

Development of Radiation-curable Resin based on Natural Rubber**

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43000 Kajang, MALAYSIAAbstract

A new radiation curable resin based on natural rubber has been developed. The resin was based on the reaction between low molecular weight epoxidised natural rubber and acrylic acid. When formulated with reactive monomers and photoinitiator, it solidified upon irradiation with UV light. The resin may find applications in coating for cellulosic-based substrates and pressure-sensitive adhesive.

INTRODUCTION

Malaysia is one of the world's biggest producer of natural rubber [1]. There has always been great interest in the modifications of natural rubber as a means of improving the properties of it as well as to develop new materials. Various products such as chlorinated [2], hydrochlorinated [3], epoxidised [4,5], grafted [6] and liquid [7,8] natural rubber have been reported.

* A lecture prepared for the Workshop on Surface Finishing by Radiation Curing Technology, being held at Kompleks PUSPATI, Bangi, 8-9 September, 1993.

Natural rubber consists of long chain molecules, each with repeated unsaturated double bonds at every five carbon atoms [9]. The unsaturated double bond is the functional group of the rubber molecule which can be reacted to form new materials [10,11,12,13].

Recently, epoxidised natural rubber (ENR) has been commercially produced by a local company. Its development was originally carried out at MRPRA in late 1970s before shifting to RRIM for scale-up studies in 1980s.

The company produces two grades of ENR i.e. ENR-25 (epoxide content of 25 mole %) and ENR-50 (epoxide content of 50 mole %). Both products are in the form of solid with estimated weight average molecular weight, \bar{M}_w , of over 300,000. To make the products more useful, methods have been established by RRIM and UKM to lower the molecular weight of ENR. The availability of low molecular weight ENR enables studies to be carried out to prepare radiation-curable resin based on natural rubber [14]. For this country, besides palm oil [15], rubber holds a promising potential to be the next renewable raw material substitutes for industrial chemicals especially radiation curable resins.

The majority of the radiation curable resins currently commercially available are products of non-renewable petroleum-based synthetic raw materials. This report briefly describes basic formulations necessary for a newly developed low molecular weight epoxidised natural rubber acrylate (ENRA) to be used as UV curable resin.

EXPERIMENTAL

Materials: Low molecular weight epoxidised natural rubber (ENR) with various molecular weights were supplied by courtesies of Dr. Ibrahim Abdullah, Chemistry Department, UKM and Dr. Sidek Dulngali, RRIM. The former were prepared from ENR supplied by Guthrie Corp. Berhad, Chemara, Negeri Sembilan. For this formulation work the resin was prepared from low molecular weight ENR-25 supplied by UKM with \bar{M}_w and \bar{M}_n of 147,000 and 39,000 respectively. Acrylic acid which contained 200 ppm hydroquinone monomethyl ether (Merck, 99%) and toluene (Merck, 99%) were used as received. Triethylamine (Merck, 99%), p-methoxyphenol (Aldrich, 98%) were used as catalyst and inhibitor respectively.

Two monomers i.e. tripropylene glycol diacrylate (TPGDA) and trimethylol propane triacrylate (TMPTA); three photoinitiators and photoactivator i.e. benzophenone (BP) and 1-benzoylcyclohexanol (Irgacure 184) and N-methyl diethanol amine (N-MDEOA) were used for formulation.

Synthesis Apparatus: The apparatus involved were 1 L round-bottomed flask equipped with a condenser, a thermometer, a mechanical stirrer and a dropping funnel.

Synthesis Procedure: The low molecular weight ENR sample was first dissolved in toluene in a reaction flask to a required percentage (v/w). 0.5 or 1.0% p-methoxyphenol was mixed with 1.0% triethylamine before adding to the reactants.

The mixture was stirred and heated up to 100°C. Then acrylic acid was added dropwise. The temperature was maintained throughout the reaction. The progress of the reaction was monitored by measuring the acid number of the mixture.

