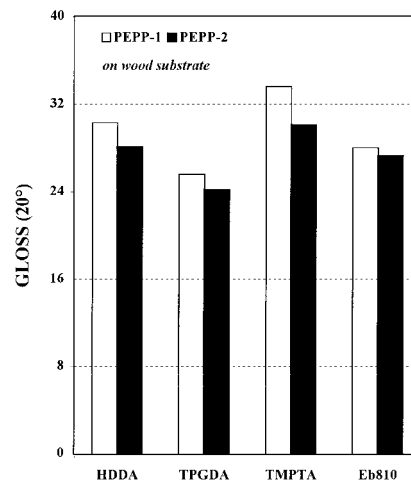


Figure 8 Gloss (20°) of UV-cured films coated on wood substrate under UV radiation.

HDDA, Eb810, and the lowest gloss was showed for diluent TPGDA, when the hardness of the coated material (wood substrate) was measured by the pendulum hardness method on the treated wood sample, the highest hardness was exhibited by the presence of TMPTA (Fig. 9), followed by HDDA, and Eb810. The lowest hardness was achieved with the film cured on wood substrate (surface) in the presence of TPGDA. This trend of film hardness is similar to the film hardness determined with the film cured on a glass plate under a UV lamp (Fig. 2).

Results of adhesion, cross-cut adhesion, scratch (macro), and abrasion (weight loss %) are shown in Table II. It can be seen that the coated

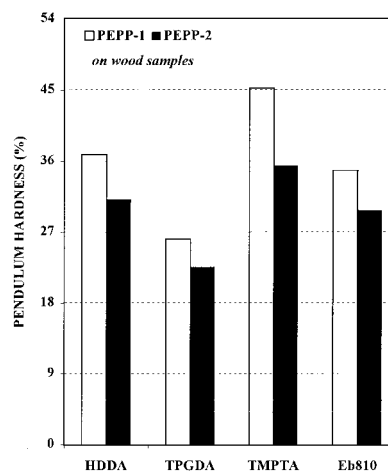


Figure 9 Pendulum hardness (%PH) of UV-cured films coated on wood substrate under UV radiation.

Table II Some Physical Properties of Coated Wood Substrate under UV Radiation

Properties		Substrate	HDDA	TPGDA	TMPTA	Ebecryl 810
i.	^a Adhesion % (cellular tape)	Wood	100	100	100	100
ii.	^a Adhesion % (cross head)					
	1 mm × 1 mm	Wood	2	2	3	3
	2 mm × 2 mm		0	0	0	0
iii.	^a Scratch : macro (g)	Wood	200	200	250	250
iv.	Abrasion (weight loss %)					
	PEPP-1	Wood	0.99	1.02	0.72	0.78
	PEPP-2		1.01	1.18	0.77	0.86
v.	Gloss (60°)					
	Blank	Wood	3.5	3.5	3.5	3.5
	Treated PEPP-1		73.3	60.6	74.8	71.2
	Treated PEPP-2		69.0	58.3	71.8	70.4
	Gloss (20°)	Wood				
	Blank		1.0	1.0	1.0	1.0
	Treated PEPP-1		30.3	25.6	33.6	28.8
	Treated PEPP-2		28.0	24.2	30.1	28.0

^a Adhesion, crosscut adhesion, and scratch properties of PEPP-1 and PEPP-2 are similar.

film has good adhesion characteristics on the wood surface. Regarding hardness characteristic properties, it is interesting to note that all of the cured films attained good hardness on coated materials (wood substrate) (Fig. 9) compared to the hardness of cured films coated on a glass plate (Fig. 2).

Solvent and Chemical Resistance of the Cured Film

The coated and cured wood (rubber) samples were also observed to exhibit solvent and chemical re-

sistance properties. Table III shows the effect of various solvents and chemicals on the cured film. The cured films of palm oil-based polyester acrylate prepolymers were resistant to all solvents and chemicals used. This led to the inference that the double bond of the formulation was fully cured under the UV lamp.

