

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

Concentrated natural rubber latex with 60% dried rubber content was purchased from Rubber Research Institute of Thailand. ϵ -Caprolactone (CL), ethylene glycol 99.8% and tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) ~95% were purchased from Sigma-Aldrich. Polylactide 4032D was purchased from Naturework. Cetyltrimethylammonium bromide (CTAB) $\geq 98\%$ was purchased from Merck Millipore. Lactide monomer (LA) (99.5% purity) was purchased from Shenzhen Bright China Industrial Co., Ltd. Bentonite based organoclay was obtained from Thai Nippon Chemical Industry Co., Ltd.

3.2 Experimental Procedures

3.2.1 Synthesis of Core-shell Particles

Concentrated NR latex was diluted to 5% dried rubber content. Then, 1 M CTAB solution was added into the diluted latex until concentration of CTAB was 2.8 mM. Ethylene glycol and $\text{Sn}(\text{Oct})_2$ were added into the mixture as initiator and catalyst respectively (Storey, R.F. and Sherman, J.W. 2002). The mixture was heated to 90 °C then CL and LA were sequentially starve-fed into mixture. The polymerization was allowed for 9 hr. The synthesized particles were washed with distilled water and dried. Overall monomers content was fixed at 100 mM, mole ratio between ϵ -caprolactone and lactide was varied from 30:70 to 70:30. The initiator to monomers mole ratio was also varied from 0.5:100 to 2.0:100. The synthesized rubber was named with series of number following monomers ratio and initiator ratio, such as 505010 mean admicelled rubber with 50:50 CL to LA ratio and initiator at 1.0:100.

3.2.2 Core-shell Nanocomposite Preparation

The admicellar synthesized latex (core-shell structure of NR-PCL/PLA) with monomer ratio of 50:50 and initiator to monomer ratio of 1.0:100 was chosen to incorporate with organoclay. The organoclay was dispersed in distilled water by vigorous stirring and mixed with the synthesized latex. Then, the mixture was vigorously sheared and dried into rubber-organoclay nanocomposites. The content of organoclay in the core-shell latex was varied from 5-20 wt%. Nanocomposite was named as same as admicelled rubber following by number of clay content.

3.2.3 Blending and Specimens Preparation

The admicellar synthesized particles and its various nanocomposites of 10 wt% were blended with PLA pellets of 90 wt% in co-rotating twin-screw extruder (LABTECH) with temperature profile from feed hopper to die as following: 150,160 and 165 °C and screw speed at 25 rpm. Extrudate was cooled in water bath and cut into pellets. The blend nanocomposites had clay content of 0.5-2.0 wt%. Then, the pellets were compressed by LABTECH LP20 instruments using heating at 180 °C, pressure of 2000 psi for 10 min and then cooled to room temperature. Impact specimens were prepared followed ASTM D256, and dynamic mechanical analysis specimens were prepared with dimension 10 mm x 50 mm x 3 mm.

3.3 **Characterization and Testing**

3.3.1 Electron Microscope

Core-shell particles existence and their size was observed by using transmission electron microscope (TEM; JEOL JEM-2100). The specimens were prepared by dropping and drying of diluted latex on copper grid.

The morphology of blends was observed with HITASHI TM 3000 scanning electron microscope (SEM) with voltage 5 kV. The specimens for morphology observation were prepared by cryo-fractured impact specimens in liquid nitrogen, then, coated them with platinum particles.

3.3.2 Fourier-transform Infrared Spectroscopy

Shell polymer of synthesized rubber particles were determined infrared spectra by using Thermo Nicolet NEXUS 670 to investigated chemical functional groups. Dried synthesized rubber particles were extracted for shell layer by chloroform. Then, the solutions were casted to be thin films which were used as specimens.

3.3.3 Thermogravimetric Analysis

Thermal stability of synthesized particles was evaluated by using Perkin-Elmer Pyris Diamond TG/DTA instrument. The 3-7 mg of samples was feed in platinum pan and heated from 30 to 700 °C under nitrogen atmosphere with heating rate of 10 °C/min. Thermograms were investigated for degradation temperature (T_d) of synthesized particles.

3.3.4 Differential Scanning Calorimetry

Thermal properties of blends were evaluated by using METTLER DSC822^e instrument. The 4-10 mg of samples was loaded in aluminum pan. The samples were first heated from 30 to 120 °C with heating rate of 3 °C/min. Then, they were cooled from 120 to 30 °C with cooling rate of 3 °C/min. Second heating was carried out with temperature range and heating rate as same as the first heating. Thermograms were investigated for glass-transition temperature (T_g), melting temperature (T_m) and crystallinity of blends.

3.3.5 Dynamic Mechanical Analysis

The blends were evaluated dynamic mechanical properties by using GABO EPLEXOR 100 N dynamic mechanical analyzer. The testing was carried out by using temperature scan mode from -100 to 100 °C with heating rate at 2 °C/min and frequency at 1 Hz under nitrogen atmosphere. The results were analyzed for storage modulus, $\tan \delta$ and glass transition temperature

3.3.6 Impact Testing

Izod impact testing was carried out with Zwick 5113 pendulum impact tester. The specimens were notched before testing. Result was reported following ASTM D256.

3.3.7 Tensile Testing

PLA blends were shaped into dog bone followed ASTM D638 type I. Then, testing was carried out by Instron Model 4206 Universal Testing Machine with head speed at 20 mm/min.