Formulation Procedure: When the acrylation reaction terminated at certain acid number, toluene was replaced with a reactive monomer i.e. TPGDA or TMPTA by rotary evaporation. Then the complete formulations were prepared by adding other relevant chemicals as indicated in Tables 3 to 5. Their viscosities were measured using a Well-Brookfield DV II viscometer model RVTDV-II CP with a spindle # CP-41. The formulations were later coated onto 10cm by 10cm glass plates using a drawdown bar coater (RDS 30, Webster) to give 30 μm thickness and then cured with a 20 cm width IST Minicure 200 machine fitted with a UV lamp of 80 W/cm and an operating current at 7.0 amp. When cured, the samples were subjected to a number of simple instantaneous qualitative tests i.e. tackiness and finger marring. The hardness of the cured films was measured with a Byk Labotron Pendulum Hardness Tester (Konig method). Gel fraction was measured by soxhlet extraction method.

Molecular Weight Measurement: It was done using Waters GPC 200 machine equipped with four prepacked Styragel columns. Tetrahydrofuran and polystyrene were used as a solvent and standard respectively.

IR Measurement: The functional groups of ENR and its acrylated derivative were measured with a Nicolet 60SX Fourier Transform

infra-red spectrophotometer.

Chemical Resistance Tests or Chemical Spot Tests: The tests were carried out using chemicals such as 5% acetic acid, 50% ethanol, 1% sodium carbonate, 10% sulphuric acid and 10% sodium hydroxide.

RESULTS AND DISCUSSION

Acrylation Reaction: Theoretically speaking, almost any epoxide group can be acrylated given the right conditions [16]. But in case of ENR there are several conditions to be observed in order to minimise the risks of gelation during synthesis. Table 1 summaries the synthesis data as a result of these various conditions.

In an ordinary natural rubber, there is only one functional group i.e. the C=C double bond. When the rubber is epoxidised in correct conditions, only epoxide groups are formed [4]. In other conditions, complex products containing hydroxyl and ring-opened structures are also obtained [17,18]. Depolymerization of the rubber shows the formation of hydroxyl group [19]. In the case of acrylation process, some changes in IR peaks are expected such as new peaks attributable to acrylate group and diminishing of epoxide peaks [15].

But only three functional groups are of importance to us i.e. epoxide group (-CHOCH-) in ENR and the other two are acrylate ($\text{CH}_2=\text{CH}-\text{COO}-$) and hydroxyl (-OH) groups in low molecular weight

ENRA. These functional groups are clearly shown by IR spectroscopic technique in Table 2. When acrylation process takes place the epoxide peaks (1250 and 881 cm^{-1}) almost disappeared and new peaks (1664 , 1638 , 986 and 809 cm^{-1}) representing acrylate group appeared.

The reaction is illustrated by the equation below;

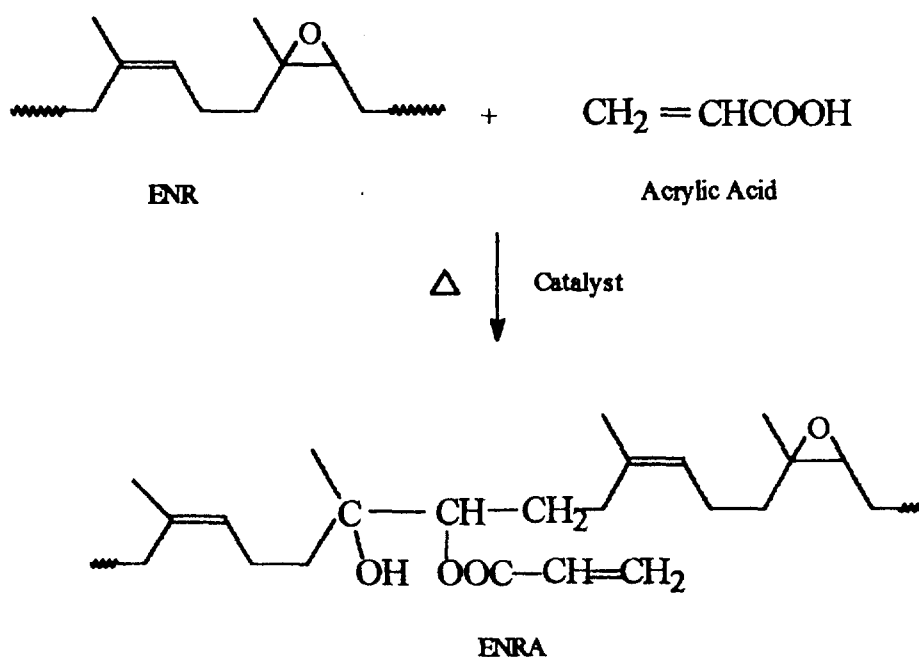


Table 2(c) shows the IR data of cured low molecular weight ENRA film. From this table it can be observed that the peaks attributable to the acrylate double bond have been used up. Upon irradiation in the presence of benzophenone, low molecular weight ENRA is capable of undergoing radical polymerization through its double bond from its newly attached acrylate group to form crosslinked network which is the basis of the radiation curing of

surface coatings.

