

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Materials

Natural rubber latex (NRL) treated with high ammonia and content of dry rubber at 60wt% was purchased from Chemical & Materials Co., Ltd. Carboxylated styrene-butadiene latex (XSBRL) was purchased from Jorakay Corporation Co., Ltd. Commercial sodium silicate (CSS) was purchased from PanReac AppliChem ITW Reagents. Rice husk ash (RHA) that is by-product from biomass power plants was purchased from Chia Meng Co., Ltd. Hydrochloric acid (HCl) was purchased from RCI Labscan Co., Ltd. Sodium hydroxide (NaOH) and acetic acid (CH₃COOH) were purchased from CARLO ERBA Reagents. Vinyltriethoxysilane (VTES) was purchased from Sigma-Aldrich Co., Ltd. Stearic acid (SA), zinc oxide (ZnO), N-Cyclohexyl-2-benzothiazole sulfenamide (CBS), and sulfur (S) were supported by Chemical Innovation Co., Ltd. Portland cement Type I was produced by Asia Cement Pub Co., Ltd. Sodium dodecyl sulfate (SDS) was purchased from LOBA Chemie Pvt. Ltd. Sand with a particle size less than 1.18 mm was supported by Concrete Technology Laboratory at Suranaree University of Technology.

3.2 Experimental

3.2.1 Preparation of RSi and CSI

3.2.1.1 Extraction of rice husk sodium silicate (RSS)

The RHA was purified by leaching RHA with 1M HCl solution at 90°C by using magnetic stirrer for 3 hours to remove some metallic oxides. Then the purified RHA was filtered by using filter paper, washed with DI water until the pH was neutral, and dried by using hot-air oven at 110°C for 12 hours. The RSS was prepared by extracting silica from the purified RHA that was obtained from the previous process with 1M NaOH solution at 90°C. The purified RHA was stirred by using magnetic stirrer

for 12 hours to obtain the yield of silica about 68%. And then the filter paper was utilized to filter the residue of purified RHA and obtain the RSS with clear solution.

3.2.1.2 Precipitation of RSi and CSi

The RSi was prepared by precipitating silica in RSS with 1M CH₃COOH solution at room temperature under stirring on over-head stirrer throughout the process. The CH₃COOH solution was dropped into RSS until the pH was neutral to obtain the RSi. The CSi was also prepared by following from the previous process.

3.2.2 Characterization of RSi and CSi

Before characterization, the RSi and CSi were washed with DI water several times and filtered by using filter paper. Then the prior RSi and CSi were dried by using hot-air oven at 110°C for 12 hours and grounded by using mortar to obtain the dried RSi and CSi with fine particles.

3.2.2.1 Fourier transform infrared spectrometer (FTIR)

The functional groups of dried RSi and CSi were analyzed by using the FTIR (Bruker, TENSOR 27) in wavenumber range of 4000 to 400 cm⁻¹ with resolution of 4 cm⁻¹ and number of scans of 64. All the samples were mixed with potassium bromide (KBr) by using agate mortar and pressed into pellets to obtain the test specimens with smooth surface for transmittance measurements.

3.2.2.2 Energy dispersive X-Ray fluorescence spectrometer (EDXRF)

The EDXRF (HORIBA Scientific, XGT-5200) was used to analyze the chemical compositions of dried RSi and CSi.

3.2.2.3 X-Ray diffractometer (XRD)

The XRD diffractograms of dried RSi and CSi were analyzed by using the XRD (Bruker, D2 PHASER) in 2θ range of 10 to 70 degrees.

3.2.2.4 Branauer-Emmett-Teller (BET) analysis

The characteristics of dried RSi and CSi in terms of BET surface area, total pore volume, and average pore diameter were analyzed by using the BET method (Micromeritics, ASAP 2020). All the samples were degassed at 160°C for 24 hours before analysis.

3.2.2.5 Dynamic light scattering (DLS) measurement

The average particle sizes of RSi and CSi were measured by using the DLS (Malvern Panalytical, Zetasizer Nano ZS). All the samples were dispersed in ethanol by using an ultrasonic probe before the measurement.

3.2.2.6 Field Emission Scanning Electron Microscope (FESEM)

For this characterization, the RSi and CSi were dispersed in ethanol by using an ultrasonic probe. Then the prior RSi and CSi were dropped on the aluminum tape and allowed to dry overnight in the electronic desiccator.

The images of dried RSi and CSi were acquired using FESEM (Carl Zeiss, AURIGA). All the samples were coated with carbon before the observation.

