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UV Curable Urethane Acrylate Resin from Palm Fatty Acid Distillate

Kim Teck Teo, Aziz Hassan and Seng Neon Gan*

Chemistry Department, University of Malaya, 50603 Kuala Lumpur, Malaysia.

* Corresponding author. Tel:+603 79674241; Fax:+603 79674193

Email Address: sngan@um.edu.my

Abstract

Palm fatty acid distillate (PFAD) is a by-product from the refining of crude palm oil. It comprises mainly of free fatty acids, having around 45% of palmitic and 33% oleic acids as the major components. Ultra-violet (UV) curable urethane acrylate (UA) oligomers could be synthesized from PFAD by the following procedure. A hydroxyl terminated macromer was first prepared by reacting PFAD with a mixture of isophthalic acid, phthalic anhydride, neopentagylcol (NPG) and pentaerythritol. The macromer is then reacted with 2-hydroxylethylacrylate (2HEA) and toluene diisocynate (TDI) to generate a resin containing acrylate side chains for UV curable application. A series of UA resins were prepared by using 15, 25, 45, 55 and 70% of PFAD respectively. The UA resin has Mw in the range of 3200 to 27000. They could be cured by UV irradiation at intensity of 225mW/cm^2. Glass transition temperature (T_g) of the cured film was measured by differential scanning calorimeter (DSC), and hardness of the film was determined by pendulum hardness tester according to ASTM4366. The resins were used in wood coating application. All of the cured films showed good adhesion, hardness and chemical resistant for resins using up to 55% PFAD; however the resin at 70% did not cure properly.

Keywords: PFAD; urethane acrylate; crosslinking, UV curing, chemical resistant; film hardness.

Introduction

Coating industry has always been searching for technological improvements, to achieve greater efficiency, productivity and lower cost. There are significant contributions made by the resin industry and its ancillaries, particularly in improved curing rates and film properties. Coating system without organic solvent would enjoy a cost reduction and at the same time being more environmental friendly. Thus radiation curing techniques offer advantages such as energy saving, free of volatile solvent and fast curing cycle. One pack system UV curable resin is a rapidly growing technology within the coating, adhesive and related industries. It has found a large variety of applications due to its distinctive advantages such as high efficiency, environmental friendliness and energy saving [1,2,3]. The main components in UV curable formulation are the unsaturated oligomer, monomer diluents and photoinititator.

Most commercial UV curable formulations are based on combination of acrylic oligomers and monomers [4,5], urethane acrylate [6,7] and polyester acrylate [8], and epoxy acrylate [9,10]. Properties of UV curable coatings are determined by the type of oligomers employed in the formulation. Currently most of the commercially available resins are petroleum-based and lacking in environmental friendliness and sustainability.

Depletion of petroleum reserves and increasing environmental concerns have stimulated the revolution to explore materials from readily available, renewable and inexpensive natural resources, such as carbohydrates, oils, fats and proteins. These renewable materials are going to play noteworthy roles in the development of sustainable green chemistry. Oils and fats of vegetable and animal origins have been the renewable materials for coating and ink industry.

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Elaeis guineensis, is the oil palm plant that produces fruit with high oil yield. In Malaysia, it is grown commercially and has been an important crop that contributes to the economy of the country. About 90% of palm oil is used for food, and about 10% for non-edible products as soaps and detergents. The traditional vegetable oils like linseed, soyabean and castor oils have been commercially used for the synthesis of alkyds, epoxides and polyesteramides [11]. Less commonly, cashew nut, karanja, annona squmosa, natural rubber seeds have also being investigated for producing polyurethane, polyesteramide and alkyd resins [12,13]. Recently, there were several reports on palm oil based-resins. For example, an excellent baking enamel was produced from a water-reducible palm stearin alkyd combined with melamine resin [14,15]. The problem of insufficient unsaturation could be overcome through the incorporation of maleic anhydride or fumaric acid into the alkyd structures, to make them UV-curable [16,17]. Further exploration of palm oil derivatives has produced many new coating resins having various film properties [18,19,20,21]. In 2014, an US patent was granted for a palm oil-based polyurethane oligomer for use as restorative dental material [22].

Crude palm oil consists of about 94% triglycerides, 3-5% of free fatty acids and about 1% of other minor constituents. The palm fatty acid distillate (PFAD) is the by-product from refining of crude palm oil. It comprises mainly of free fatty acids, having around 45% of palmitic and 33% oleic acid as the major components, and it has been using in the making of soap and animal feed, and certain oleo chemicals. Vitamine E could be extracted from PFAD [23]. Gapor has developed a process for producing high purity (>90%) Squalene[24]. This valuable compound is useful in heath supplements, cosmetics, and in pharmaceutical industry. In recent study, PFAD has been explored as biodiesel feed stock [25]. Many studies utilizes various types of catalysts, such as SO_4^{2-}/TiO_2-SiO_2, and modified Zirconia compounds [25,26,27]. Malaysian palm oil refineries are producing more than 750,000 MT of PFAD annually as a by-product, which is being sold at a discounted price as compare to RBD Palm

oil at USD200 – 250 per metric tonne for usage in animal feed [28,29]. There was no report of its application in coating. This project has aimed to synthesize PFAD urethane acrylate with different PFAD content. The urethane acrylates (UA) were investigated as UV curable resins for wood coating applications.

1. Experimental

2.1 Materials

The PFAD was a kind gift from Sime Darby Group, Malaysia. This commercial PFAD was used without further treatment. 2,2-dimethyl-1,3-propanediol (neopentaglycol, NPG) was purchased from LG Chemicals, Korea; 2,2-bis(hydroxylmethyl)1,3-propanediol (Pentaerythritol) from Perstop AB, phthalic anhydride from Nanya Plastic Taiwan, purified isophthalic acid from MGC Chemicals, Japan, mono-butyl tin oxide from Arkema, toluene diisocyanate (80/20 TDI) from Bayer AG, 2-hydroxy ethyl acrylate (2-HEA) from BASF, xylene from Exxonmobil, Tripropylene glycol diacarylate (TPGDA), triphenyl phosphine (TPP) and 4-methoxy phenol from Sigma Aldric Chemicals, Speedcure 73 (2-hydroxy-2-methylpropiophenone) from Lambson UK. Tetrahydrofuran (THF) from Thermo Fisher Scientific,USA. Epon 828 from Hexion, USA. All Chemicals were used as received.

2.2 Synthesis

2.2.1. Synthesis of PFAD hydroxyl-terminated macromer.

A hydroxyl-terminated macromer was first synthesized by one batch reaction of PFAD, isophthalic acid, phthalic anhydride, neopentagylcol and pentaerythritol. The procedure is a modified process that had been described elsewhere [30].

