MINT R&D Seminar 2000
October 17-19, 2000 MINT, Bangi.

RADIATION CURABLE PRESSURE SENSITIVE ADHESIVES (PSA) FORMULATIONS FROM PALM OIL BASED RESIN

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Abstract

Various low glass transition temperature (T_g) acrylate and methacrylate monomers were mixed with epoxidised palm oil acrylate (EPOLA) with the ratio of 50/50 prior to curing with electron beam (EB) irradiation. Methacrylate monomers such as dicyclopentenyloxyethyl methacrylate (DCPOEMA) and isobornyl methacrylate (ISBMA), although displaying relatively higher adhesive properties compared to others were finally excluded from being further utilised as monomers for PSA because of a very slow curing speed. Literally, it is suggested that poorer adhesive performances of the cured films made from 50/50:EPOLA/monomer mixture as compared to that of 100% monomer was attributed to the lack of compatibility between EPOLA and the particular monomers. Further compatibility investigations were continued using formulations prepared via prepolymer route cured by ultraviolet (UV) irradiation and the results showed that several monoacrylate monomers with polar and non-polar groups exhibited high curing speed as well as good compatibility with EPOLA as shown by their cured film properties such as surface tackiness, peel adhesion and creep resistance. It is also suggested that these monomers were acting as surfactants for EPOLA which consequently enhance their compatibility upon mixing.. Earlier results of the studies on the use of several tackifiers such as poly(vinylmethylether) (PVME), liquid epoxidised natural rubber (LENR) and acrylic oligomer based active tackifier (IRR-153) in the PSA formulations showed that the addition of tackifiers, particularly 3 to 50% IRR-153 into the PSA formulations (while maintaining palm oil contents at 50%) significantly improved the adhesive properties of cured films. The use of tackifiers also reducing or eliminating the needs to employ prepolymer method in preparing PSA formulations since most of their viscosities are already above the optimum level (>500 Cps at 25° C).

Abstrak

Beberapa monomer akrilat dan metakrilat bersuhu peralihan kaca (T_g) rendah telah diformulasikan dengan minyak sawit terepoksida berakrilat (EPOLA) pada nisbah 50/50 sebelum dilakukan penyinaran alur elektron (EB). Monomer metakrilat seperti dwisiklopentenil oksi etil metakrilat (DCPOEMA) dan isobornil metakrilat (ISBMA), walaupun telah menunjukkan ciri-ciri adhesif yang lebih baik jika dibandingkan dengan lain-lain monomer tetapi telah diketepikan untuk kajian seterusnya disebabkan kadar pematangan yang sangat perlahan. Pakar-pakar umumnya berpendapat sifat-sifat adhesif yang lebih rendah terhasil dari formulasi 50/50:EPOLA/monomer berbanding dengan 100% monomer adalah disebabkan kurangnya keserasian diantara EPOLA dan monomer tersebut. Hasil kajian keserasian monomer:EPOLA seterusnya menggunakan kaedah prepolimer menunjukkan beberapa monomer monoakrilat yang mempunyai kumpulan polar dan non-polar telah mempamirkan kadar pematangan yang tinggi disamping keserasian yang bertambah sebagaimana dibuktikan oleh sifat-sifat adhesif seperti kemelekatan, rekatan kupas dan rintangan rayap yang semakin unggul. Juga dicadangkan monomer-monomer ini bertindak sebagai agen aktif permukaan untuk EPOLA yang membolehkan percampuran berlaku dengan lebih mudah. Keputusan awal kajian formulasi PSA menggunakan resin pemelekat seperti poli(vinil metil eter) (PVME), getah asli terepoksida cecair (LENR) dan pemelekat aktif oligomer akrilik (IRR-153 menunjukkan, penambahan 3-50% IRR-153 kedalam formulasi PSA (dengan mengekalkan kandungan resin minyak sawit pada 50%) dengan ketaranya dapat memperbaiki sifat-sifat adhesif matang. Penggunaan resin pemelekat juga dapat mengurang atau menghapuskan kebergantungan kepada kaedah prepolimer dalam penyediaan formulasi PSA memandangkan resin yang terhasil telah mencapai paras kelikatan yang mencukupi (> 500 Cps at 25°C).

1.0 INTRODUCTION

Pressure sensitive adhesives (PSA) form a permanently tacky film after drying of liquid formulations by means of evaporation (conventional method) or radiation (UV/EB) curing. Bonding is effected by slightly pressing the adhesive surface onto the adherend. Conventional PSA can be classified as either **non-permanent (272.2 to 907.2 g/in of 180° peel adhesion)** or **permanent (above 907.2 g/in of 180° peel adhesion).** Adhesives included in the former category find utility in the manufacture of removable tapes, labels, protective laminants and other less durable products, whereas the more permanent adhesives are used for plastic decals, backings for floor tiles, etc. (Perkins 1980).

In 1999 the market segment for the radiation curable PSA in North America and Europe combined was estimated at 2,000 tons/year which is app. 2% of the total radcure products used by the region, whereas, the growth rate of the market segment was forecasted at approximately 15% in Europe and 20% in North America (Lawson 1999; Homer 1999).

The amount of PSA to be applied depends on the adsorptivity of the backings and the requirements imposed on the bonding properties. The dry coat weight for cellular plastics, polymer films and metal foils normally varies between 20-80 g/m^2, while very absorbent substrates such as paper, fabrics, antidrumming board etc. require higher coat weights of 100-300 g/m^2 (Eisenträger and Druschke 1977).

Previous works (Mohd. Hilmi *et al.* 1997; Mohd. Hilmi *et al.* 1998) carried out at the Malaysian Institute for Nuclear Technology Research (MINT), on the studies to investigate the potential use of palm oil based acrylated resins namely EPOLA and palm oil based urethane acrylate (POBUA) for the production of radiation (UV/EB) curable PSA were mainly focused on the use of ISBMA as a monomer. However, the requirements of around 200 to 300 kGy and 2.25×10^{13} to 4.125×10^{13} MeV/cm^2 (6 to 11 times of UV light exposures from a 200 watt/cm, 20 cm UV machine with the condition of 7.5 A current and 4m/min conveyor speed) dose or energy for curing using EB and UV respectively were considered rather high and might lead to overcuring and subsequently the risk of degradation to the irradiated films, especially when using EB irradiation, where, dose variations are less flexible when compared to UV. Employment of N-vinyl-2-pyrrolidone (NVP) into formulations to some extent increased the curing speed but at the expense of adhesive properties. The poor creep resistance results showed by UV/EB curable PSA made of 60/40:EPOLA/ISBMA mixture (Mohd. Hilmi *et al.* 1998) could be considered a setback in determining the properties of PSA. The introduction of tackifying agents such as; poly(vinylmethylether) (PVME), hydrogenated rosin (HR) and aliphatic hydrocarbon resin (AHR) into formulations did little in improving these properties.

The present study is conducted with the aims of searching for new monomers which are most compatible with EPOLA as well as possessing high curing speed without compromising the adhesive properties of PSA such as tackiness, peel adhesion and creep resistance. This study will also searching for methodology of enhancing viscosity of PSA formulations, i.e., either by employing prepolymer method (Karmann and Zöllner 1995) or addition of extremely high viscosity tackifier resin such as IRR-153. It is understood that the optimum viscosity (over 500 Cps at 25°C) of the formulations will minimize flow, adsorption and evaporation rate during coating process which will subsequently produce cured adhesive films with desired thickness of around 10-125 μm (depends upon applications). The curing conditions (inert or air atmospheres) of PSA formulations, whether or not they play active roles in determining the adhesive properties of cured films will also be investigated.

