

CHAPTER III EXPERIMENTAL

3.1. Materials

NatureWork 4042D PLA resin and ethylene glycol (Carlo Erba) were used in the glycolysis reactions. Chloroform, methanol, tetrahydrofuran solvents (HPLC grade) were obtained from Lab Scan. Chloroform-D (D 99.8 %) was purchased from Cambridge Isotope Laboratories.

Commercial high ammonia (HA)-preserved NR latex concentrate (60% dry rubber content (DRC) was purchased from Rayong Bangkok Rubber, Thailand. Nonylphenylpoly(ethylene glycol); Nonidet P40 (Fluka, Biochemika), 85% formic acid (Carlo Erba, RPE), 30% aqueous solution of hydrogen peroxide (BDH, AR), and 25% ammonium hydroxide (Loba, AR) were used as received. Stannous Octoate, $\text{Sn}(\text{Oct})_2$ (Wako), used as catalyst for ENR crosslinking, tetrahydrofuran and toluene solvent (AR grade) were obtained from Lab Scan for solvent extraction method.

NatureWork 4043D PLA resin was used as PLA matrix in melt blending with the cured ENR developed in this current work.

3.2 Instruments and characterizations

3.2.1 Sample preparation:

- Moving Die Rheometer (MDR, TechPro MD+)
- Internal mixer (C-AREON TUT, MX105-D40DL50)
- Compression molding (C-AREON TUT, PR20-W300L300 HD-WCL)

3.2.2 Mechanical testing

- Universal testing machine (TINIUS OLSEN, H5KT)
- Impact tester (Comtech Testing Machines, QC-639EN)

3.2.3 Characterizations

- NMR spectroscopy (Bruker Biospin DPX-300)



- MALDI-TOF mass spectrometer (Bruker Daltonics MALDI-TOF/TOF mass spectrometer Autoflex II)

- FTIR spectroscopy (Nicolet 6700)

A single-reflection ATR accessory equipped with diamond crystal with a face angle of 45° was employed. The resolution is 2 cm⁻¹ with 64 scans.

- Differential scanning calorimetry (DSC, Mettler Toledo STARc DSC 1)

The thermograms were recorded from -60 to 200 °C, followed by cooling to -60 °C. After keeping isothermally at -60 °C for 5 min, the samples were re-heated to 200 °C. All DSC measurements were conducted under N₂ atmosphere with a scanning rate of 20 °C/min.

- Thermogravimetric analysis (TGA, Mettler Toledo TGA/SDTA 851)

The thermograms were recorded from 50 to 800 °C, under N₂ atmosphere with a scanning rate of 20 °C/min.

- Gel Permeation Chromatography (GPC, WATERS 600 Controller)

The samples are dissolved with THF solvent and conducted with a flow rate of 1 ml/min.

- Scanning electron microscope (SEM, JEOL (JSM-6610LV)

The impact fractured samples are prepared and coated with platinum before morphological testing at 2,500 X.

3.3. Synthesis and characterization of PLA glycolysate (GPLA)

OH-capped GPLA glycolyzed products with various molecular weights (MW) were prepared by glycolysis of commercial PLA resin (cPLA) resin by ethylene glycol (EG), as summarized in Table 3.1. The resulting GPLAs were dissolved in chloroform



and precipitated in methanol to remove excess EG. The products were then dried and stored in a desiccator for further use.

Table 3.1 Glycolysis conditions of PLA resin.

Reaction Number	PLA:EG (wt/wt)	Temp (°C)	Time (min)
1	1 : 0.5	175	60
2	1 : 0.5	195	60
3	1 : 1	195	30

Molecular weight (MW) of GPLAs and cPLA were determined by GPC. Chemical structures of GPLAs were characterized by ^{13}C -NMR spectrometer using chloroform-D as solvent, MALDI-TOF mass spectrometer and FTIR spectrometer. 1ul of GPLA dissolved in THF was mixed with 1ul of sodium chloride aqueous solution (2 mg/ml) and 15 ul of Dithranol in THF (15 mg/ml). Then 1ul of the GPLA mixture was used for MALDI with linear positive mode, with protein mix or 12 kDa programs.

Number average molecular weight (\bar{M}_n) of GPLA were examined by nuclear magnetic resonance (NMR) spectroscopy and MALDI-TOF Mass spectroscopy (MALDI-TOF MS) [58]. The OH end group contents of GPLA, determined from ^{13}C -NMR spectra, were used in the calculations of degree of polymerization (DP) and \bar{M}_n , as follows:

$$DP = \frac{C^d + C^{d'} + C^{d''}}{C^d} \quad (\text{Equation 3.1})$$

$$\bar{M}_n = 72(DP) + 62 \quad (\text{Equation 3.2})$$

Where C^d : in-chain methine; $-\text{OCHCH}_3\text{C}=\text{O}$ at 68.9 ppm.