Based on the above experimental results and discussion, the polymeric films thus prepared by using palm oil prepolymer PEPP-1 incorporated with different reactive diluents on the wood surface showed better properties compared to the

Table III Solvent and Chemical Resistance Properties of Coated Wood Substrate under UV Radiation

Solvent/Chemicals	Formulations							
	RA ₁	RA ₂	RA ₃	RA ₄	CA ₁	CA ₂	CA ₃	CA ₄
Acetone	✓	✓	✓	✓	✓	✓	✓	✓
Coffee	✓	✓	✓	✓	✓	✓	✓	✓
Tea	✓	✓	✓	✓	✓	✓	✓	✓
10% EtOH	✓	✓	✓	✓	✓	✓	✓	✓
50% EtOH	✓	✓	✓	✓	✓	✓	✓	✓
5% NaOH	✓	✓	✓	✓	✓	✓	✓	✓
10% NaOH	✓	✓	✓	✓	✓	✓	✓	✓
1% Na ₂ CO ₃	✓	✓	✓	✓	✓	✓	✓	✓
5% CH ₃ COOH	✓	✓	✓	✓	✓	✓	✓	✓
5% H ₂ SO ₄	✓	✓	✓	✓	✓	✓	✓	✓
10% H ₂ SO ₄	✓	✓	✓	✓	✓	✓	✓	✓

✓ = Solvent and/or chemical resistant.

polymeric films prepared with the prepolymer PEPP-2.

CONCLUSIONS

1. For radiation-curable wood-coating applications, the formulations of PEPP-1 and PEPP-2 incorporated with reactive diluents TMPTA and HDDA were found to be most suitable for wood coating application.
2. Films cured by UV radiation made of PEPP-1 and PEPP-2 on the rubber wood surface (substrate) have the same adhesion, scratch, solvent, and chemical-resistant properties. Hardness, gloss, and abrasion properties of prepolymer PEPP-1-based coated materials were better than for prepolymer PEPP-2-based coating.

In general, it can be concluded that radiation curable palm oil-based polyester acrylated prepolymers, namely PEPP-1 and PEPP-2, are promising candidates for wood coating applications.

This work was financially supported by the Palm Oil Research Institute of Malaysia (PORIM), under the project agreement of USM-PORIM. Therefore, the author gratefully acknowledge PORIM for financial support and USM for giving permission to work at the PORIM laboratory. Our sincere thanks are also given to the Director-General of PORIM for his permission to publish this article.

REFERENCES

1. Mills, M. R. *An Introduction to Drying Oil Technology*; Pergamon: Oxford, 1952.
2. Morgans, W. *Outlines of Paint Technology*; Halsted Press: New York, 1990.
3. Lanson, H. J. *Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc.: New York, 1978, 3rd ed., vol. 2.
4. Ohlson, R. *Lipid Technol* 1993, Mar/Apr, 34.
5. Kumar, R. N.; Goh, T. J.; Abubakar, A.; Rozman, H. D. *RadTech Asia95 International Conference on Radiation Curing (Proceeding)*, 20–24 November, 1995.
6. Bhabhe, M. D.; Athawale, V. D. *Prog Org Coat* 1997, 30, 207.
7. Homer, D. C. E. *RadTech Asia '99, International Conference on Radiation Curing (Proceeding)*, 24–26 August, 1999.
8. Lewis, L. N.; Katsamberis, D. *J Appl Polym Sci* 1991, 42, 1515.
9. Montoe, B. M. In *Radiation Curing: Science and Technology*; Pappas, S. P., Ed.; Plenum: New York, 1992, p. 399.
10. Rybny, B. B.; De Fazio, C. A.; Shahidi, J. K.; Trebellas, J. C.; Vona, J. A. *J Paint Technol* 1974, 46, 60–69.
11. Hashimoto, K.; Saraiya, S. J. *J Radiat Curing* 1981, January, 4–15.
12. Hilmi, M.; Hussin; Hamirin; Mazni; Azman. *J Sains Nuklear Malaysia* 1990, 8, 149.
13. Halvorsen, C. *American Ink Market* 1992, 29–31.
14. Azam Ali, M.; Ooi, T. L.; Salmiah, A.; Ishiaku, U. S.; Ishak, Z. A. Mohd. *PORIM Int. Palm Oil Congress, Oleochemical Technology, Kuala Lumpur, Malaysia, 2–6 February, 1999.*
15. Azam Ali, M.; Ooi, T. L.; Salmiah, A.; Ishiaku, U. S.; Ishak, Z. A. Mohd. *RadTech '99 Asia 7th International Conference on Radiation Curing (Proceeding)*, 24–26 August, 1999.
16. Singapore Pat. No. PI 9502302, 1997.
17. Malaysia Pat. No. P-9610425-2, 1998.
18. Speckhard, T. A.; Hwang, K. K.; Lin, S.; Tsay, S.; Koshiba, M.; Ding, Y.; Cooper, S. L. *J Appl Polym Sci* 1985, 30, 647.
19. Charlesby, A. *Proc Roy Soc* 1954, A222, 60, 542; A224, 120.
20. Saito, O. *J Phys Soc Jpn* 1958, 13, 198, 1451, 1465.