

CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Chemical: Natural Rubber Latex

- Double centrifuge natural rubber latex (total solid content >60%wt), commercial grade from Thai Eastern Rubber Co., Ltd

3.1.2 Fillers

- Commercial graphene multilayers (particle diameter < 2 μ m) from XG Sciences (USA)

3.1.3 Chemicals and Solvents

- Tween80 from Sigma Aldrich, AR grade
- 2-methyl-4'-(methylthio)-2-morpholinopropiophenone; MMMP (λ_{\max} = 310 nm) from Sigma Aldrich, AR grade
- Trimethylol-propane 3-mercaptopropionate; TMPTMP from Sigma Aldrich, AR grade
- Toluene from Carlo ERBA, reagent grade

3.2 Equipments

- Raman spectrometer (NT-MDT, NTEGRA Spectra)
- X-ray Diffraction Spectrometer, XRD (Rigaku, DMAX 2200)
- Fourier Transform Infrared Spectrometer, FT-IR (Nicolet, Nexus 670)
- Thermogravimetric analyzer, TGA (Thermo, TGA Q 50)
- Melt Rheometer (Rheometric Scientific, Ares)
- Scanning Electron Microscope, SEM (FE-SEM, JSM-7001F)
- Electrometer (Keithley, 6517A) with a custom-built two-point probe

3.3 Experimental

3.3.1 Preparation of Graphene/NR Composite

TMPTMP, as a crosslinking agent, concentrations were varied at 0.1, 0.5, 1.0, 2.0, 3.0, 5.0, 7.0, 10.0, 15.0, and 20.0 %v/v of NR. MMMP, as a photoinitiator, concentration was set up to be 3:1 ratio of TMPTMP. First, TMPTMP and MMMP were mixed together with a magnetic stirrer until homogeneity was obtained. Then TWEEN 80, as a surfactant, was added in to 20 ml DI water and magnetically stirred for 5 min. Graphene was slowly added in TWEEN 80 solution to make a graphene solution. Crosslinker and photoinitiator were added into latex (20 ml) and stirred until homogenous, called the latex mixture. Lastly, graphene solution was added to the latex mixture. The compounded latex was magnetically stirred for 1 h. before curing with UV radiation. NR films and composite were subsequently investigated under the effects of crosslinking concentration, crosslinking time, and graphene concentration.

3.4 Characterizations

3.4.1 Raman Spectrometer (NT-MDT, NTEGRA Spectra)

Raman spectroscopy was used to verify graphene due to the ability to identify and characterize all the members of the carbon family. The characterizations were nondestructive, fast, with high resolution and give the maximum structural and electronic information. The indications of graphene were measured by the Raman spectroscopy (NT-MDT, NTEGRA Spectra) with 632.8 nm excitation laser, objective lens 100x, and accumulate time 60s from National Nanotechnology Center.

3.4.2 X-ray Diffraction Spectrometer. XRD (Rigaku, DMAX 2200)

The wide angle X-ray diffraction microscope (XRD, Rigaku, DMAX 2200) was used to study the crystal structure below the nanometer scale. The CuK-alpha radiation source was operated at 40 kV/30 mA. K-beta filter was used to eliminate interference peak. Divergence slit and scattering slit 0.5 deg together with 0.3 mm of receiving slit were set on the instrument. The graphene powder was

placed onto a sample holder and the measurement was continuously run. The experiments were recorded by monitoring the diffraction appearing in the diffraction angle (2θ) range from 10 to 80 with a scan speed 5 deg/min and a scan step 0.02 deg.

3.4.3 Fourier Transform Infrared Spectrometer, FT-IR (Nicolet, Nexus 670)

Fourier Transform Infrared Spectroscopy (FT-IR Nicolet, Nexus 670) was used to investigate the characteristic vibration frequencies of the molecules in order to determine the molecular structure of the samples. This technique employed was the absorption mode with 32 scans a resolution of $\pm 4 \text{ cm}^{-1}$, covering a wavelength range of $400\text{-}4000 \text{ cm}^{-1}$, using deuterated triglycine sulfate as a detector. Optical grade KBr powder was used as a background material to characterize the graphene. The sample powder was ground with KBr and pressed to form pellets before testing. In addition, NR films were characterized for the functional groups by using the Attenuated total reflectance (ATR) mode.

3.4.4 Thermogravimetric Analyzer, TGA (Thermo, TGA Q 50)

A thermogravimetric analyzer (Thermo, TGA Q 50) was used to determine the thermal behavior of the NR films. The thermal behavior was examined by weighting the sample of 4-5 mg and loaded into a platinum pan. The mass change under the temperature scan from 30 to 550 °C at a heating rate of 10 °C/min and under the nitrogen flow was monitored and recorded.