$C^{d'}$: terminal methines; $\text{HOCHCH}_3\text{COOCHCH}_3\text{C}=\text{O}$ at 69.4 ppm

$C^{d''}$: terminal methines; $\text{HOCHCH}_3\text{C}=\text{O}$ at 66.6 ppm.

\bar{M}_n value of GPLAs were also calculated from MALDI-TOF mass spectra [59, 60], by using Equation 3.3, where N_i and M_i are the abundance and mass of fragmented species, respectively.

$$\bar{M}_n = \frac{\sum (N_i M_i)}{\sum N_i} \quad (\text{Equation 3.3})$$

3.4 Synthesis and characterization of ENR

ENR with 20% epoxidation was synthesized from commercial high ammonia (HA)-preserved NR latex concentrate. NR latex with 60% DRC (100 g) was diluted to 30% DRC with de-ionized water (100 ml) and Nonidet P40 (3 g). After gentle stirring in a glass reactor at room temperature for 1 h, the mixture was neutralized by 85% formic acid (1 ml), and then acidified with an excess of the acid (9.7 ml). After raising the temperature to 40°C, a 30% aqueous solution of hydrogen peroxide (72.8 ml) was added within a duration of 15–20 min, and the reaction temperature was kept at 50°C for 12 h. At the end of the reaction, the pH of the latex was adjusted to 10 by using a 25% NH_4OH solution. Aliquots were immediately precipitated in methanol, washed with de-ionized water and dried under vacuum at room temperature overnight [7].

Chemical structure of the synthesized ENR was characterized by ^1H NMR using toluene- d_6 solvent, FTIR spectroscopy, and MALDI-TOF mass spectroscopy. 1ul of rubber solution (in toluene) was mixed with 1ul of silver trifluoroacetate aqueous solution (2mg/ml) and 15 ul of Dithranol in THF (15 mg/ml). 1ul of rubber mixture was used for MALDI with linear positive mode, with protein mix or 12 kDa programs.

The epoxide content was calculated from ^1H NMR spectra [61], as follows:

$$\text{Epoxide content (\%)} = \left[\frac{I_{2.7}}{(I_{2.7} + I_{5.1})} \right] \times 100 \quad (\text{Equation 3.4})$$

Where $I_{2.7}$: epoxy methine proton ; $-\text{C}(\text{O})-\text{CH}-\text{CH}_2-$

$I_{5.1}$: olefinic proton ; $-\text{C}=\text{CH}-\text{CH}_2-$

3.5 Preparation of GPLA-cured ENR

OH-capped GPLAs (with \overline{M}_n of 44 000, 10 000, and 2 000 g/mol, determined from GPC), denoted by G44, G10, and G2, were used as macromolecular crosslinkers for ENR by chemical reaction and reactive crosslinking processes. Effects of GPLA chain lengths and GPLA/ENR feed compositions on structures and properties of the cured ENR products were examined. A simple mixture of GPLA/natural rubber (NR) was used as a control sample. Curing conditions and sample notations are summarized in Table 3.2.

Table 3.2. Curing conditions and sample notations of ENR and NR by GPLA.

Samples		Composition in feed (wt%)		Composition in feed (mol%)		Composition in feed (wt%)	
		GPLA	ENR	GPLA	ENR	GPLA	NR
Chemical curing reaction	Reactive curing process						
G2ER11	G2ET11	50	50	97.3	2.7	-	-
G2ER12	G2ET12	33	67	94.7	5.3	-	-
G2ER14	G2ET14	20	80	90.0	10.0	-	-
G10ER11	G10ET11	50	50	87.8	12.2	-	-
G10ER12	G10ET12	33	67	78.0	22.0	-	-
G10ER14	G10ET14	20	80	64.3	35.7	-	-
G44ER11	G44ET11	50	50	62.1	37.9	-	-
G44ER12	G44ET12	33	67	44.6	55.4	-	-
G44ER14	G44ET14	20	80	29.0	71.0	-	-
uncuredENR _p	uncuredENR _r	0	100	0	100	-	-
-	G44NT14	-	-	-	-	20	80

Note:

ENR cured with GPLA by chemical reaction is named as GxERy.

ENR cured with GPLA by reactive crosslinking process is named as GxETyz.

Where x represents molecular weight of GPLA in the unit of 10^{-3} g/mol

yz represents weight ratio of GPLA:ENR

3.5.1 Curing of ENR via chemical reactions

GPLA and ENR were dried under vacuum/inert gas for 1 h, and then dissolved in dried THF at 50°C. The GPLA:ENR weight ratios were varied from 1:1, 1:2, to 1:4, as summarized in Table 3.2. $\text{Sn}(\text{Oct})_2$ (1% by weight of GPLA) was added to the solution and the curing reaction was carried out at 80°C for 24 h. A film sample was prepared by casting the product solution on a Teflon plate and evaporating THF solvent at room temperature for 5 days.