PEAD and Neopentaglycol were charged into a 2L round bottom flask, fitted with a decanter and stirrer. The mixture was heated slowly to 100°C until all material melted, and subsequently pentaerythritol, isophthalic acid, phthalic anhydride and mono-butyl tin oxide were added. Constant stirring at 250 rpm was maintained and the temperature was raised gradually. Water from the condensation reactions started to evolved around 180°C and was decanted out. Temperature was raised and maintained at 240°C. Progress of the reaction was monitored by measuring the acid value and viscosity of a small sample taken from the reactor at different reaction intervals. The sample was dilute with xylene to 80% solid content before its viscosity was measured by Brookefield viscometer (model DVI). Acid value was determined by titration of a known weight with standardized alkali according to ASTM D4662-93 Method. When the acid value has fallen below 10 mgKOH/g, heating was turned off and allowed to cool down to 100ºC, before the PFAD macromer was transferred to a storage container and diluted with TPGDA to 70% solid content and kept for further modification. Five macromers were synthesized with PFAD content of 15, 25, 45, 55 and 70% respectively, the recipes of reactions are as shown in Table 1.

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Table1. Formulations of PFAD hydroxyl terminated macromers.

Raw material (wt g^{-1})	Formulation				
	M1	M2	M3	M4	M5
PFAD	150.0	266.1	447.4	546.9	689.4
NPG	399.6	300.0	233.7	203.8	149.9
Pentaerythritol	-	59.2	59.7	59.7	70.0
Isophthalic acid	180.0	177.4	159.1	139.2	50.0
Phthalic anhydride	224.8	224.8	99.4	49.7	40.0
Mono-butyl tin oxide	0.4	0.4	0.7	0.7	0.7

2.2.2 PFAD Urethane Acrylate Oligomer (UA)

The PFAD urethane acrylate oligomer was synthesized via reactions of PFAD macromers (M1-M5) with 2HEA and TDI. The procedure is as follow. 95.9 g of TDI was charged into a four necked flask equipped with a mechanical stirrer, dropping funnel with a condenser capped with a drying tube, thermometer and a nitrogen inlet. The flask was heated to 35^0C in a water bath. 63.4 g 2HEA and 0.1 g 4-methoxyphenol were mixed in a separate flask and the mixture dosed into the flask using dropping funnel over a period of 2 hours. The progress of the reaction could be checked by both the FTIR spectrum and determining the isocyanate value by titration. When the isocyanate content reached half of the initial value, the -OH peak in the FTIR spectrum would have disappeared, and the specified amount of the PFAD macromer was charged into the reaction mixture. The temperature was raise to 97˚C to accelerate the reaction,

which was stopped when residual isocyanate content has dropped to less than 0.05%. Then 64.0 g of TPGDA was added and the final resin was ready for further evaluation. Table 2 summaries the compositions of the urethane acrylic oligomers UA1, UA2, UA3, UA4 and UA5 prepared from the PFAD macromers M1, M2, M3, M4 and M5 respective.

Table 2. Composition of PFAD urethane acrylate

Raw material	Formulation				
wtg^{-1}	UA1	UA2	UA3	UA4	UA5
TDI	95.9	95.9	95.9	95.9	95.9
2-HEA	63.4	63.4	63.4	63.4	63.4
4-methoxy phenol	0.1	0.1	0.1	0.1	0.1
M1	840.6	-	-	-	-
M2	-	840.6	-	-	-
M3	-	-	840.6	-	-
M4	-	-	-	840.6	-
M5	-	-	-	-	840.6

2.2.3 UV curable formulation.

The UV curable formulation were prepared by mixing the urethane acrylic oligomer UA at 80.00% (w/w) , Speedcure 73 at 3.00% (w/w) and 17.00% (w/w) TPGDA.

2.3 Characterization

2.3.1 Molecular weight measurement

Molecular weights of samples were measured by a Shimadsu GPC with tetrahydrofuran as the mobile phase (set at 1.0 ml min^{-1}). Monodisperse polystryrene standards were used for the calibration of the column.

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2.3.2 FTIR analysis

FTIR spectra were recorded by using ATR technique on a Perkim Elmer Spectrum Two FTIR spectrometer. The polymer was coated directly onto the ATR diamond plate and the spectrum was recorded.

2.3.3 Viscosity measurement

A Brookefield viscometer (model DVI) was used to measure the sample dynamic viscosity at temperature 25°C. The sample of macromer was diluted to 70% of oligomer content with TPGDA before viscosity measurement.

2.3.4 Glass Transition Temperature

To determine T_g of the resin and cured film, samples were encapsulated in 40 µL aluminium pan and analysed using Shimadzu DSC (model DSC-60) at heating rate 20°C min^{-1}.

2.3.5 Pendulum Hardness

The hardness of the UV cured film was measured with Sheen konig pendulum hardness tester according to ATSM 4366.

2.3.6 Acid Value, Isocyanate Value and Hydroxyl Value

The resin acidity (acid value), isocyanate value and hydroxyl value were determined by standard titration method according to ASTM D4662-93, ISO 14896/3 and ASTM D1957-86 (2001) respectively.

2.3.7 Gloss measurement

The gloss of the cured film was measured with BYK tri-gloss meter according to ASTM D523 for non-metallic substrate. The gloss level was report as gloss unit (GU) from the measurement.

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2.3.8 Adhesion

The film adhesion was performance accordingly to ASTM D3359-09 test method B. The adhesion performance was rated according to the Table 3.

Table 3. Classification of Adhesion results

Percentage of area removed	0% none	< 5%	5-15%	15-35%	35-65%	> 65%
Classification	5B	4B	3B	2B	1B	0B

2.3.9 Pencil Hardness

The hardness of the cured film was measured by pencil hardness accordingly to ASTM D3363. The pencil hardness scale is as follow, where 6B denotes the softest and 6H being the hardest: Pencil Hardness Scale : 6B-5B-4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H

2.4 Monitoring of UV Curing

UV curing was carried out by casting the formulated UA resin, using a bar coater of 20µm, onto a glass panel, which was then irradiated with the UV at 10 cm distance from the source at the specified exposure time, from 5 until 60 seconds. The extent of cure at each instant was correlated to the hardness and T_g of the film.