UV Curing of Low Molecular Weight ENRA:

In these formulation studies, di- and trifunctional monomers were used i.e. TPGDA and TMPTA, respectively. They act as solvent and crosslinker.

Table 3 shows the effects of a single photoinitiator, BP and a combination of BP and a synergist, N-MDEOA on cured properties of low molecular weight ENRA using TPGDA as a reactive monomer.

From Table 3, it clearly indicates that the cure rate increases as the N-MDEOA content increases but at the expense of the gel fraction and the pendulum hardness. It is believed that the ability of N-MDEOA in enhancing the initiation reaction lies with its hydroxyl group which provides a source of readily extractable hydrogen [20]. The addition of N-MDEOA to BP repressed oxygen inhibition and enabled the latter to perform as effectively in air as in nitrogen [21]. On the other hand, single BP imparts higher gel fraction and pendulum hardness but the cure rate is slower as demonstrated by formulation A1.

With the addition of trifunctional acrylate i.e. TMPTA, the hardness and the cure rate were not improved as normally the case. Instead, the data in Table 4 indicate that their physical properties have been somewhat affected by the addition of TMPTA.

Table 5 illustrates the effects of Irgacure 184 and BP. The combination of both is commercially available as Irgacure 500

which is used for reducing an air inhibition effect in the absent of amines [22]. As shown by formulation B1 in Table 5, the cure rate increases more than double that of A1 - the one without Irgacure 184. At the same time, Irgacure 184 also reduces the negative effect of TMPTA on the pendulum hardness as shown by formulation B4. In short, with Irgacure 184, the physical properties of the coatings are found to be better than the formulations with the combination of BP and N-MDEOA.

The formulations also show good chemical resistance to a number of chemicals tested.

In other development [27], we used rubberwood as a substrate to be coated with natural rubber-based formulation. The formulation and performance of the coating film are given in Tables 6 and 7, respectively. The results show that its performance is comparable to commercial resins.

CONCLUSIONS

Since the preparation of new resin requires the use of solvent, the amount of solvent needed depends on the molecular weight of the starting material, ENR. The lower the molecular weight, the higher the concentration of ENR solution possible.

From formulation studies, several conclusions can be made such as;

i. Diacrylate monomer, TPGDA delivers better performance than

triacrylate, TMPTA.

- ii. Irgacure 184 is better photoinitiator for the new resin.
- iii. New resin based formulations show good chemical resistances.
- iv. Their gel fraction is readily acceptable.

This new resin has potential to find applications in;

- a. Coatings for wood-based substrates (e.g. fillers and top-coats), paper and board, and
- b. Pressure-sensitive adhesives.

ACKNOWLEDGEMENTS

In carrying out this work, we are grateful to many people namely the members of UTN's Surface Coatings Group; Guthrie Corp. Berhad, Chemara; Dr. Ibrahim Abdullah, UKM; Drs. Sidek Dulngali and Esah Yip, RRIM; Mr. T. Sasaki, JAERI, Japan and UTN's Research Committee.

Last but not least, we acknowledge financial support from the IRPA Code # 2-06-05-012.

* More detailed reports are being published in *Nucl. Sci. J. Malaysia, Vol. 11(1), 1993.*

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Table 1 : Some data of the preparation of low molecular weight ENRA.

