will expand the range of applications.

## II. Materials and Methods

### A. Materials

High-ammonia NR latex (60% dry rubber content (DRC)) was purchased from the Department of Agriculture, Thailand. All other chemicals were purchased from Sigma-Aldrich and used as received unless otherwise noted. NVCL was purified by recrystallization in methanol. Organic solvents (Labscan, AR) were used as received. Deionized (DI) water was used throughout the experiments. PNVCL was synthesized from NVCL via free radical polymerization using AIBN and used as a reference.

### B. Deproteinization of NR latex

NR latex (100 g) used in this study was commercial high ammonia latex (60% DRC). The incubation of the latex was performed with 0.1 wt% urea (0.2 g) in the presence of 1 wt% sodium dodecyl sulfate (SDS, 2 g) dissolved in DI water (100 g). This mixture was then incubated for 30 min with continuous stirring at room temperature. After that, the resulting latex was purified by centrifugation at 10,000 rpm for 1 h at 25 °C. The cream fraction was re-dispersed in 1 wt% SDS and washed twice by centrifugation to prepare DPNR latex (32% DRC).

### C. Grafting of NVCL on DPNR backbone

The DPNR latex (5 g) was placed in 100 mL round-bottom flask. Then, SDS (0.15 g) as an emulsifier and potassium hydroxide (KOH, 0.15 g) diluted in DI water was added while vigorous stirring. Subsequently, NVCL monomer (50-150 phr with respect to dry rubber content) was added continuously and the reaction mixture was heated at 80 °C for at least 30 min with continuous stirring. Next, AIBN (5-15 phr with respect to dry rubber content) as an initiator was dissolved with a slight amount of toluene and slowly charged into the reactor. The polymerization reaction was performed at the desired polymerization temperature (80-100 °C). The reaction mixture was allowed to react for a specified length of time (4-8 h). After that, the reaction mixture was cooled down to room temperature and coagulated by using 5 wt% acetic acid solution. The modified product was purified by soxhlet extraction in acetone for 24 h to remove contaminants, unreacted monomer and homopolymer. The grafted product was dried under vacuum at 60 ºC overnight. After drying, the grafted product was dissolved with chloroform-d for investigating grafting efficiency. The 1H-NMR intensity of the product was used to determine grafting efficiency percentage. Grafting efficiency (%) was determined from 1H-NMR spectra using the following equation:

$$Grafting\ efficiency\ (\%) = \frac{I_{4.4}}{I_{5.2}} \times 100\ , \qquad (1)$$

where $I_{4.4}$ was the integrated signal area of the proton in –NCH– of the α position of PNVCL unit and $I_{5.2}$ was the integrated signal area of the unsaturated methyne proton of polyisoprene backbone chain.

### D. Determination of LCST

The grafted material and dry DPNR were cut into small pieces (0.75x0.75 cm2) and compressed to remove air bubbles and reduce porosity by sandwiching them between two glass slides and heating at 60 °C for 24 h. The samples were immersed in deionized water for 2 h at a range of temperatures from 28 to 38 °C. After removing the surface liquid gently with tissue paper, the weight of the materials was measured and the swelling percentage was calculated to determine the LCST from the following equation:

$$Swelling\ (\%) = \frac{W_2 - W_1}{W_1} \times 100\ , \qquad (2)$$

where $W_1$ and $W_2$ was the weight of the material before and after immersion, respectively.

### E. Characterization

CHN data was obtained using CHN-2000 LECO analyzer. 1H (400 MHz) nuclear magnetic resonance (NMR) spectra were obtained using an AVANCE Bruker NMR spectrometer with chloroform-d as a solvent. The Fourier transform infrared (FT-IR) spectra were obtained using a Perkin Elmer FT-IR (Spectrum GX model) and NaCl salt windows. The surface elements of the sample were investigated using an X-ray photoelectron spectrometer (XPS; AXIS ULTRADLD, Kratos analytical, Manchester UK.) The base pressure in the XPS analysis chamber was about 5x10-9 torr. The samples were excited using X-ray hybrid mode at a 700x300 µm spot area with a monochromatic Al Kα1,2 radiation at 1.4 keV. The X-ray anode was run at 15kV 10mA 150 W. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45o with respect to the sample surface.

## III. Results and Discussion

### A. Synthesis and charaterizations of grafted copolymer

NVCL-grafted DPNR (NVCL-g-DPNR) was prepared via free radical grafting in aqueous system using AIBN as an initiator. NR latex was deproteinized prior to grafting reaction because deproteinization removed surface protein, leading to higher grafting efficiency. Deproteinization was carried out using urea as a deproteinizing agent [24]. The DPNR was characterized using CHN analysis. It was found that the nitrogen content in DPNR was less than that of NR by 43% while carbon and hydrogen remained almost unchanged (Table 1). This result indicates that deproteinization of NR removed approximately 50% of protein from NR latex, comparable with previous study [25].

TABLE I: Elemental analysis of NR and DPNR

| Sample name | Chemical composition | | |
|---|---|---|---|
| | Carbon (%) | Hydrogen (%) | Nitrogen (%) |
| DPNR | 84.19 | 12.88 | 0.43 |
| NR | 84.79 | 12.68 | 0.76 |

Grafting of NVCL onto DPNR was carried out in an aqueous system using AIBN as free radical initiator (Figure 1). The formation of grafting copolymer is believed to proceed by two possible pathways: a reaction between the free radicals and double bonds of the isoprene units and a hydrogen abstraction mechanism [26, 27]. The NVCL-g-DPNR was purified by