2.5 Chemical Resistance of cured film.

The UA cured films were subject to wood coating standard for chemical resistance test. The UA coating was applied on rubber wood panel and cured by irradiation with UV light for 60 s. The cured panel was conditioned at room temperature for 1 hour before carrying out the chemical resistant test. 10 ml of chemical reagent was dropped onto the cured film and allowed to stand for 24 hours, to minimize the evaporation of the reagent, it was covered with a plastic cap. The reagent was then wiped off with a dry clean cloth, surface was then dried for 15 minutes before making observation and reporting. The reagents commonly applied by

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Industrial Wood coating standard include coffee, tea, dish washing solution, acetone, cooking oil, 1% ethanol aqueous solution (wt/wt), vinegar (8% acetic acid, v/v), 10% ammonia solution, 5% sodium hydroxide (NaOH) solution (wt/v) and 5% hydrochloric (HCl) solution (w/v).

2. Results and Discussions

3.1 Synthesis of PFAD macromer

The hydroxyl terminated PFAD macromere was synthesized from the reactions between PFAD, neopentylglyco, pentaerythritol, isophthalic acid and phthalic anhydride. A plausible structure of the macromer is shown in scheme 1.

Scheme1. The plausible structure of PFAD macromer

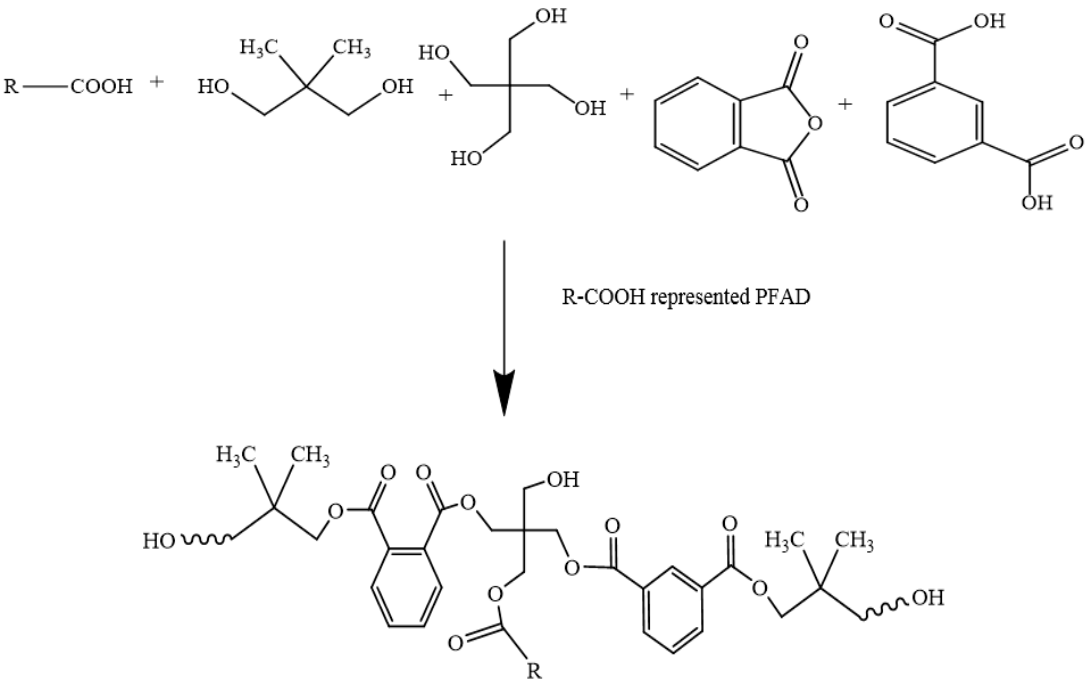

Figure 1. Acid value as function of reaction time.

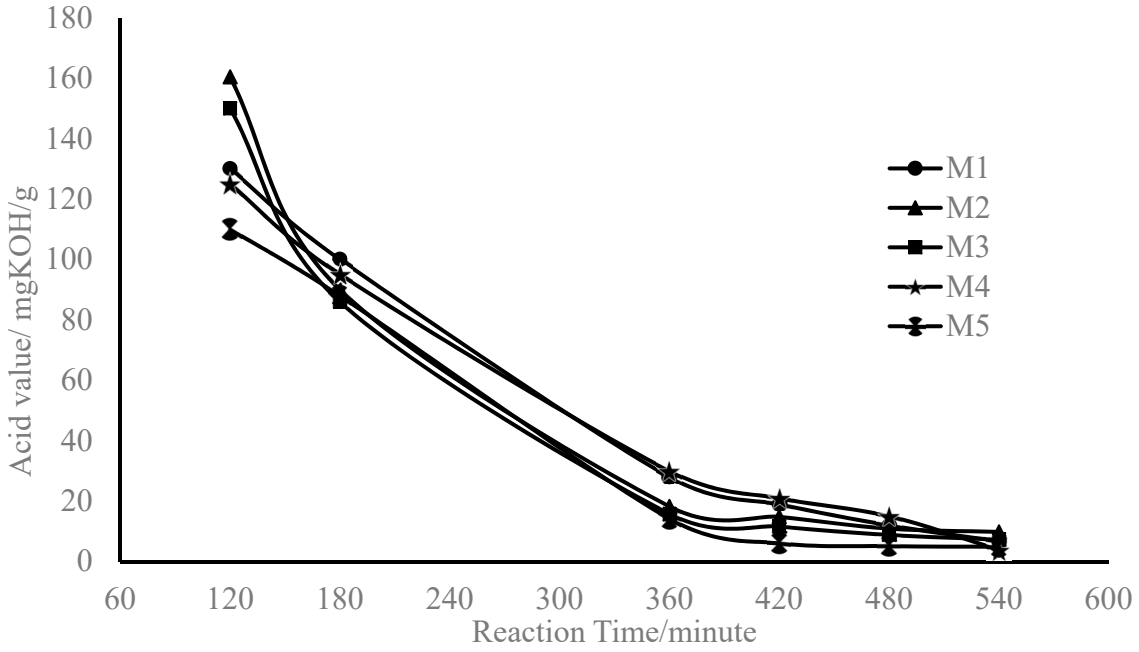

Figure 1 shows the change in acid value with reaction time during the synthesis of the macromers. With reference to Table 1, the PFAD content in increasing order is M1<M2<M3<M4<M5, and all the macromers have showed the similar reaction trend, being fast at initial stage from 120-360 min and reached constant AV after 420 min. Between 180-360 minutes, the acid value of all macromers were decreasing at comparable rates, all of them have reached acid value <10 mgKHO/g.

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Table 4. Molecular weight of the 5 macromers.