3.2.3 Preparation of rubber composite

3.2.3.1 Mixing and drying of rubber sheet

1) NR/RSi sheet

The RSi at 0, 5, 10, and 20 phr was poured into NRL and mixed by using over-head stirrer at room temperature for 15 minutes to obtain the mixture. Then each prior mixture was poured onto tray and dried by using hot-air oven at 60°C for 72 hours to obtain the NR/RSi sheet with constant weight.

2) NR/VTES/RSi sheet

First, the RSi at 0, 5, 10, and 20 phr was combined with VTES by dropping VTES into RSi at a ratio of 1/10, which was the optimal ratio of VTES onto RSi. The previous process was prepared by using over-head stirrer at room temperature for 15 minutes. Then the prior product was poured into NRL and mixed by using over-head stirrer for 15 minutes to obtain the mixture. And then the NR/VTES/RSi sheet was prepared by pouring each mixture onto tray and drying in a hot-air oven at 60°C for 72 hours.

3) NR/XSBR/RSi sheet

First, the NRL was blended with XSBR at a ratio of 2/1, which was the optimal blending ratio of NRL with XSBR. The homogeneous rubber latex blend was prepared by using over-head stirrer for 15 minutes. Then the rubber latex blend was mixed with RSi at 0, 5, 10, and 20 phr for 15 minutes under stirring on over-

head stirrer to obtain the mixture. And then each mixture was poured onto tray and dried by using hot-air oven at 60°C to obtain the NR/XSBR/RSi sheet with constant weight.

3.2.3.2 Compounding and vulcanizing of rubber composite

All the rubber sheets were compounded with chemicals that were shown in Table 3.1. The two-roll mill was used to compound each rubber sheet with chemicals for 15 minutes to obtain the rubber compound. Then each prior rubber compound was vulcanized by using compression molding machine at 150°C with an optimal curing time that was determined by using a moving die rheometer (MDR) to obtain the rubber composite.

Table 3.1 Rubber compounding chemicals.

Chemical	Function	Content (*phr)
Stearic acid (SA)	Activator	2
Zinc oxide (ZnO)	Activator	5
N-cyclohexyl-2-benzothiazole sulfonamide (CBS)	Accelerator	2.5
Sulfur (S)	Crosslinking agent	1

*phr refers to part per hundred of rubber.

3.2.4 Characterization of rubber composite

3.2.4.1 Cure characteristics

The cure characteristics such as minimum torque, maximum torque, scorch time, and optimal cure time of rubber composites were determined by using a MDR (GOTECH, M-2000AN) according to ASTM D2084 with a temperature of 150°C.

3.2.4.2 Mechanical properties

The modulus at 100% elongation (M100), modulus at 300% elongation (M300), tensile strength, and percentage of elongation at break of rubber composites were measured according to ASTM D412 with the type C test specimen,

as shown in Figure 3.1, by using a universal testing machine (UTM, INSTRON, Model:5565) with a load cell of 5 kN and crosshead speed of 500 mm/min.

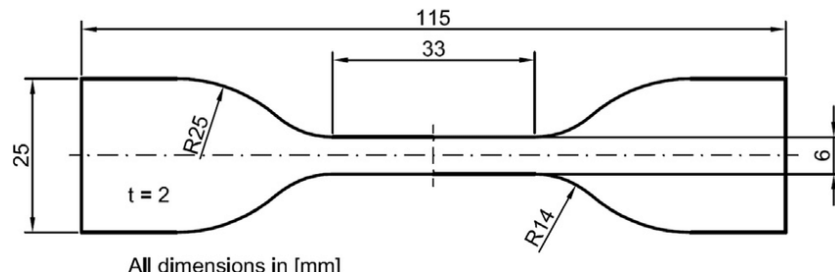


Figure 3.1 Dimensions of the type C test specimen according to ASTM D412 (Staudt et al., 2018).

The hardness of rubber composites were measured according to ASTM D2240 by using a hardness tester (Bareiss, HPE II) with the Shore A test method.

3.2.4.3 Morphological properties

The secondary electron images of rubber composites were acquired using a FESEM (Carl Zeiss, AURIGA). The tensile fracture surfaces of rubber composites were coated with gold before the observation.

3.2.5 Preparation of polymer-modified mortar (PMM)

The sample codes and mixing proportions of PMM are listed in Table 3.2. The ratios of cement to sand (C/S), water to cement (W/C), and SDS to polymer (SDS/P) were fixed at 0.50, 0.55, and 0.10, respectively. The polymer was added to cement at a polymer to cement (P/C) ratio of 0.00, 0.05, 0.10, and 0.20. All the samples were mixed according to ASTM C305 by using mortar mixer at room temperature. The mixing procedures are as follows:

- 1) Place all the mixing water in the bowl.
- 2) Add the cement to the water then start the mixer and mix at the slow speed of 140 rpm for 30 seconds.
- 3) Add the entire quantity of sand slowly over 30 seconds period, while mixing at slow speed of 140 rpm.