2.0 EXPERIMENTAL

2.1 **Materials**

2.11 Oligomers/resins

EPOLA oligomer used in the present work was prepared in MINT Laboratory through acrylation of the epoxidised palm oil pruducts (EPOP). The acid number (AN), molecular weights (MW) (measured using Tosoh made GPC, model HLC-8020) and T_g (measured using Shimadzu Thermal Analyser, Model DSC-50) of EPOLA are around 29.81, 3200 and -5.0°C respectively. The viscosity of EPOLA, measured using a Brookfield Viscometre Model RVTDV-IICP was about 1200 Cps at 25°C.

Poly(vinylmethylether) (PVME) having MW and T_g (data supplied by manufacturer) around 99,000 and -31°C (242 K) respectively, supplied as 50 wt. % solution in water by Aldrich Chemical Co., USA, liquid epoxidised natural rubber (LENR) having MW and T_g around 38,000 and app. -60 ° C respectively, supplied as 48 wt. % in toluene by MINT Laboratory and IRR-153 which is an acrylic oligomer diluted with 10% tripropylene glycol diacrylate (TPGDA) having extremely high viscosity of ± 220,000 Cps at 60°C supplied by UCB Chemicals (M) Sdn. Bhd. were used as tackifiers. Prior to use, PVME and LENR need to be dried (e.g. vacuum oven at 60° C for 24 hours) while IRR-153 was used as received.

2.12 Monomers/diluents

Most monomers i.e., dicyclopentenyloxyethyl methacrylate (DCPOEMA), isodecyl acrylate (i-DA), isodecyl methacrylate (i-DMA), lauryl methacrylate (LMA), acrylic acid (AA), isobornyl acrylate (ISBOA), isobornyl methacrylate (ISBMA), isooctyl acrylate (i-OA), isononyl acrylate (i-NA), 2-ethylhexyl acrylate (2-EHA), n-butyl acrylate (n-BA), isobutyl acrylate (i-BA), N-vinyl-2-pyrrolidone (NVP) and 1,6-hexanediol diacrylate (1,6-HDDA) employed in this work were supplied by Aldrich Chemical Co., USA, while, phenol diethoxylate acrylate (M-101), phenol tetraethoxylate acrylate (M-102), nonylphenol monoethoxylate acrylate (M-111), nonylphenol tetraethoxylate acrylate (M-113), nonylphenol poly(n=2.5)propoxylate acrylate (M-117), 2-ethylhexyl carbitol acrylate (M-120), 2-hydroxy-3-phenoxy-propyl acrylate (M-5700) and 2(2-ethoxyethoxy)ethyl acrylate (IRR-184) were supplied by Toagosei Chemical Industry Co., Ltd., Japan and UCB Chemicals (M) Sdn. Bhd., Malaysia respectively. Lastly, dimethylaminopropyl acrylamide (DMAPAA) was supplied by Kohjin Co., Ltd., Japan.

2.13 Other additives

Photoinitiator namely Darocure® 1173 (D-1173) product used in UV curing applications was supplied by CIBA-GEIGY Corporation, USA and used as received.

2.2 **Application and Irradiation**

The PSA coating materials with the recipes (based on weight percent) of EPOLA:monomer(± tackifier)/ISBOA/AA/D-1173=50:50 of 85%/10%/5%/0.1% of the total weight, were prepared either through normal mixing method or prepolymer method. The latter involves the formation of partially polymerised resins by purging the above recipes with N_2 gas while intermittently exposed to UV irradiation (a 400 watt, Mercury Lamp UV Irradiation Source of Photochemical Reactors Ltd., U.K.) uniformly along the flanks of the transparent vessel when finally prepolymers (partially polymerised mixtures) were formed as marked by the increased in viscosity. Additional photoinitiator (D-1173), i.e., up to 3% was added before coating the high viscosity prepolymer syrups onto polyethylene terephthalate (PET) films (30-40 μm thickness) with a baker type applicator marked # 2 (50 μm thickness, the parametre used throughout experiments) giving around 20-50 μm thickness of dried films (vary with formulation viscosities). The coated syrups both covered [with transparent silicone treated PET films (inert atmosphere)] or uncovered (air atmosphere) were exposed to UV irradiation by using a

200 watt/cm, medium pressure mercury vapour lamp of IST®-UV Dryer (Switzerland) at 10m/minute giving app. 1.31 x 10^{12} MeV/cm^2 energy per pass, while, the usually low viscosity PSA resins prepared through normal mixing method were subjected to EB irradiation (without covering) by using a 15 cm wide Curetron® (NHV, Japan) at an acceleration voltage of 200 kV, a beam current of 2 mA and a conveyor speed of 22.5 m/min under nitrogen atmosphere giving app. 10 kGy (1 Mrad) per pass.

2.3 **Measurements and Testing**

The viscosity of the PSA formulations are measured using a Brookfield Viscometre Model RVTDV-IICP at 25°C. The 180° peel strength was evaluated following Pressure Sensitive Tape Council Test Method Number 1 (PSTC-1) (Perkins 1980) test in which a strips of 1 inch width adhesive tape was pasted onto a stainless steel panel (SUS 304) and peeling off at a crosshead speed of 300 mm/min by using a Strograph-RI (Toyoseiki Co., Ltd.) 24 hours after pasting and pressing with a 1.8 kg roller. The surface tackiness was measured by using a Probe-Type Tackiness Tester (Rhesca Co., Ltd., Japan) which followed the "IPC-SP-819 IIW SUB-COMMISSION 1A" standard (specified by the supplier), where a 5 mm diameter stainless steel probe being contacted with a specimen for 1 second followed by being peeled off at a speed of 30 mm/sec. The creep resistance was conducted via the Pressure Sensitive Tape Council Test Method Number 7 (PSTC-7) (Perkins 1980) test procedure in which one inch square tape sample is applied to a stainless steel surface mounted in a vertical position after which a 500 gram weight is attached to the tape and the time to failure is measured.