Formulation	Molecular weight (Dalton)
M1	2400
M2	5100
M3	8000
M4	2800
M5	2600

The M_w each macromer is shown in Table 4. In general, molecular weight of alkyd resin is known to be affected by its oil-length in the formulation [30]. In this case, from M1 to M3, %PFAD increases from 15- 45%, M_w has shown an increasing trend, from 2400 to 8000. However for M4 and M5, at %PFAD of 55 and 70% respectively, Mw has dropped to around 2700. In this series of study, the macromer attained optimum M_w with formulation of M3, containing 45% PFAD at 8000.

Figure 2. FTIR spectrum of M1, M2 and M3 macromer.

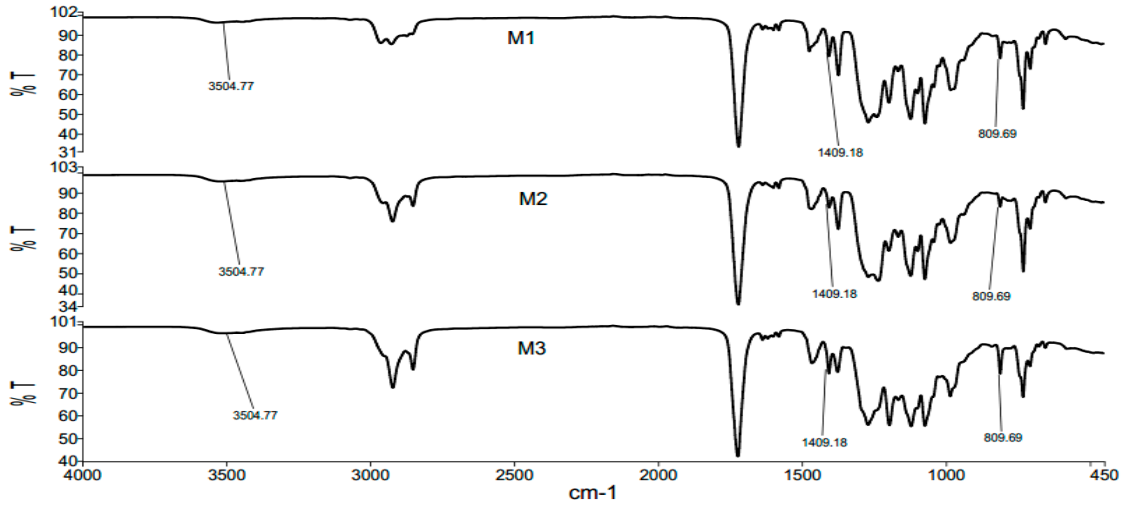

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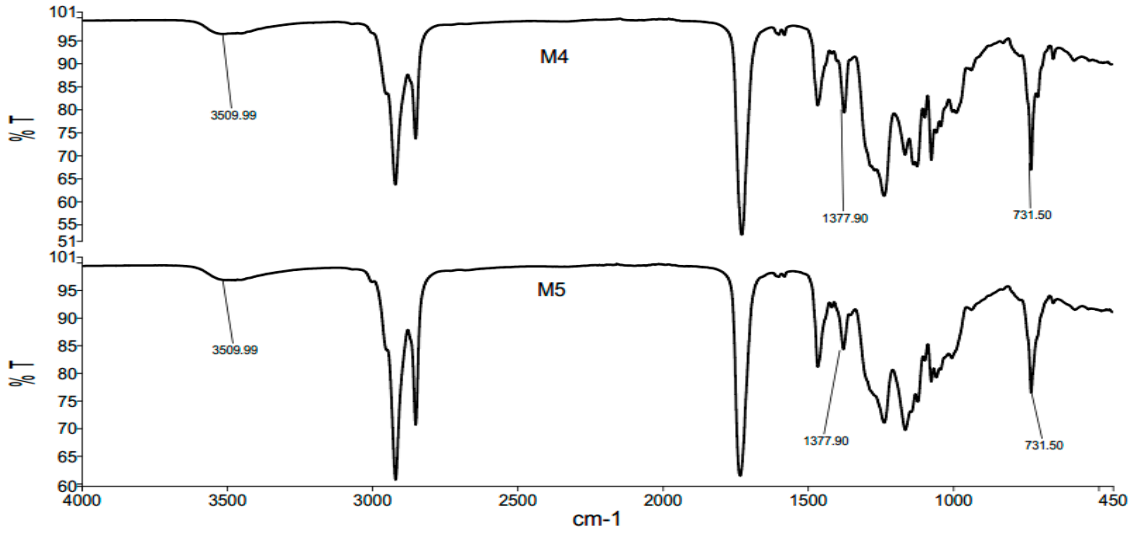
Figure 3. FTIR spectrum of M4 and M5 macromer.



The FTIR spectra of the macromers were showed in Figure 2 and 3. The -OH stretching occur 3500 cm^{-1}. The peaks at 2852-2956 cm^{-1} are associated with the symmetric and asymmetric stretchings of C-H the aliphatic $–CH_2$ and $–CH_3$. Other bands included C=O at 1722 cm^{-1}, and C-O-C stretching at 1120-1230cm^{-1}. In Figure 2, the M1, M2 and M3, peaks of -C=C- of acrylate at 1409 and 809 cm^{-1} are contributed by the diluents TPGDA. The dilution of this three macromers were necessary as the neat macromers showed extremely high viscosity and not possible for subsequent grafting process. Figure 3 shows the spectra of M4 and M5, which were not diluted with TPGDA, hence the acrylate peak not observed. .The characteristic properties of the PFAD macromer are summarized in Table 5.

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Table 5. Properties of PFAD macromers

Description	M1	M2	M3	M4	M5
Oligomer content/%	70.0	70.0	70.0	100	100
Reactive diluent/%	30.0	30.0	30.0	-	-
Viscosity@25°C/poise	218.0	70.1	40.0	15.8	5.3
Acid value/mgKOHg^{-1}	6.7	9.8	7.3	3.9	4.9
Molecular weight/Mw	2400	5100	8000	2800	2600
Polydispersity/Q	1.38	2.23	2.28	1.40	1.21

3.2 PFAD Urethane Acrylate (UA)

The PFAD macromer was reacted with TDI and 2-HEA to produce the UA resin. TDI contains –NCO at ortho and para positions, and the para-NCO is 8 times more reactive than ortho-NCO at temperature below 30˚C [31,32]. The adduct of TDI and 2HEA was first produced at temperature below 30˚C. The consumption of NCO was being monitored through the reduction of peak at 2270cm^{-1} in the FTIR spectrum. The plausible reaction path of PFAD urethane acrylate formation is shown in scheme 2.