3.4.5 Determination of Crosslink Density

Dried rubber sheets were prepared by casting the latex on glass plates and cured under UV radiation at various crosslinking times and crosslinking ratios. The thin films were cut into small pieces (1 cm^2) and then immersed in toluene (150 mL) until the swelling reaches the equilibrium (3 days). The mole percent uptake of solvent, weight loss, and crosslinking density of crosslinked NR were calculated from the following equations:

$$\text{Mole percent uptake of solvent} = \frac{W_t - W_0}{M_w} \times 100 \quad (3.1)$$

where W_0 and W_t are the weights of dried and swollen samples, respectively. M_w is the molar mass of toluene (92.14 g mol^{-1}).

$$\% \text{ Weight loss} = \frac{M_i - M_d}{M_i} \times 100 \quad (3.2)$$

where M_i and M_d are the weight of dried rubber before and after soaking in toluene.

$$v_e = \frac{-[\ln(1-V_r) + V_r + \chi_1 V_r^2]}{[V_1(V_r^3 - V_r)/2]} \quad (3.3)$$

where v_e is effective number of chains in a real network per unit volume, V_r is volume fraction of polymer in a swollen network in equilibrium with pure solvent and is calculated as:

$$V_r = \frac{\text{Weight of dry rubber} / \text{density of dry rubber}}{\text{Density of dry rubber} + \frac{\text{Weight of solvent absorbed by sample}}{\text{Density of solvent}}} \quad (3.4)$$

χ_1 is polymer-solvent interaction parameter (0.391) and V_1 is molecular volume of solvent.

3.4.6 Melt Rheometer (Rheometric Scientific, Ares)

The mechanical properties of graphene/NR composites were measured by a rheometer (Rheometric scientific, Ares) with the extensional fixture at room temperature. In this experiment, the transient mode was applied and the stress was monitored during stretching, at strain rate 0.01 s^{-1} , as a function of strain. From the results, a stress vs. strain curve was obtained. An evaluation of the mechanical properties of the film was focused on the modulus, the yield strength, and the yield strain.

The electrical conductivity of graphene/NR composites was measured and determined with the same fixture as in the mechanical testing. DC voltage was applied with DC power supply (Instek, GFG 8216A) connected to a digital

multimeter (Tektronix, CDM 250) to monitor the voltage input. The electrical conductivity during stretching was calculated through the following equation:

$$\sigma = \frac{1}{R} \times \frac{l}{A} = \frac{l}{V} \times \frac{l}{A} \quad (3.5)$$

where, σ = electrical conductivity (S/cm), R = resistivity ($\Omega \times \text{cm}$), l = length of specimen (cm), A = cross-section area of specimen (cm^2), I = current (Ampere), and V = applied voltage (volt).

In addition, length and area of specimen depend on the stretching which was calculated based on the incompressible material assumption via the following equation:

$$\gamma = -\frac{\epsilon_{22}}{\epsilon_{11}} = -\frac{\epsilon_{33}}{\epsilon_{11}} = 0.5 \quad (3.6)$$

$$t_x = t_0(1 - \epsilon_{33}) = t_0(1 + 0.5\epsilon_{11}) \quad (3.7)$$

$$w_x = w_0(1 - \epsilon_{33}) = w_0(1 + 0.5\epsilon_{11}) \quad (3.8)$$

$$l_x = l_0(1 + \epsilon_{11}) \quad (3.9)$$

$$\epsilon_{11} = \frac{\Delta l}{l_0} = \frac{l_x - l_0}{l_0} \quad (3.10)$$

where γ = the Poisson ratio (for rubber = 0.5), $\epsilon_{11,22,33}$ = the strains in x, y, z axes, t = the thickness of specimen (cm), w = the width of specimen (cm), l = the length of specimen (cm). Subscript x means at the value at any strain, and subscript 0 means at strain = 0.

3.4.7 Scanning Electron Microscope (FE-SEM. JSM-7001F)

A field-emission scanning electron microscope (FE-SEM, JSM-7001F) was used to examine the morphological structure and to investigate the dispersion of the graphene in the NR matrix. The film was placed on the holder with an adhesive tape and coated with a thin layer of gold using an ion sputtering device

for 100 sec prior to observation under FE-SEM. The scanning electron images were investigated by using an acceleration voltage of 20 kV with a magnification in the range of 2k - 60k times.

3.4.8 Atomic Force Microscope (AFM, Park System, XE-100)

The topology of the composite was obtained by using the atomic force microscope (AFM, Park System, XE-100) in air under ambient conditions. For the conventional AFM, the non-contact mode was operated with the cantilever (NSC36) tapping at scan rate of 0.5 Hz and applied Z-servo gain of 10. The micro-scale dispersion of graphene in the NR matrix can be observed from the topology.

3.4.9 Two – point probe Technique

An electrometer (Keithley, 6517A), with a custom-built two-point probe, was used to measure the electrical conductivity of graphene powder. The calculation is the inversion of specific resistivity (ρ) that indicates the ability of material to transport electrical charge. The meter consisted of a probe making contact on the surface of the sample in a disc shape. This probe was connected to a power supplier source for a constant source and for reading current. The applied voltage was plotted versus the resultant current to determine the linear Ohmic regime of each sample based on the Van der Pauw method. The applied voltage and the current in the linear Ohmic regime were converted to the electrical conductivity of the sample using equation (3.11) as follow:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{I}{K \times V \times t} = \frac{\text{slope}}{K \times t} \quad (3.11)$$

where σ is the specific conductivity (S/cm), ρ is the specific resistivity ($\Omega \cdot \text{cm}$), R_s is the sheet resistivity (Ω), I is the resultant current (A), K is the geometric correction factor, V is the applied voltage (V), and t is the thickness of the disc sample (cm).