3.0 RESULTS AND DISCUSSION

3.1 **Choice of Monomers-Fox Equation**

Various low T_g monomers, most of them with T_g below -30°C such as listed in Tables 1(a) and 1(b) were mixed with EPOLA (with $T_g \sim -5.0$°C) at 50/50:EPOLA/monomer ratio following the Fox equation (Ward 1983) to produce mixed materials with an expected cured film's T_g around < -20°C. The Fox equation is described below:

$$1/T_g=W_1/T_{g1}+W_2/T_{g2}\ldots\ldots\ldots$$

and $W_1+W_2=1$ (weight fraction)

where, W_1, W_2; weight fraction of each content
T_g; glass transition of a compound (mixture)
T_{g1}, T_{g2}; glass transitions for each component (content)
(T_g is in unit of Kelvin, not in Celcius)

Table 1 (a): List of Monomers Used In PSA Formulations

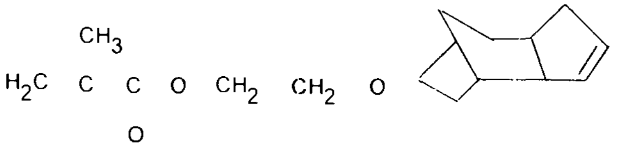
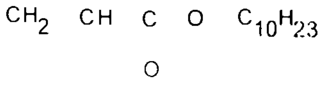
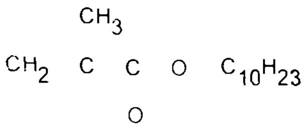
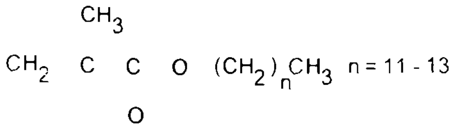
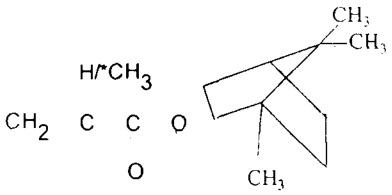
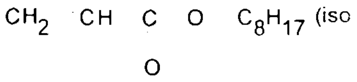
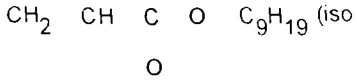
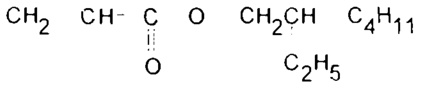
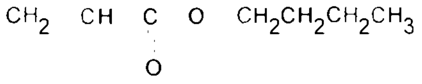
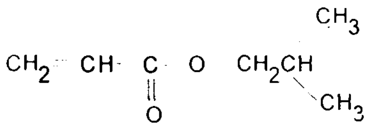
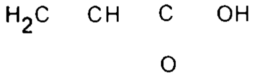
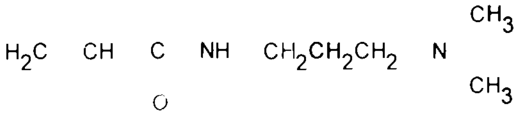
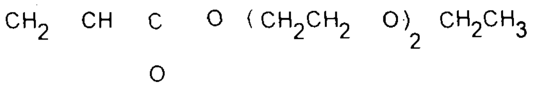
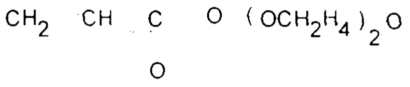
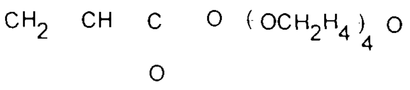
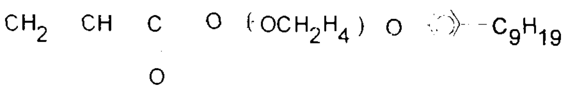
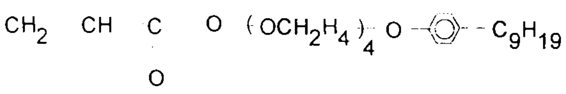
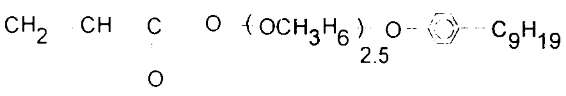
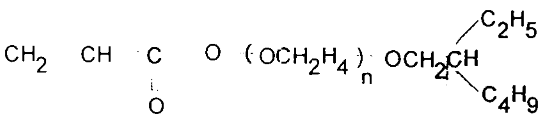
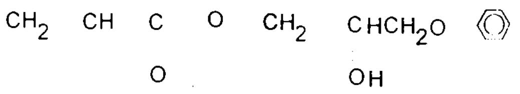
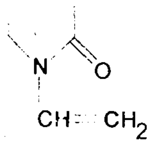
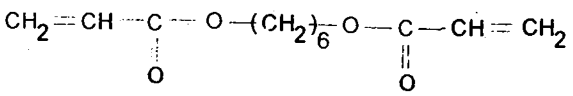
Chemical names (Abbreviations)	Chemical Structures	MW	Viscosity (Cps/25^{0}C)	T_g (^{0}C) (Homopolymers)
DCPOEMA	 $H_2C\ \overset{CH_3}{C}\ \underset{O}{C}\ O\ CH_2\ CH_2\ O$	262	17	25 - 35
i - DA	 $CH_2\ CH\ \underset{O}{C}\ O\ C_{10}H_{23}$	212	2	- 55
i - DMA	 $CH_2\ \overset{CH_3}{C}\ \underset{O}{C}\ O\ C_{10}H_{23}$	226	20	- 70
LMA	 $CH_2\ \overset{CH_3}{C}\ \underset{O}{C}\ O\ (CH_2)_nCH_3\ n = 11 - 13$	254	-	- 65
ISBOA/ *ISBMA	 $CH_2\ \overset{H/*CH_3}{C}\ \underset{O}{C}\ O$	208/ *222	7.5	* - 144
i-OA	 $CH_2\ CH\ \underset{O}{C}\ O\ C_8H_{17}$ (iso	184	14	- 45
i-NA	 $CH_2\ CH\ \underset{O}{C}\ O\ C_9H_{19}$ (iso	-	-	-
2-EHA	 $CH_2\ CH-\underset{O}{\overset{}{C}}\ O\ CH_2\underset{C_2H_5}{CH}\ C_4H_{11}$	184	1-54	- 85
n-BA	 $CH_2\ CH\ \underset{O}{C}\ O\ CH_2CH_2CH_2CH_3$	-	-	- 54
i-BA	 $CH_2\ CH\ \underset{O}{C}\ O\ CH_2\overset{CH_3}{\underset{CH_3}{CH}}$	-	-	- 40

Table 1(b): List of Monomers Used In PSA Formulations

Chemical Names/ Trade Names (Abbreviations)	Chemicals Structures	MW	Viscosity Cps (25^0C)	Tg (^0C)
AA	 $H_2C\ \ CH\ \ \underset{O}{C}\ \ OH$	72.06		
DMAPAA	 $H_2C\ \ CH\ \ \underset{O}{C}\ \ NH\ \ CH_2CH_2CH_2\ \ N\begin{matrix}CH_3\\CH_3\end{matrix}$	156.11		
IRR - 184	 $CH_2\ \ CH\ \ \underset{O}{C}\ \ O\ (CH_2CH_2\ \ O)_2\ \ CH_2CH_3$	188	4.7	- 70
M - 101	 $CH_2\ \ CH\ \ \underset{O}{C}\ \ O\ (OCH_2H_4)_2O$		16	- 8
M - 102	 $CH_2\ \ CH\ \ \underset{O}{C}\ \ O\ (OCH_2H_4)_4\ O$		30	
M - 111	 $CH_2\ \ CH\ \ \underset{O}{C}\ \ O\ (OCH_2H_4)\ O$ — C_9H_{19}		70	17
M - 113	 $CH_2\ \ CH\ \ \underset{O}{C}\ \ O\ (OCH_2H_4)_4\ O$ — C_9H_{19}		90	- 20
M - 117	 $CH_2\ \ CH\ \ \underset{O}{C}\ \ O\ (OCH_3H_6)_{2.5}\ O$ — C_9H_{19}		110	- 3
M - 120	 $CH_2\ \ CH\ \ \underset{O}{C}\ \ O\ (OCH_2H_4)_n\ OCH_2CH\begin{matrix}C_2H_5\\C_4H_9\end{matrix}$		5	- 65
M - 5700	 $CH_2\ \ CH\ \ \underset{O}{C}\ \ O\ \ CH_2\ \ \underset{OH}{CHCH_2O}$		140	17
NVP		111	2.07	175
1,6 - HDDA	 $CH_2=CH-\underset{O}{C}-O-(CH_2)_6-O-\underset{O}{\overset{}{C}}-CH=CH_2$	226.3	20 - 35	