Scheme 2. The plausible reaction path fo PFAD urethane acrylate formation.

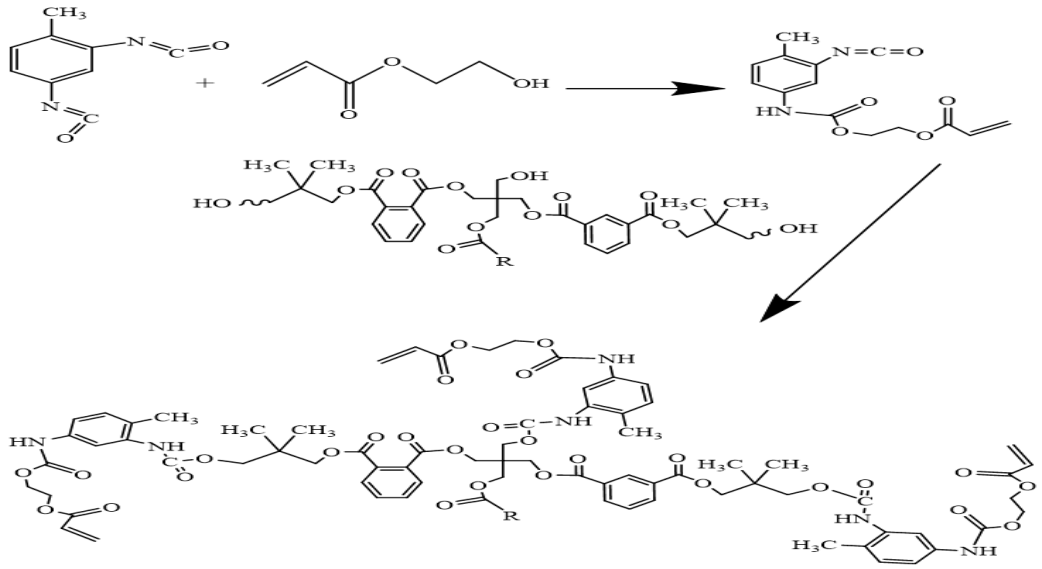

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Figure 4. NCO value during synthesis of PFAD urethane acrylate.

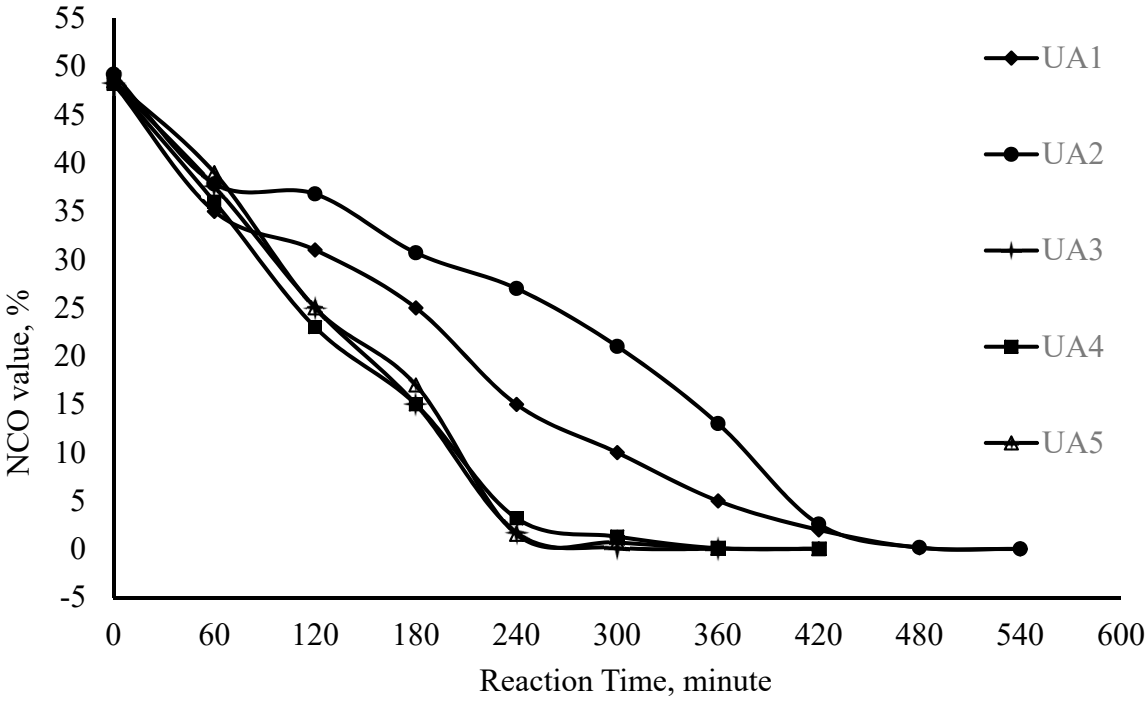

Figure 4 shows the change in % NCO with reaction time during the synthesis of PFAD urethane acrylate. The initial NCO of 49.2% has reduced gradually and reached 0.05% at the end of polymerization process. At time interval of 120 minutes, UA1 and UA2 show slower rate of formation as compared to UA3, UA4 and UA5 presumably due to the effect of viscosity. The high viscosities of M1 and M2 have reduced the mobility of TDI adduct during the grafting process and resulted in slower reaction rate to form UA1 and UA2 respectively. The low viscosity oligomer M3, M4 and M5 has provide better mobility medium for TDI adduct to react, as clearly reflected by the fast reduction rate of NCO value particularly from reaction time of 60-240 min.