No.	Sample	Source	\bar{M}_w	\bar{M}_n	SC,%	OOC,%	Epoxide: AA ratio	Cat. %	Inh. %	Reaction time (hr)	Initial AN	Final AN	% AN reduction
1.	LENR-25	UKM	380,000	82,000	27.6	5.04	1:1.2	1.0	1.0	61	166	64.0	61.4
2.	LENR-25	UKM	380,000	82,000	27.6	5.04	1:1.2	1.0	1.0	116	166	55.4	66.6
3.	LENR-50	UKM	232,000	62,000	21.9	5.26	1:1.2	1.0	1.0	7	172	153.9	10.5
4.	LENR-50	UKM	232,000	62,000	21.9	5.26	1:1.2	1.0	1.0	15	172	141.5	17.7
5.	LENR-50	UKM	232,000	62,000	21.9	5.26	1:1.2	1.0	1.0	41.5	172	103.5	39.8
6.	LENR-50	RRIM	19,478	5,847	50	7.43	1:0.2	1.0	1.0	20	65.1	49.4	24.1
7.	LENR-50	RRIM	19,478	5,847	50	7.43	1:0.1	1.0	0.5	13	24	14.9	37.9
8.	LENR-50	RRIM	19,478	5,847	50	7.43	1:0.1	1.0	0.5	11	25	17.2	31.2
9.	LENR-50	RRIM	19,478	5,847	50	7.43	1:0.2	1.0	0.5	28	72	49.0	31.9

Notes :- SC = Solution Concentration
 OOC = Oxirane Oxygen Content (before reaction)
 AN = Acid Number
 Cat = Catalyst
 Inh = Inhibitor
 AA = Acrylic Acid

P106

Table 2 : IR data of low molecular weight ENR-25, low molecular weight ENRA-25 and cured low molecular weight ENRA-25.

ν cm ⁻¹	Low molecular weight ENR-25 Assignment (a)	
3453.7	-OH	stretch.
2962.5	-CH	stretch.
2926.7	-CH	stretch.
2857.6	-CH	stretch.
1726	C=O	from lactone (?)
1664.8	C=C	stretch. of cis-1,4 [23]
1450	-CH ₂ -	deform. mode [23,24]
1377.5	-CH ₃ -	deform. mode [17]
1322.3		
1250.4	C-O	stretch. from epoxy [4]
1133.2	C-H	in-plane bend [17]
1081.4	C-O	stretch. from cyclic ether [17]
1036.0		
872.2	C-O	stretch. from epoxy [4]
836.9	C=C	vibration of cis-struct. [23,25]
741.8	C=C	vibration of cis-struct. [23]

.../more

ν cm ⁻¹	Low molecular weight ENRA-25 (washed) Assignment (b)	ν cm ⁻¹	Cured low molecular weight ENRA-25 Assignment (c)
3476.9	-OH (free) stretch.	3467 (broad)	-OH (free) stretch.
2962.8	-CH stretch.	2962.6	-CH stretch.
2926.7	-CH stretch.	2930.6	-CH stretch.
2856.7	-CH stretch.	2859	-CH stretch.
2728.2	-OH (bonded) stretch.	2360.7	CO ₂ peaks
		2340.8	CO ₂ peaks
1726	C=O	1732.3	C=O
1664.2	} external double bond and C=C of cis-1,4 [23]	1668.2	} reduced double bond peaks
1637.6		1654	
1450.0	-CH ₂ -	1450.5	-CH ₂ -
1404.3	C=C external double bond (exomethylene group, scissoring =CH ₂)		
1376.9	CH ₃ -	1377	CH ₃ -
1295.7		1316	
1269.7	} $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O} \end{array}$ stretch.	1255.4	C-O stretch. from epoxy (reduced)
1192.2		1165.5	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O} \end{array}$ stretch.
1062.1	C-O stretch. from cyclic ether (reduced)	1072.6 1029.7	cyclic ether (?)
985.5	CH ₂ =CHR out of plane bending		
880.7	C-O stretch. from epoxy (reduced), [4]	886.3	C-O stretch. from epoxy
836	C=C vibration of cis-struct.	837	C=C vibration of cis-struct.
809.1	C=C acrylic double bond [26]	745.4	C=C vibration of cis-struct.

Table 3 : Formulations of low molecular weight ENRA-25: Synergistic effects of N-methyl diethanol amine (N-MDEOA) with BP.

FORMULATIONS	A1	A2	A3	A4	A5
OLIGOMER - Low molecular weight ENRA, %	20	20	20	20	20
MONOMER - TPGDA, %	75	75	75	75	75
- TMPTA, %	0	0	0	0	0
PHOTOINIATOR, %					
Benzophenone	5	4	3	2	1
N-methyl diethanol amine	0	1	2	3	4
VISCOSITY 25°C (cps)	1100	1100	1100	1100	1100
CURRENT, mA	7.0	7.0	7.0	7.0	7.0
CONVEYOR SPEED, m/min	2	2	2	2	2
NO. OF PASSES TO CURE (to a tack-free finish)	3X	2X	1X	1X	1X
PENDULUM HARDNESS, %	48.8	32.9	31.1	31.7	26.2
GEL FRACTION, %	95.2	92.3	94.5	94.0	90.7
CHEMICAL TEST (Yes/No)*					
Acetic acid, 5%	Y	Y	Y	Y	Y
Ethanol, 50%	Y	Y	Y	Y	Y
Sodium Carbonate, 1%	Y	Y	Y	Y	Y
Sulphuric Acid, 10%	Y	Y	Y	Y	Y
Sodium Hydroxide, 10%	Y	Y	Y	Y	Y

* Yes means the spot is not affected and vice versa.