3.2 **EB Irradiation-Search For Monomers**

Table 2 shows the properties of PSA formulations prepared via normal mixing method cured by EB. Most of the monomers used exhibited high curing speed except for the methacrylates, i.e., DCPOEMA, ISBMA, i-DMA and LMA. Among the acrylate monomers, ISBOA shows the fastest curing rate and highest tackiness which qualifies it to be further utilised as a speed enhancer in other formulations together with acrylic acid (AA) which was later introduced as a hardener (might copolymerises with other monomers in the present of photoinitiator and UV light). Although, the adhesive properties shown by DCPOEMA and ISBMA were reasonably high but their slow curing speed hinders them from being considered for further use in PSA formulations.

Table 2: Properties of PSA Formulations By EB Curing-Baker Type Bar Coater # 2 (50 µm) (Following Ordinary Mixing Method)

Components	**Composition % By Weight**										
	AD 1	**AD 2**	**AD 3**	**AD 4**	**AD 5**	**AD 6**	**AD 7**	**AD 8**	**AD 9**	**AD 10**	**AD 11**
EPOLA	50	50	50	50	50	50	50	50	50	50	50
DCPOEMA	50										
2 – EHA		50									
n – BA			50								
i – BA				50							
ISBMA					50						
ISBOA						50					
i – DA							50				
i – DMA								50			
i – OA									50		
i – NA										50	
LMA											50
Properties											
Dose (# Passes)	9	2	2	1	10	1	3	> 20 not cure	2	2	> 11 not cure
Viscosity (Cps/25°C)	179.5	-	-	-	134.4	-	-	57.2	36.8	44.1	-
Tackiness (gf)	126.7	30.4	25.0	14.9	33.3	181.6	30.5	-	23.8	24.2	-
Peel Adhesion (g/in)	15	1	2	2	100	8	3	-	3	3	-
Mode of Failure	CRF	CRF	CRF	CRF	BF	BF	CRF	-	CRF	CRF	-

Note : CRF (Clean Release Failure); BF (Backing Failure) Dose : 30 kGy/ Pass

3.3 **UV Curing-Prepolymer Method**

Further search for good compatibility monomers was conducted by using UV irradiation since its machine is less complicated to handle as compared to that of EB and the dose or light intensity is easier to control, i.e., by merely changing the conveyor speed or varying the # of passes, giving only small variations in intensity (measured by using UV Curing Radiometre) and hence reduces the risk of overcuring and consequently degradation to the cured films as compared to the bigger intensity differences in case of EB irradiation, which otherwise might cause the adverse effects.

The prepolymer method as described in sec. 2.2 was employed on all formulations. The behaviour of formulations AD12 to AD14 shown in Table 3 indicates that the adhesion properties were superior when using baker-type applicator with thickness indicator # 2 (50 µm). Thus this parametre was used throughout experiments. Table 3 also displayed the effect of EPOLA/monomer ratio on adhesive properties as shown by formulations

AD15 to AD20; where PSA formulations made of 100% monomers although showed rather slow curing speed but their adhesive properties i.e., tackiness and peel strenght were superior. Sudden decline in adhesive properties when adding 25% to 50% EPOLA illustrated that these monomers are incompatible (hardly miscible) with EPOLA oligomer.

Table 3: Properties of PSA Formulations Following Prepolymer Method By UV Curing In Inert.

Components	Composition % By Weight								
	AD 12	AD 13	AD 14	AD 15	AD 16	AD 17	AD 18	AD 19	AD 20
EPOLA					50	25	50	25	
i- NA	100	100	100						
n – BA				100	50	75	50	75	100
NVP							15	15	15
ISBOA	10	10	10	10	10	10			
AA	5	5	5	5	5	5			
D - 1173	3	3	3	3	3	3	3	3	3
Properties									
Coat. Thickness (μm)	25	37.5	50	50	50	50	50	50	50
Dose (# Passes)	3	3	3	13	6	4	2	6	25
Viscosity (Cps/25°C)	948.0	948.0	948.0	184.0	152.0	38.0	-	-	-
Tackiness (gf)	298.9	402.3	441.7	413.2	128.2	168.5	32.0	81.5	277.8
Peel Adhesion (g/in)	80	150	210	2500	10	20	5	4	600
Mode of Failure	CRF	CRF	CRF	BF	CRF	CRF	CRF	AF	CRF

Note : CRF (Clean Release Failure); BF (Backing Failure); AF (Adhesive Failure)
Dose : 1.31 x 10^{12} MeV/cm^2 per pass

Table 4 further explains that the prepolymer method was more superior than that of normal mixing since it produces PSA formulations with higher viscosities, better curing speed and better adhesive performances. The most notable one is that when using baker-type applicator marked # 2 (50 μm) for coating, the PSA formulations made from prepolymer route produced cured films with favourable thickness of 42-48 μm as compared to only 25-30 μm for normal mixing method. It is suggested that the increased viscosities of the formulations made by prepolymer method minimised the flow of wet resins on the substrates after coating and thus maintaining the predetermined coating thickness. Also, the formation of prepolymers as marked by the increased in viscosities will similarly enhance adhesive properties such as; surface tackiness and peel adhesion.

Table 4: Properties of PSA Formulations By UV Curing In Inert- A Comparison Between Normal Mixing and Prepolymer Methods

Components	Composition % By Weight					
	AD 21	AD 22	AD 23	AD 24	AD 25	AD 26
EPOLA		50	25		50	25
M – 101	100	50	75	100	50	75
ISBOA	10	10	10	10	10	10
AA	5	5	5	5	5	5
D – 1173	3	3	3	3	3	3
	Prepolymer	**Method**		**Normal**	**Mixing**	**Method**
Properties						
Dried film Thickness (μm)	48	43	42	25	30	28
Dose (# Passes)	4	5	5	5	6	6
Viscosity (Cps/25°C)	281.0	166.4	118.8	13.1	99.5	35.1
Tackiness (gf)	268.5	88.8	82.1	74.4	77.0	78.3
Peel Adhesion (g/in)	100	5	8	10	5	5
Mode of Failure	CRF	CRF	CRF	CRF	CRF	CRF

Note : CRF (Clean Release Failure) ; Dose : 1.31 x 10^{12} MeV/cm^2 per pass

3.4 **Surfactants Like Monomers**

Current experimental results displayed that common monomers [Table 1(a)] commercially employed in PSA formulations such as; 2-EHA, n-BA, i-BA, i-DA, i-OA and i-NA showed very poor compatibility with EPOLA as shown by the sudden drop in adhesive properties when 25 to 50% EPOLA was added to the formulations (see Table 3). So, it is necessary to continue searching for monomers with better compatibility without compromising the essential requirements of PSA properties such as; high curing speed and reasonably high adhesive performances.