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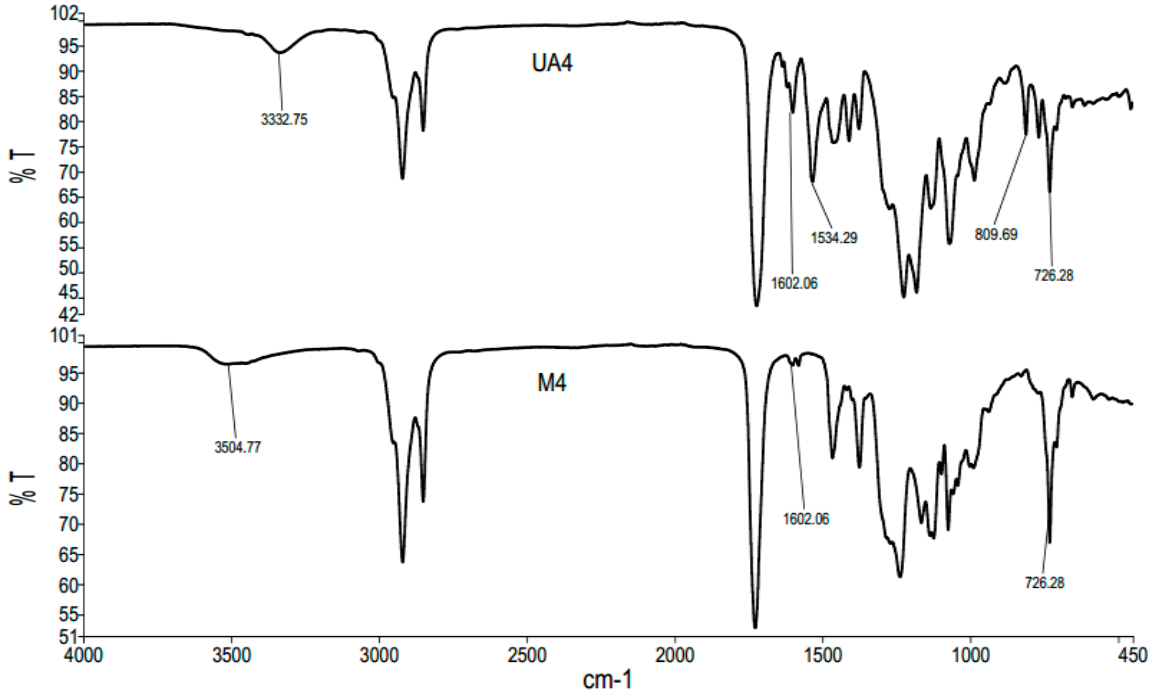
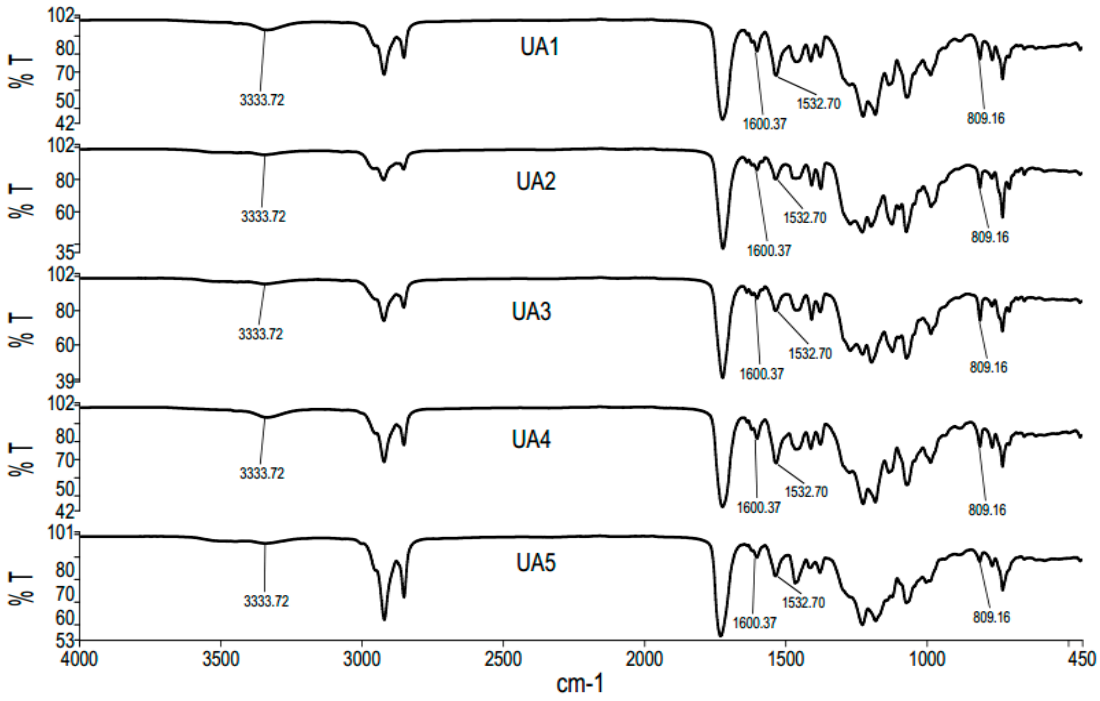
Figure 5. Comparison of FTIR spectra between M4 and UA4.



For illustration, Figure 5 shows the FTIR spectra of the macromer M4 and final urethane acrylate of UA4. The shift of peak at 3500 to 3350 cm^{-1} was due to the reaction of OH and NCO to form the urethane linkage. The NH deformation at 1531 cm^{-1} and acrylate double bond at 810 cm^{-1} were observed on UA4 but not on M4.

Figure 6 shows the spectra of all the UA resins. The shift of OH peak at 3500 cm^{-1} to 3350 cm^{-1} and NH deformation at 1532cm^{-1} confirms the formation of urethane linkage after the grafting reaction.

Figure 6. FTIR spectrum of UA1, UA2, UA3, UA4 and UA5.



The molecular weight of polymer relative to polystyrene standards were determined by GPC. The M_w of UA is generally higher than its macromer. The increase is due to the reactions of the macromer with TDI and 2-EHA. Properties of the UA resins are summarized in Table 6.

(Take in Table 6)

3.3 T_g of the UV cured film by DSC method

The clear coat was applied onto glass panel by a bar coater to achieve a thickness of 25μm and expose to UV irradiation at specified durations. Tg of the cured film was determined by DSC.

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Figure 7. Tg of the UA cured film at different UV curing time.