Table 4 : Formulations of low molecular weight ENRA-25: The effects of TMPTA.

FORMULATIONS	A6	A7	A8	A9	A10
OLIGOMER -					
Low molecular weight ENRA, %	20	20	20	20	20
MONOMER - TPGDA, %	65	65	65	65	65
- TMPTA, %	10	10	10	10	10
PHOTOINIATOR, %					
Benzophenone	5	4	3	2	1
N-methyl diethanol amine	0	1	2	3	4
VISCOSITY 25°C (cps)	1040	1040	1040	1040	1040
CURRENT, mA	7.0	7.0	7.0	7.0	7.0
CONVEYOR SPEED, m/min	2	2	2	2	2
NO. OF PASSES TO CURE (to a tack-free finish)	5X	3X	2X	1X	2X
PENDULUM HARDNESS, %	45.5	24.7	31.7	26.8	24.4
GEL FRACTION, %	94.6	94.6	93.6	93.5	91.5
CHEMICAL TEST (Yes/No)*					
Acetic acid, 5%	Y	Y	Y	Y	Y
Ethanol, 50%	Y	Y	Y	Y	Y
Sodium Carbonate, 1%	Y	Y	Y	Y	Y
Sulphuric Acid, 10%	Y	Y	Y	Y	Y
Sodium Hydroxide, 10%	Y	Y	Y	Y	Y

* Yes means the spot is not affected and vice versa.

Table 5 : Formulation of low molecular weight ENRA-25 : The effects of Irgacure 184 and BP.

FORMULATIONS	B1	B2	B3	B4
OLIGOMER -				
Low molecular weight ENRA, %	20	20	20	20
MONOMER - TPGDA, %	75	75	65	65
- TMPTA, %	0	0	10	10
PHOTOINITIATOR, %				
Benzophenone	2.5	0	2.5	0
Irgacure 184	2.5	5	2.5	5
VISCOSITY 25°C (cps)	940	940	1000 (est.)	1000 (est.)
CURRENT, mA	7.0	7.0	7.0	7.0
CONVEYOR SPEED, m/min	4	4	4	4
NO. OF PASSES TO CURE (to a tack-free finish)	2X	2X	3X	3X
PENDULUM HARDNESS, %	30.8	40.1	30.2	39.3
GEL FRACTION, %	93.6	94.6	93.4	94.5
CHEMICAL TEST (Yes/No)*				
Acetic acid, 5%	Y	Y	Y	Y
Ethanol, 50%	Y	Y	Y	Y
Sodium Carbonate, 1%	Y	Y	Y	Y
Sulphuric Acid, 10%	Y	Y	Y	Y
Sodium Hydroxide, 10%	Y	Y	Y	Y

* Yes means the spot is not affected and vice versa.

Table 6: Natural rubber-based formulation for rubberwood substrates [27].

Liquid epoxidised natural rubber acrylate (LENRA-50)	20%
TPGDA	65%
TMPTA	10%
Benzophenone	2.5%
Irgacure 184	2.5%
Total	100%

Table 7: The properties and performance of the coating film from natural rubber-based resin (LENRA-50) [27].

Type of Test	Properties/performance
Viscosities (cps)	430
Gel content (%)	93.7
Gloss (%)	80.3
Pencil hardness	H
Pendulum hardness (%)	34.7
Adhesion (%)	82
Impact resistance [*]	3.2
Scratch resistance (kg)	1.44
Abrasion resistance	0.0036
Heat resistance [*]	5
Chemical resistance:	
Acetic acid 5%	good
Citric acid	good
Sulphuric acid 10%	good
Sodium carbonate 1%	good
Sodium chloride 10%	good
Sodium hydroxide 1%	good
Ethanol	good
Acetone	good