4) Stop the mixer, change to medium speed of 285 rpm and mix for 30 seconds.

5) Stop the mixer and let the mortar stand for 90 seconds. During the first 15 seconds of this interval, quickly scrape down into the batch any mortar that may have collected on the side of the bowl.

6) Finish by mixing for 60 seconds at medium speed of 285 rpm.

Then the fresh mortars were cast in molds and allowed to harden for 1 day. The prior hardened mortars were demolded and immersed in tap water for curing, as shown in Figure 3.2. The curing time of all the samples was fixed at 28 days. Then the cured mortars were taken out of the tap water and allowed to dry at room temperature for 3 hours to obtain the PMM without water on the surface.



Figure 3.2 Curing of the test specimens.

Table 3.2 Sample codes and mix proportions of PMM.

Sample	C/S	W/C	SDS/*P	*P/C
Unadded PMM	0.50	0.55	-	-
0.05PMM	0.50	0.55	0.10	0.05
0.10PMM	0.50	0.55	0.10	0.10
0.20PMM	0.50	0.55	0.10	0.20

*P refers to the mixture of 2NR/XSBR/5RSi.

3.2.6 Characterization of polymer-modified mortar (PMM)

3.2.6.1 Mechanical properties

1) Tensile properties

The PMM specimens with a briquette-shape were used to test in tension mode according to ASTM C190 by using flexural/tensile testing machine (ELE International) with a load of 10 kN. Figure 3.3 represents the dimensions of briquette-shape test specimen according to ASTM C190.

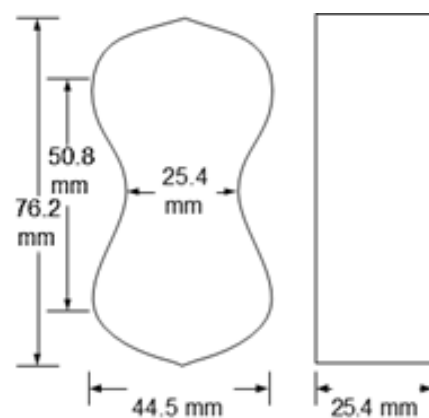


Figure 3.3 Dimensions of the briquette-shape test specimen according to ASTM C190 (<https://www.lceted.com/2021/08/laboratory-tests-on-cement.html>).

2) Compressive properties

The cube specimens of PMM with dimensions of 50 x 50 x 50 mm were used to test in compression mode according to ASTM C109 by using a semi-automatic compression machine (ELE International, ADR Touch SOLO 2000) with a pace of 100 kN/s. The equation that was used to calculate the tensile strength and compressive strength of PMM is:

$$S_T \text{ or } S_C = \frac{P}{A}$$

Where:

S_T or S_C = tensile strength or compressive strength (MPa),

P = total maximum load (N), and

A = area of loaded surface (mm²).

3) Flexural properties

The PMM specimens with a prism shape in dimensions of 40 x 160 x 40 mm were used to test in flexure mode according to ASTM C348 by using flexural/tensile testing machine (ELE International) with a load of 10 kN. The flexural strength of PMM was calculated by following the equation:

$$S_F = 0.0028P$$

Where:

S_F = flexural strength (MPa), and

P = total maximum load (N).

3.2.6.2 Water absorption

Before this characterization, the cube specimens of PMM with dimensions of 50 x 50 x 50 mm were dried in a hot-air oven at 110°C for 24 hours. Then the dried PMM specimens were allowed to cool at room temperature for 3 hours to obtain the PMM specimens with ambient temperature surfaces.

The water absorption of PMM was measured according to ASTM C1403. The PMM specimens were immersed in tap water for different immersion times of 0.25, 1, 4, and 24 hours. The equation that was used to calculate the water absorption of PMM is:

$$A_t = (W_t - W_0) \times \frac{10000}{(L_1 \times L_2)}$$

Where:

A_t = the water absorption (g/100 cm²),

W_t = the weight of the specimen at time t (g),

W_0 = the initial weight of the specimen (g),

L_1 = the average length of the test surface of the mortar specimen cube (mm), and

L_2 = the average width of the test surface of the mortar specimen cube (mm).

3.2.6.3 Morphological properties

The images of PMM were acquired using a FESEM (Carl Zeiss, AURIGA). The compressive fracture surfaces of PMM were coated with gold before the observation.