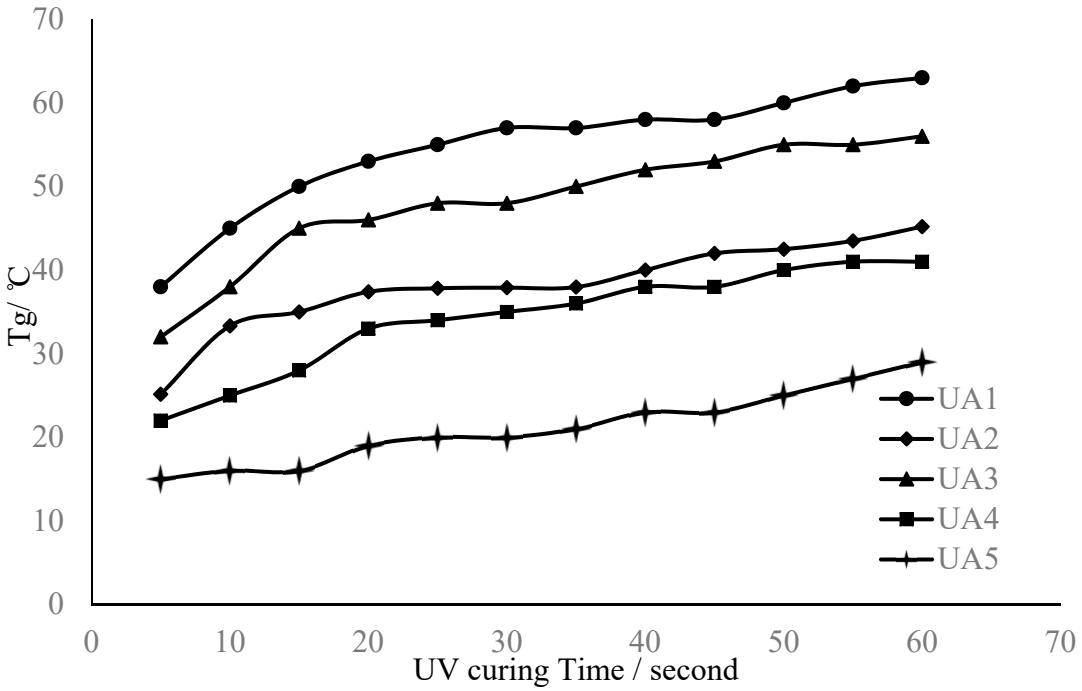

Figure 7 shows the change in T_g of the film at different UV curing time. Generally, all formulations show accelerated photopolymerization at 5 to 20 s UV exposure. Subsequently curing has decreased as the acrylate double bond is being used up. In addition, the curing reaction is accompanied by sharp increase in viscosity and would reduce the mobility of the reactant with further reduction of rate of reaction. As shown in Figure 7, the %PFAD in UA has great influence on the T_g of the cured film. Generally T_g is reduced with higher % PFAD. Film of UA5 shows the lowest T_g (29°C) after 60s of UV irradiation. Film of UA3 has the higher T_g value among UA2 to UA5. In case of UA1, 15%PFAD seems to have less influence on cured T_g of cured film. Its highly reactive polyester backbone has dominant contribution to the T_g , thus UA1 has attained the highest T_g (63°C) as compared to other four UA resins.

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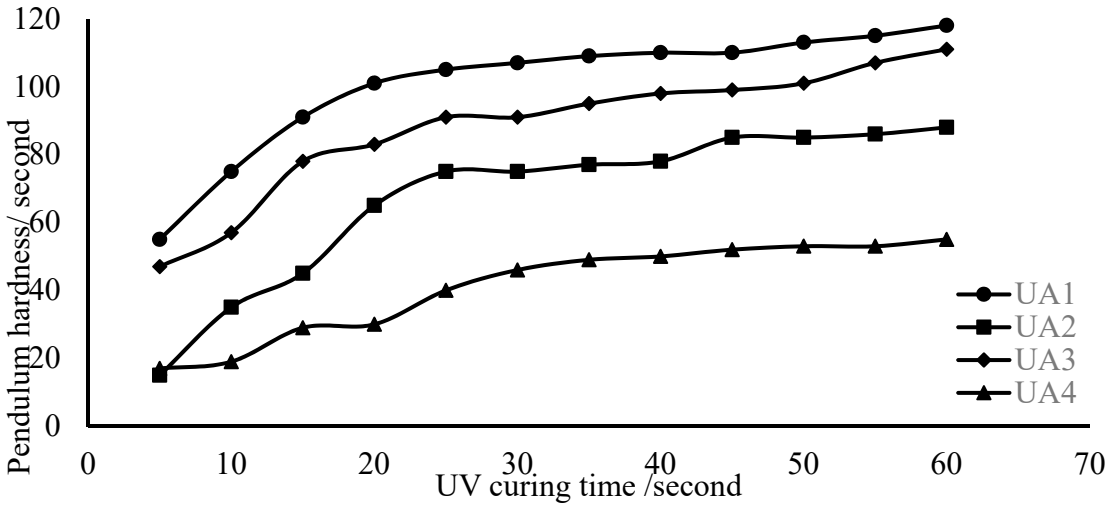
3.4 Pendulum hardness of the UV cured film

The film at different stages of UV curing was subjected to pendulum hardness test by using Sheen Konig pendulum tester according to ASTM 4366. The results are shown in Figure 8.

Figure 8. Pendulum hardness of the UA cured film at various UV curing time.



Only four oligomers UA1 to UA4 have films with measureable hardness. UA5 has formed soft film after the UV curing process, as reflected by its low film Tg. In general, the hardness, as well as the Tg of the cured film increased during the photo induced polymerization process. They are mainly depending on the cross-link density and the nature of the UV curable acrylate. Similar to T_g property, the hardness of the film was influence by %PFAD. Thus. UA1 with lowest %PFAD and highly reactive polyester backbone has showed good hardness development as compared to other UAs and achieved the final pendulum hardness of 118s. As %PFAD increases, UA3 has showed optimum cured film property and achieved the final film hardness of 111s. On the other hand, UA2 and UA4 have showed quite similar hardness after 5s of UV curing time but the hardness development of UA2 has increased faster as compared to UA4 from UV curing time of 10 to 30s. At 30s curing time, UA2 and UA4 have achieved pendulum hardness of 77s and 49s respectively. Their final pendulum hardness were recorded at 88s and 55s for UA2 and UA4 respectively. Further analysis of UA2 and UA4

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showed that the different was due its M_w where UA2 was having higher M_w of 7500 dalton as compared to UA4 at only M_w of 3800 dalton.

3.5 Chemical resistant of UV-cured film.

All wood panels were coated with formulation described in section 2.2.3. The initial cured film properties and appearance were summarized in Table 7 and final properties and appearance were showed in Table 8 and Table 9.

Table 7. The initial cured film properties

Properties	UA1	UA2	UA3	UA4	UA5
Film appearance	Glossy	Glossy	Glossy	Glossy	Tacky
60° Gloss unit (GU)	97.1	93.4	92.9	93.3	NA
Crosshatch adhesion	5B	5B	5B	5B	NA
Pencil hardness	H	F	H	HB	NA

Results from Table 7 showed that all cured films were having good initial properties except UA5. UA1 to UA4 showed glossy appearance with gloss measurement ranging from 93GU to 97GU except UA5 showing tacky appearance. All cured films have excellent adhesion on wood panel with grade of 5B recorded. In pencil hardness scale, UA1 and UA3 showing hardness of H, follow by UA2 of F and UA4 of HB.

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Table 8. The cured film appearance of various composition of UA after 24 hours chemical aging.