Incompatibility results from the existence of high surface tension between two immiscible media (Zahariah *et al.* 1997). In order to promote the miscibility, this surface tension must be removed or reduced and this can only be done by the so called surface active agents or surfactants which are amphiphilic compounds consisting of a hydrophobic (hates water) and a hydrophilic (loves water) moieties. The presence of this two moieties within a molecule causes it to partition preferentially at the interface between fluids of different polarity and hydrogen bonding and thus lowers the interfacial energy or surface tension (Thambirajah 1998) which later improves miscibility or compatibility.

Table 5: Properties of PSA Formulations By UV Curing In Inert-Baker Type Bar Coater # 2 (50 μm)
(Following Prepolymer Method)

Components	**Composition % By Weight**									
	AD 27	**AD 28**	**AD 29**	**AD 30**	**AD 31**	**AD 32**	**AD 33**	**AD 34**	**AD 35**	**AD 36**
EPOLA	**50**	**50**	**50**	**50**	**50**	**50**	**50**	**50**	**50**	**50**
M – 101	**50**									
M – 102		**50**								
M – 111			**50**							
M – 113				**50**						
M – 117					**50**					
M – 120						**50**				
M – 5700							**50**			
IRR – 184								**50**		
DMAPAA									**50**	**45**
PVME										**5**
ISBOA	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
AA	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**
D – 1173	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
Properties										
Dose (# Passes)	**5**	**5**	**5**	**6**	**6**	**7**	**3**	**3**	**4**	**8**
Viscosity (Cps/25^{0}C)	**166.4**	**138.4**	**217.1**	**249.0**	**330.9**	**139.5**	**290.5**	**114.3**	**3,570**	**10,670**
Tackiness (gf)	**88.8**	**54.6**	**196.3**	**125.0**	**199.4**	**122.0**	**140.6**	**59.3**	**404.3**	**448.1**
Peel Adhesion (g/in)	**5**	**5**	**190**	**15**	**40**	**8**	**75**	**5**	**175**	**280**
Creep Resistance (hr) ^{a}25^{0}C	**> 72 Intact**	**> 72 Intact**	**> 72 Intact**	**> 72 Intact**	**> 72 Intact**	**> 72 Intact**	**>72 Intact**	**< 1 min.**	**> 72 Intact**	**> 72 Intact**
^{a}60^{0}C	**> 72 Intact**	**> 72 Intact**	**> 72 Intact**	**> 72 Intact**	**> 72 Intact**	**> 72 Intact**	**> 72 Intact**	**-**	**> 72 Intact**	**>72 Intact**
^{b}25^{0}C	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**Int.,> 72**
Mode of failure	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**

Note : CRF (Clean Relaese Failure); Dose :1.31 x 10^{12} MeV/cm^2 Per pass; a: 500g load; b: 1 kg load

Ethoxylated/propoxylated nonyl phenol acrylates and other monomers having polar and non-polar groups as listed in Table 1(b) were later chosen as monomers for PSA not only because of their low T_g but it was also tought that they are capable of functioning like surfactants (Glotfelter 1997) and thus promote compatibility. In general, most of these monomers have shown reasonably high curing speed (see Table 5) with the exception of long chain 2-(ethyl)hexylcarbitol acrylate, M-120, (formulation AD32) and formulation AD36 which could be due to the addition of 5% PVME into DMAPAA monomer. As for the adhesive performances four monomers namely; nonylphenol monoethoxylate acrylate (M-111), nonylphenol tetraethoxylate acrylate (M-113), nonylphenol poly(n=2.5)propoxylate acrylate (M-117), 2-hydroxy-3-phenoxy-propyl acrylate (M-5700) and dimethylaminopropyl acrylamide (DMAPAA) exhibited a reasonably high adhesive properties i.e., tackiness and peel adhesion, where the most outstanding performances were shown by DMAPAA (also known for its readily copolymerises with most common monomers through the reactive amino group) and secondly by M-111 monomers. All of them also displayed a clean release mode of failure during peel tests. When samples were subjected to creep resistance or holding tests at 25°C (room temperature) and 60°C, all the films were remained intact to the steel panel after 72 hours.

3.5 Effect of Multifunctional (MF) Monomer and Tackifiers On Properties of PSA

Brief studies on the effect of MF monomer has been performed and the initial results shown in figures 1 and 2 indicated that the addition of MF monomer i.e., 1,6-HDDA, into formulations improves the adhesive properties. Further studies will be conducted in detail to investigate the effect of employing various other common MF monomers such as; tetraethyleneglygol diacrylate (TEGDA), polyethyleneglycol diacrylate-400 (PEGDA-400), trimethylolpropane triacrylate (TMPTA) and pentaerythritol triacrylate (PETA) at different concentrations on the adhesive properties.

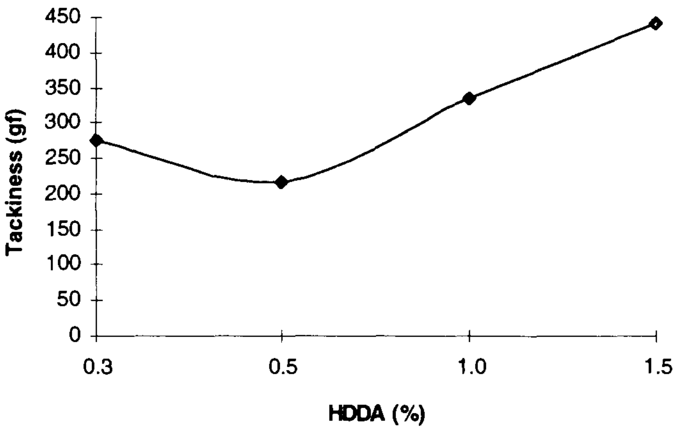


Figure 1 : Crosslinker (HDDA) Concentration of PSA Formulation (AD 14) vs Tackiness

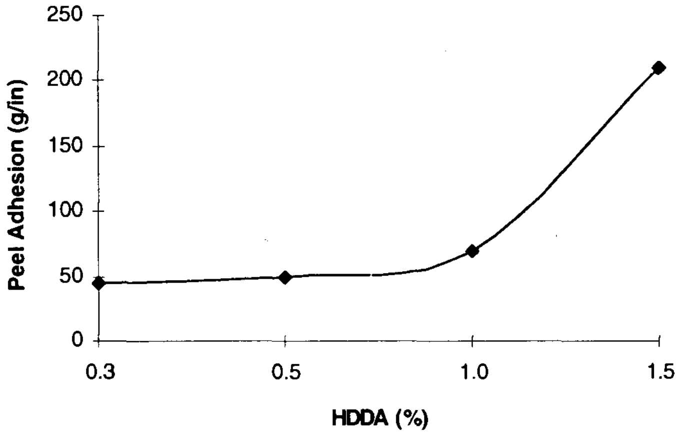


Figure 2 : Crosslinker (HDDA) Concentration of PSA Formulation (AD 14) vs Peel Adhesion