3.5.2 Curing of ENR via reactive crosslinking in Moving Die Rheometer (MDR)

GPLA and ENR mixtures were separately prepared by dissolving in dried THF. $\text{Sn}(\text{Oct})_2$ catalyst (1 wt. % of GPLA) was then added to the GPLA solutions. The mixture was gently stirred at 80°C for 1 h, and subsequently mixed with ENR solution (at 30°C) at given weight ratios. Homogeneous solid samples were obtained by evaporation of the solvent under vacuum [9]. The dried mixture samples were used in assessments of their crosslinking behaviors. GPLA/ENR mixtures (5 g) were examined by a Moving Die Rheometer (MDR) at 80°C for 30 min, in accordance with ISO 6502. Elastic and viscous torques of the samples were measured as a function of curing time. Loss tangent ($\tan\delta$) of the cured samples were calculated and compared with that of a GPLA/NR simple mixture (G44NT14) and pure ENR (uncured ENR_f).

3.6 Characterizations and testing of GPLA-cured ENR products

3.6.1 Sequential solvent fractionation

The efficiency of both curing processes were examined by sequential solvent fractionation of the cured products, employing THF and toluene as solvents. The unreacted GPLAs and uncured ENR were first extracted by Soxhlet extraction using THF at 80°C for 24 h. (denoted by S_{THF}). The THF-insoluble fraction was then extracted by toluene at room temperature for 7 days. The toluene soluble and insoluble fractions (denoted by S_{TO} and I_{TO}), corresponding to “grafted” and fully



“crosslinked” ENR fractions, were recovered by removing toluene solvent in a vacuum oven at room temperature until a constant weight was reached [9]. The weight percentage of each fraction was calculated based on the mass of the original sample.

3.6.2 Solvent swelling method

The crosslink density of the remaining toluene-insoluble fraction (I_{Tot}) was measured by using a solvent swelling method. A piece of sample (0.2 g.) was immersed in toluene (20 ml.) at room temperature in a dark cabinet. At an equilibrium swelling time (about 7 days), the test piece was removed, wiped with filter papers, and its weight (W_{eq}) was recorded. The swelling percentage was calculated, as follows:

$$\text{Swelling(\%)} = \frac{W_{eq} - W_0}{W_0} \times 100 \quad (\text{Equation 3.5})$$

Where W_0 = weight of original sample (g)

W_{eq} = weight of swollen sample at an equilibrium time (g)

3.6.3 Gel content determination

The degree of crosslinking of the cured products was determined by toluene extraction at room temperature for 7 days. The test piece was then removed and dried in a vacuum oven, in which its final weight (w) was recorded. The gel content was calculated, as follows:

$$\text{Gel content(\%)} = \frac{w_1}{w_0} \times 100 \quad (\text{Equation 3.6})$$

Where w_0 = weight of original sample (g)

w_1 = weight of dried sample after toluene extraction (g)

3.6.4 Chemical structure

Chemical structures of the cured samples and the extracted products were examined by $^1\text{H-NMR}$, MALDI-TOF MS, and FTIR spectroscopy. Thermal properties of the cured products were examined by using DSC and TGA.

3.6.5 Tensile properties

Tensile specimens were prepared and tested in accordance with ISO 37. GPLA-cured ENR materials were firstly prepared by reactive mixing the specified composition of GPLA and ENR in a cam-type internal mixer. The mixing was conducted at 80°C , for 30 min with a rotor speed of 50 rpm. Then, they were compressed into thin films, with a thickness of about 0.2 mm. The rubber samples are prepared at 160°C , for 10 min. Tensile strength, Young's modulus, elongation at break, and breaking energy were measured with 1000N load cell from film specimens of 10mm wide. A cross-head speed of 200 mm/min and a gage length of 50 mm were employed.

3.7 Preparation and testing of GPLA/ENR/PLA blends

Potency in toughening PLLA with GPLA-cured ENR is the main purpose of this section. Therefore the GPLA/ENR/PLA blends were developed by the following procedures. GPLA and NatureWork 4043D PLLA resin were dried in a vacuum oven at 60°C for 24 h. Then, GPLA and ENR at weight ratio of 1:2 were reactive blending in a cam-type internal mixer using $\text{Sn}(\text{Oct})_2$ (1wt% of GPLA) as a catalyst. The mixing was carried out at 80°C for 30 min with a rotor speed of 50 rpm. Subsequently, the GPLA-cured ENR products were removed from the mixing chamber, cut into small flakes and further used for blending with PLA.

NatureWork 4043D PLLA resin was allowed to melt at 160°C for about 5 min, and then mixed with GPLA-cured ENR flakes for another 10 min with a rotor speed of 50 rpm. It is note that PLA does not completely melt at these condition [62]. The weight percentage of cured ENR was varied from 0 to 15 wt%. The blends were pulverized into flakes, and then compressed for tensile testing (ASTM D882) and



notch Izod impact testings (ASTM D256). the PLA blend samples are prepared at 180 °C, for 18 min. Morphology of the blend samples was examined on the cross-section of failure samples (from impact testing) by SEM.