Chemical test	UA1	UA2	UA3	UA4
Coffee	UC	UC	UC	UC
Tea	UC	UC	UC	UC
Dish washing solution	UC	UC	UC	Fading and whitish mark
Acetone	UC	UC	UC	UC
Cooking oil	UC	UC	UC	UC
1% ethanol aqueous solution	UC	UC	UC	UC
Vineger	UC	UC	UC	Slight fading
10% ammonia solution	UC	UC	UC	Slight fading
5% NaOH solution	Fading and whitish mark	Fading and whitish mark	Fading and whitish mark	Fading and whitish mark
5% HCL solution.	UC	UC	UC	Slight fading

UC=unchanged.

In Table 8, cured films of UA1, UA2 and UA3 exhibit good chemical resistant with unchanged of film appearance after 24 hours aging with almost all the chemicals. Generally, the films have showed poor alkaline resistant ranging from 15 to 55%. Fading and whitish mark was observed on the cured film when using 5% NaOH solution aging. At 55% and 70% PFAD, the oligomer shows more poorer film properties as compared to UA1, UA2 and UA3. Fading and whitish mark were observed on dish washing solution and 5% NaOH solution. The cured film showed slight fading in vinegar, 10% ammonia solution and 5% HCL solution aging test at oligomer with 55% PFAD.

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Table 9. The cured film properties of various composition of UA after 24 hours chemical aging.

Chemical test	UA1		UA2		UA3		UA4	
	Crosshatch adhesion	Pencil Hardness	Crosshatch adhesion	Pencil Hardness	Crosshatch adhesion	Pencil Hardness	Crosshatch adhesion	Pencil Hardness
Coffee	5B	H	5B	F	5B	H	5B	HB
Tea	5B	H	5B	F	5B	H	5B	HB
Dish wash solution	5B	H	5B	F	5B	H	3B	2B
Acetone	5B	H	5B	F	5B	H	5B	HB
Cooking oil	5B	H	5B	F	5B	H	5B	HB
1% ethanol solution	5B	H	5B	F	5B	H	5B	HB
Vinegar	5B	H	5B	F	5B	H	4B	B
10% ammonia solution	5B	H	5B	F	5B	H	4B	B
5% NaOH solution	3B	HB	3B	B	3B	HB	2B	3B
5% HCL solution	5B	H	5B	F	5B	H	4B	B

Table 9 showed the results of adhesion and pencil hardness tests performed on the all cured film after 24 hours chemical aging test. For the films of UA1, UA2 and UA3, results for crosshatch adhesion and pencil hardness remain perfect except those after tin 5% NaOH solution aging. 10% of the NaOH aging cured film has detached from the substrate after the adhesion test (grade 3B). In the case of pencil hardness, cured films of UA1, UA2 and UA3 the hardness was not affected after the chemical aging, except for 5% NaOH solution. Their hardness remains unchanged at initial value of H, F and H for UA1, UA2 and UA3 respectively. Similar observation as compared to cured film appearance, UA4 crosshatch adhesion and pencil hardness shows significant reduction in performance especially in NaOH and dish washing solution. The cured film adhesion has reduced to grade 2B and 3B and hardness of 3B and 2B were recorded after aging with 5% NaOH solution and dish washing solution

respectively. Slightly reduction of cured film performance also being observed on Vinegar, 10% ammonia solution and 5% HCl solution for UA4. The crosshatch adhesion has been reduced one grade lower than initial value and pencil hardness was recorded at B on these three chemical aging tests.

Figure 9. Gloss retention after 24 hours chemical aging.

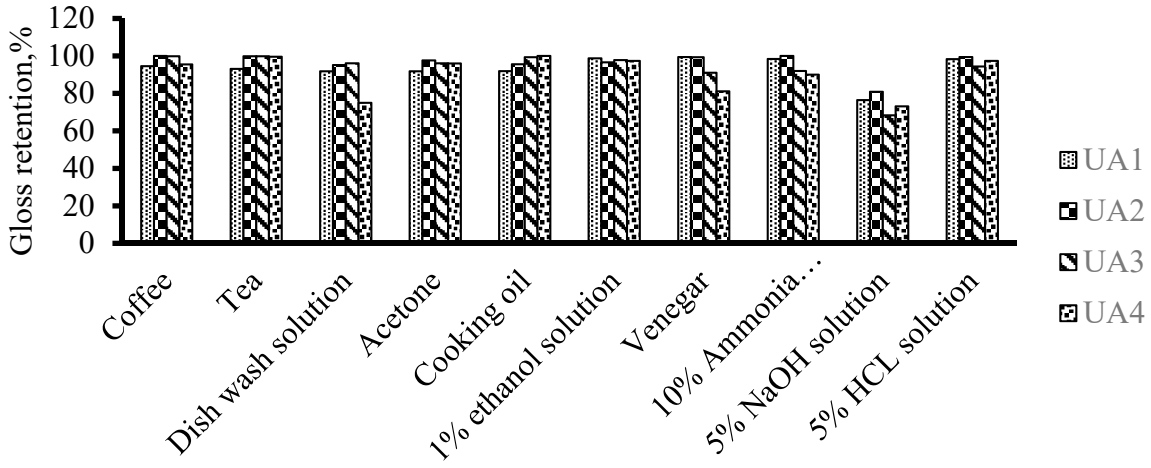

Figure 9 shows the gloss retention of the cured film after 24 hours of chemical aging. In general, all cured films that showed good chemical resistant also showed very high gloss retention. As expected the films that have performed badly in 5% NaOH solution test, showed lower gloss retention ranging from 68-81%. Except in Tea, acetone, cooking oil and 5% HCl solution aging test, UA4 showed lowest gloss retention in dish was solution, vinegar, 10% ammonia solution and 5% NaOH solution aging as compared to the other three oligomers synthesized. As shown in Figure 11, UA2 showing the highest gloss retention for all chemical aging test and follow by UA1 and UA3. This two oligomers showed quite similar performances in all chemical aging resistant tests. The high gloss retention achieved by UA resins (> 90%) was good and fit level for industrial wood coating application.

3. Conclusion

Hydroxyl terminated macromers can be synthesized with 15-70% PFAD. Further reactions of the macromers with TDI and 2-EHA have produced the novel oligomeric urethane acrylate resins that can be cured by UV irradiation. Generally, %PFAD has significant influence in the film properties. 70% PFAD the urethane acrylic does not form good film.. The urethane acrylic oligomers with 15-55% PFAD could be cured readily and have good films properties in term of adhesion, hardness and chemical resistant. PFAD is a valuable bio-resources for wood making UV-curable coatings.

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