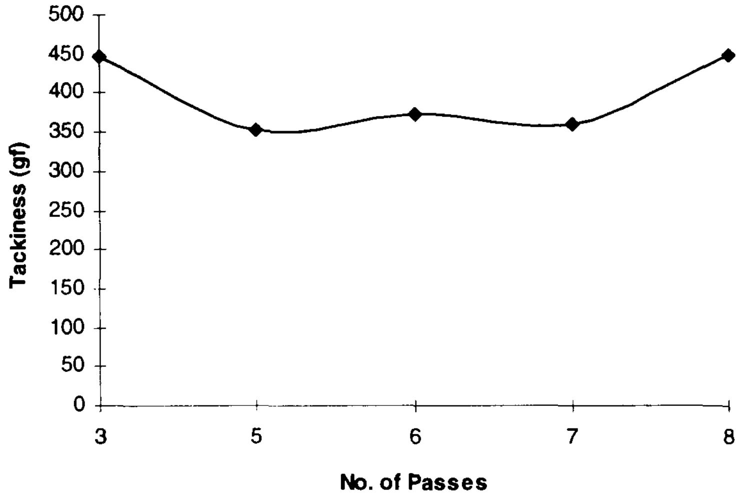


Figure 3 : Effect of Dose (# passes) On Tackiness of PSA Formulation (AD 35) Blended with 5% Tackifier (PVME)

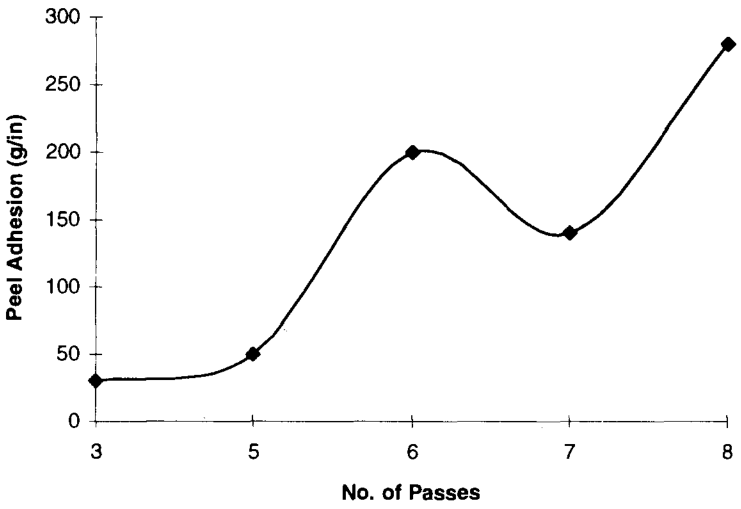


Figure 4 : Effect of Dose (# passes) On Peel Adhesion of PSA Formulation (AD 35) Blended with 5% Tackifier (PVME)

Similarly, addition of 5% PVME tackifier to the PSA formulation such as shown in Table 5 (formulation AD36) and figures 3 and 4 significantly enhanced its adhesive performances, but, at a higher irradiation dose as compared to that of without tackifier. Further studies will be performed to investigate the effect of varying PVME contents on the adhesive properties.

On the other hand, the use of LENR, prepared in MINT Laboratory (Dahlan 1998) as tackifier (see figures 5, 6 & 7) increased both the viscosities and tackiness but decreased the peel adhesion. Figure 6 shows that the use of 5-7% LENR in PSA formulations was sufficient in obtaining the maximum tackiness value. In the future studies an attempt will be made to improve the peel adhesion of LENR containing formulations by incorporating up to 1.5% MF monomers such as 1,6-HDDA, the task which is considered worthwile since LENR, similar to EPOLA is one of Malaysian indigenous product.

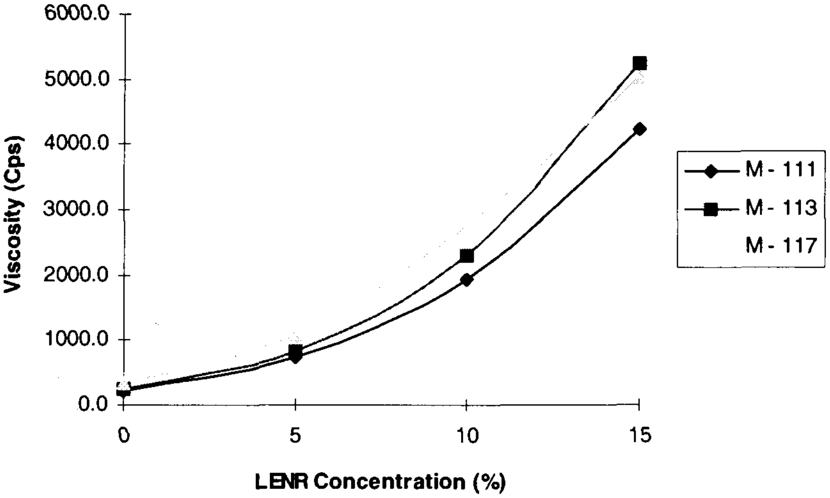


Figure 5 : LENR Concentration vs Viscosity

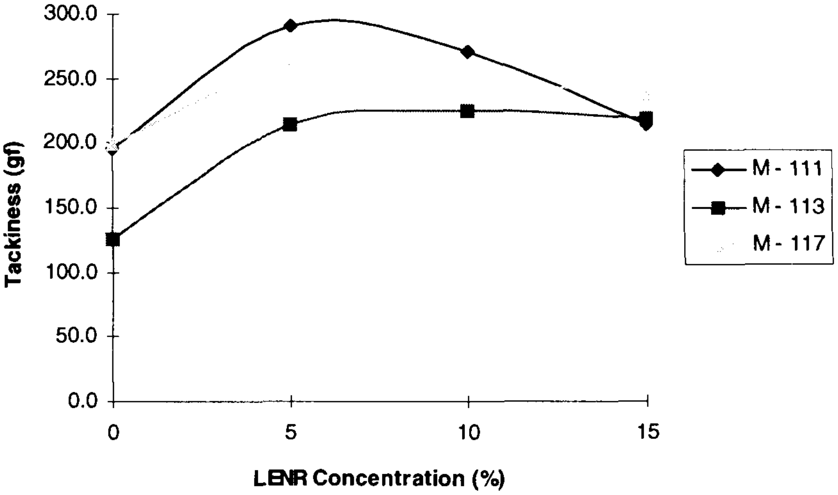


Figure 6 : LENR Concentration vs Tackiness

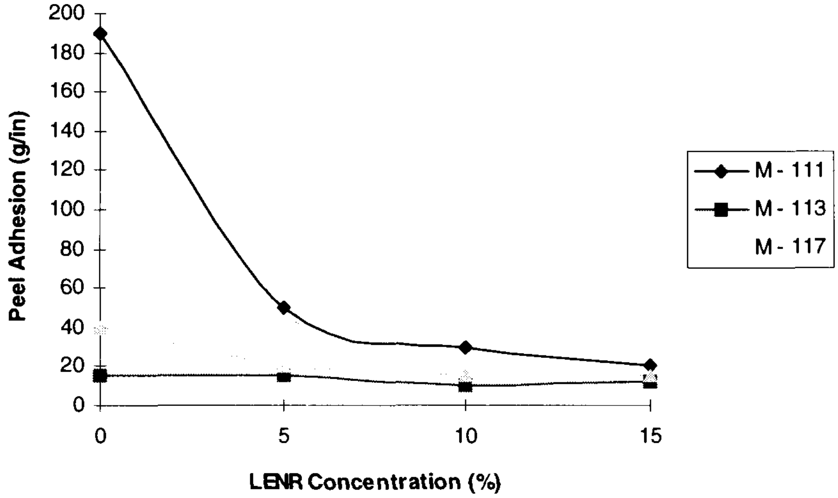


Figure 7 : LENR Concentration vs Peel Adhesion

The most outstanding adhesive performances so far were shown by formulations using IRR-153 as an active tackifier as displayed in Tables 6(a), (b) & (c). Addition of 3 to 50% IRR-153 in PSA formulations using 50% palm oil resin (EPOLA) and monomer M-111 as shown in Table 6(a) significantly increased the viscosity as well as the tackiness and peel adhesion of the cured films.

Table 6(a): Effect of Tackifier IRR-153 On Properties of PSA Formulations Cured By UV

Components		**Composition % By Weight**									
		AD37	**AD38**	**AD39**	**AD40**	**AD41**	**AD42**	**AD43**	**AD44**	**AD45**	**AD46**
EPOLA (1000 Cps/ 25°C)		**50**	**50**	**50**	**50**	**50**	**50**	**50**	**50**	**50**	**50**
M-111 (70 Cps/ 25°C)		**47**	**45**	**43**	**40**	**35**	**30**	**20**	**15**	**10**	**0**
IRR-153 (220,000 Cps/ 60°C)		**3**	**5**	**7**	**10**	**15**	**20**	**30**	**35**	**40**	**50**
ISBOA (7.5 Cps/25°C)		**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
AA		**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**
D- 1173		**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
Properties											
Dose (# Passes)	**inert**	**2**	**2**	**2**	**2**	**2**	**2**	**2**	**2**	**2**	**2**
	air		**10**	**4**	**10**	**5**	**5**	**5**	**6**	**4**	**5**
Viscosity (Cps/25°C)		**532.0**	**560.0**	**610.0**	**750.0**	**864.0**	**1440.0**	**3550.0**	**3800.0**	**7440.0**	**9620.0**
Tackiness (gf)	**inert**	**229.2**	**287.1**	**340.5**	**385.9**	**480.4**	**505.9**	**480.0**	**391.8**	**374.4**	**355.9**
	air		**355.8**	**377.0**	**561.3**	**563.2**	**586.5**	**572.2**	**569.5**	**516.5**	**407.6**
Peel Adhesion (g/in)	**inert**	**125.0**	**130.0**	**200.0**	**230.0**	**240.0**	**250.0**	**280.0**	**280.0**	**280.0**	**475.0**
	air		**430.0**	**450.0**	**450.0**	**500.0**	**670.0**	**825.0**	**570.0**	**710.0**	**850.0**
Mode of failure	**inert**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**
	air		**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**	**CRF**

Note: CRF (Clean Release Failure), Dose: 1.31 X 10^{12} MeV/cm^2 per pass

Curing in air produced higher tackiness and peel adhesion as compared to that of in inert but with the disadvantages of slightly slower curing due to oxygen inhibition effect which is inherent in the UV curing of acrylates. Apart from curing under nitrogen blanket, which is sometimes not practical due to instrument set up and limited budget allocations, utilising higher photoinitiator concentrations (3-5%) and the inclusion of Irgacure 184 into the formulations are generally recommended to solve this surface cure problems (Ciba 1999). Table 6(a) also demonstrated that in general, PSA properties showed the overall satisfactorily good performances after the addition of 5 to 50% IRR-153 tackifier where, they reached maximum level at 20-30% after which, in most cases the tackiness and peel adhesion of the cured films started to slightly decrease and level respectively. This might be due to the fact that higher IRR-153 content (above 30%) will result in higher viscosity formulations which will consequently produced higher coating thickness and subsequently insufficient UV light to produce radicals for 100% curing at the inner parts of coating layers. This shortcoming however, might be overcome by incorporating (0.5-1%) Bis Acyl Phosphine Oxide (BAPO) class of UV curing photoinitiator such as Irgacure 819 in addition to α-hydroxyketone type initiator such as Ciba's D-1173 for through curing of thicker sections (Ciba 1999).

Too thin the formulations (very low viscosity, i.e., below ~500 Cps at 25°C) might cause too much flow, evaporation and adsorption to the porous substrates such as paper, whereas, too thick the formulations (very high viscosity) might hinder smooth flow during coating process (at room temperatures) where roll-coaters are normally employed in an actual production line. Both factors contribute towards inconsistency in acquiring good wettability, uniformity of coatings and desired thickness of cured adhesive films. However, in an industrial applications, a too high viscosity formulations are usually be heated to 30-60°C to obtain a consistency low enough for smooth coating process.

Table 6(b): Effect of Tackifier IRR-153 On Properties of PSA Formulations Cured By UV

Components		**Composition % By Weight**								
		AD47	**AD48**	**AD49**	**AD50**	**AD51**	**AD52**	**AD53**	**AD54**	**AD55**
EPOLA		50	50	50	50	50	50	50	50	50
M-117 (110 Cps/ 25°C)		47	45	40						
M-5700 (140 Cps /25°C)					35	30	20			
DMAPAA (572 Cps/25°C)								47	43	45
IRR-153		3	5	10	15	20	30	3	7	15
ISBOA		10	10	10	10	10	10	10	10	10
AA		5	5	5	5	5	5	5	5	5
D-1173		3	3	3	3	3	3	3	3	3
Properties										
Dose (# Passes)	**Inert**	3	3	2	1	1	1	1	1	1
	Air	8	8	10	5	5	5	2	2	2
Viscosity (Cps/25°C)		556.0	558.0	778.0	780.0	1480.0	6880.0	3950.0	10,800.0	25,000.0
Tackiness (gf)	**Inert**	282.3	312.0	365.1	199.0	191.3	255.9	283.3	380.9	307.3
	Air	531.4	540.5	569.3	265.3	290.0	268.0	400.6	568.6	356.5
Peel Adhesion (g/in)	**Inert**	20.0	40.0	50.0	255.0	230.0	200.0	200.0	250.0	380.0
	Air	120.0	200.0	220.0	350.0	600.0	650.0	300.0	400.0	450.0
Mode of failure	**Inert**	CRF	CRF	CRF	CRF	CRF	CRF	CRF	CRF	CRF
	Air	CRF	CRF	CRF	AF	AF	AF	CRF	CRF	CRF

Note: CRF (Clean Release Failure), AF (Adhesive Failure), Dose: 1.31 X 10^{12} MeV/cm^2 per pass

Table 6(b) shows that the use of monomer DMAPAA together with tackifier IRR-153 (AD53-AD55) also produced very good curing and adhesive performances followed by formulations AD50-AD52 (monomer M-5700). The high viscosity formulation at 15% IRR-153 (AD55) might require heating (above 30°C) to provide smooth and uniform coating applications.

Table 6(c): Effect of Tackifier IRR-153 On Properties of PSA Formulations Cured By UV

Components		**Composition % By Weight**			
		AD56	**AD57**	**AD58**	**AD59**
EPOLA		**50**	**50**	**50**	**50**
IRR-184 (47 Cps/ 25°C)		**40**	**30**	**20**	**10**
IRR-153		**10**	**20**	**30**	**40**
ISBOA		**10**	**10**	**10**	**10**
AA		**5**	**5**	**5**	**5**
D- 1173		**3**	**3**	**3**	**3**
Properties					
Dose (# Passes)	**Inert**	**3**	**3**	**2**	**5**
	Air	**8**	**10**	**8**	**10**
Viscosity (Cps/25°C)		**111.0**	**364.0**	**1320.0**	**3850**
Tackiness (gf)	**Inert**		**156.2**	**220.6**	**318.3**
	Air	**128.5**	**142.2**	**167.2**	**227.2**
Peel Adhesion (g/in)	**Inert**		**80.0**	**70.0**	**150.0**
	Air		**450.0**	**430.0**	**550.0**
Mode of failure	**Inert**	**CRF**	**CRF**	**CRF**	**CRF**
	Air		**CRF**	**AF**	**CRF**

Note: CRF (Clean Release Failure), AF (Adhesive Failure), Dose: 1.31 X 10^{12} MeV/cm^2 per pass

In general, the curing and adhesive performances of PSA formulations using monomer 2(2-ethoxyethoxy)ethyl acrylate (IRR-154) together with tackifier IRR-153 shown in Table 6(c) are the least impressive of all monomers, i.e., low curing speed and relatively lower adhesive properties as compared to that of other monomers displayed in Tables 6(a) & 6(b).

4.0 CONCLUSIONS

- From this study it was found that the use of prepolymer method in PSA formulations produced better coating, curing and adhesive performances compared to the normal mixing method as has previously been employed ☺.

- So far, two monomers namely nonylphenol monoethoxylate acrylate (M-111) and dimethylaminopropyl acrylamide (DMAPAA) were found to be most compatible with EPOLA as shown by the outstanding performances of their coatings, curing and adhesive properties (of the cured films) based on 50/50:EPOLA/monomer formulations ☺.

- This study also revealed that, IRR-153 has come up as the most suitable and effective (an acrylic based active) tackifier to be incorporated into the PSA formulations as displayed by the much improved performances of their coatings, curing and adhesive properties compared to that of shown by other tackifiers ☺.

◘ The use of IRR-153 as tackifier, also reducing or eliminating the needs to employ prepolymer method in preparing PSA formulations since most of their viscosities are already above the optimum level (>500 Cps at 25° C) ☺.

5.0 ACKNOWLEDGMENT

Thanks are due to those who directly and constantly contribute to and support this work especially all staffs of Radiation Curing of Surface Coatings Project Group namely Dr. Nik Ghazali Nik Salleh and Ms. Mek Zah Salleh. Authors also, would like to appreciate all useful suggestions given by Prof. Dr. Reiner Mehnert of the Institute of Surface Modifications, Leipzig, Germany during his short visit to MINT.

Also, the authors would like to extend their gratitude to the Head of Advanced Oleochemical Technology Centre (AOTC), Malaysian Palm Oil Board (MPOB), Dr. Salmiah Ahmad and other AOTC staffs particularly Mr. Azman Rafie for their continuous support for this project, i.e., by supplying epoxidised palm oil products (EPOP). Lastly, we would like to thank Dr. Dahlan Hj. Mohd. for the permission to use the LENR and Mr. Zahid Abdullah for extending helping hands in one way or another.

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Table 6(b) shows that the use of monomer DMAPAA together with tackifier IRR-153 (AD53-AD55) also produced very good curing and adhesive performances followed by formulations AD50-AD52 (monomer M-5700). The high viscosity formulation at 15% IRR-153 (AD55) might require heating (above 30°C) to provide smooth and uniform coating applications.

Table 6(c): Effect of Tackifier IRR-153 On Properties of PSA Formulations Cured By UV

Components		**Composition % By Weight**			
		AD56	**AD57**	**AD58**	**AD59**
EPOLA		**50**	**50**	**50**	**50**
IRR-184 (47 Cps/ 25°C)		**40**	**30**	**20**	**10**
IRR-153		**10**	**20**	**30**	**40**
ISBOA		**10**	**10**	**10**	**10**
AA		**5**	**5**	**5**	**5**
D- 1173		**3**	**3**	**3**	**3**
Properties					
Dose (# Passes)	**Inert**	**3**	**3**	**2**	**5**
	Air	**8**	**10**	**8**	**10**
Viscosity (Cps/25°C)		**111.0**	**364.0**	**1320.0**	**3850**
Tackiness (gf)	**Inert**		**156.2**	**220.6**	**318.3**
	Air	**128.5**	**142.2**	**167.2**	**227.2**
Peel Adhesion (g/in)	**Inert**		**80.0**	**70.0**	**150.0**
	Air		**450.0**	**430.0**	**550.0**
Mode of failure	**Inert**	**CRF**	**CRF**	**CRF**	**CRF**
	Air		**CRF**	**AF**	**CRF**

Note: CRF (Clean Release Failure), AF (Adhesive Failure), Dose: 1.31 X 10^{12} MeV/cm^2 per pass

In general, the curing and adhesive performances of PSA formulations using monomer 2(2-ethoxyethoxy)ethyl acrylate (IRR-154) together with tackifier IRR-153 shown in Table 6(c) are the least impressive of all monomers, i.e., low curing speed and relatively lower adhesive properties as compared to that of other monomers displayed in Tables 6(a) & 6(b).

4.0 CONCLUSIONS

- From this study it was found that the use of prepolymer method in PSA formulations produced better coating, curing and adhesive performances compared to the normal mixing method as has previously been employed ☺.

- So far, two monomers namely nonylphenol monoethoxylate acrylate (M-111) and dimethylaminopropyl acrylamide (DMAPAA) were found to be most compatible with EPOLA as shown by the outstanding performances of their coatings, curing and adhesive properties (of the cured films) based on 50/50:EPOLA/monomer formulations ☺.

- This study also revealed that, IRR-153 has come up as the most suitable and effective (an acrylic based active) tackifier to be incorporated into the PSA formulations as displayed by the much improved performances of their coatings, curing and adhesive properties compared to that of shown by other tackifiers ☺.

- The use of IRR-153 as tackifier, also reducing or eliminating the needs to employ prepolymer method in preparing PSA formulations since most of their viscosities are already above the optimum level (>500 Cps at 25° C) ☺.

5.0 ACKNOWLEDGMENT

Thanks are due to those who directly and constantly contribute to and support this work especially all staffs of Radiation Curing of Surface Coatings Project Group namely Dr. Nik Ghazali Nik Salleh and Ms. Mek Zah Salleh. Authors also, would like to appreciate all useful suggestions given by Prof. Dr. Reiner Mehnert of the Institute of Surface Modifications, Leipzig, Germany during his short visit to MINT.

Also, the authors would like to extend their gratitude to the Head of Advanced Oleochemical Technology Centre (AOTC), Malaysian Palm Oil Board (MPOB), Dr. Salmiah Ahmad and other AOTC staffs particularly Mr. Azman Rafie for their continuous support for this project, i.e., by supplying epoxidised palm oil products (EPOP). Lastly, we would like to thank Dr. Dahlan Hj. Mohd. for the permission to use the LENR and Mr. Zahid Abdullah for extending helping hands in one way or another.

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