

Synthesis and Temperature-Responsive Behavior of N-vinylcaprolactam-grafted Natural Rubber

Sopitcha Phetrong, Chanon Sansuk and Peerasak Paoprasert

Abstract— Temperature-responsive polymers are smart materials because they can respond to change in surrounding temperature and are applicable for various applications. In this work, we reported a synthesis and temperature-responsive behavior of N-vinylcaprolactam-grafted deproteinized natural rubber (NVCL-g-DPNR). The grafting reaction was carried out using deproteinized natural rubber (DPNR) latex, N-vinylcaprolactam (NVCL) as monomer, and 2,2'-azoisobutyronitrile (AIBN) as free radical initiator. The temperature responsiveness of the grafted copolymers was investigated using water swelling and compared with that of pure DPNR. The lower critical solution temperature (LCST) of the grafted copolymer was found to be in the range 32-34 °C whereas the DPNR was not responsive to temperature. The temperature-responsiveness of grafted copolymer near human body temperature can be utilized to be fabricated as biomedical materials. Based on this study, the temperature-responsive natural rubber would potentially be used as a novel responsive rubber-based material in various applications.

Keywords— Temperature-responsive material, N-vinylcaprolactam, Deproteinization, Natural rubber, Grafting.

I. INTRODUCTION

Stimuli-responsive materials are smart materials because they can sense and respond to changes in environmental conditions, such as pH, temperature, light, ionic strength, electric field, and magnetic field [1]. Changes in surrounding conditions trigger a change in the physical and chemical properties of stimuli-responsive materials, such as size, shape, hydrophobicity/hydrophilicity, and degradation rate [2]. These responsive materials can therefore be used to fabricate responsive and active devices that can regulate and introduce new functionalities for various applications. Temperature is considered as one of the most widely used external stimuli in stimuli-responsive materials because it can be simply modulated by temperature-programmed equipment or ambient conditions. Temperature-responsive materials are those that generally undergo a volume transition or soluble-to-insoluble change or vice versa in solvents around the lower critical solution temperature (LCST). One of the most widely studied temperature-responsive polymers is based on poly(N-vinylcaprolactam) (PNVCL) because it possesses

LCSTs of around 32 °C in water, which is near the human body temperature [3, 4]. The non-toxicity, high water solubility, and biocompatibility of PNVCL make it applicable in various biomedical applications. In addition, PNVCL is water-soluble, biocompatible, and relatively stable against hydrolysis and does not produce toxic low molecular-weight amines due to the presence of cyclic amide instead of aliphatic amides in other polymers [5]. A range of temperature-responsive copolymers have also been prepared to increase strength and impart new properties to hybrid materials. N-vinylcaprolactam (NVCL) has been copolymerized and grafted copolymerized with several polymers, for example, chitosan [6], methacrylic acid (MAA) [7], poly(acrylic acid) (PAA) [8], and polypropylene (PP) [9]. NVCL-based copolymers thus have the potentials to be used for a wider range of applications.

Natural rubber (NR) is a well-known renewable elastomeric material obtained from the *Hevea brasiliensis* tree in the form of a milky white fluid called latex [10]. NR is a versatile material widely used in various applications. Although the presence of double bonds makes cis-polyisoprene susceptible to degradation, double bonds are places to which new functionalities can be added. Several chemical reactions have been used to modify NR which produces hybrid structures with high strength and stability. Various monomers have been grafted with NR, including glycidyl methacrylate (GMA) [11], methyl methacrylate (MMA) [12-14], styrene (ST) [15, 16], 2-hydroxyethyl methacrylate (HEMA) [17], vinyl alcohol (VA) [18], and maleic anhydride (MA) [19, 20].

Grafting of hydrophilic monomers on NR backbone remains a challenge because of the presence of surface proteins as rubber particle shells. Monomers are not well incorporated in the hydrophobic NR cores in latex and therefore often homopolymerize [21-23]. However, several monomers and polymers have been grafted with NR, the main goal has been to improve the thermal, chemical, and mechanical properties of NR. The addition of responsive functions to NR via grafting reaction has never been reported. Thus, the objective of this study was to develop a method for grafting NVCL onto NR for preparing rubber-based, temperature-responsive materials. Furthermore, in this work grafting reaction was carried out using deproteinized natural rubber (DPNR) latex and 2,2'-azoisobutyronitrile (AIBN) as an initiator. The LCST of the grafted copolymers was measured and compared with pristine NR. Based on these results, this work shows that temperature responsiveness can be introduced to NR, which

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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 °C 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:

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

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:

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

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 μ m spot area with a monochromatic Al K α 1,2 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 characterization 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

soxhlet extraction in acetone in order to remove impurities, unreacted NVCL, and PNVCCL homopolymer.

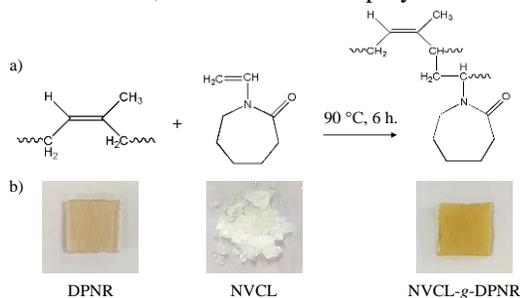


Fig. 1: a) schematic representation for the synthesis of NVCL-g-DPNR from DPNR and NVCL and b) their respective images.

The NVCL-g-DPNR was characterized using FT-IR and $^1\text{H-NMR}$ techniques and compared with the DPNR and PNVCCL. The FT-IR spectrum of NVCL-g-DPNR showed signature signals of both DPNR and PNVCCL (Figure 2). The FT-IR signals at 3440, 3255, 1631, and 1379 cm^{-1} corresponded to O-H stretching, N-H stretching, C=O stretching and C-N stretching of caprolactam ring of PNVCCL, respectively. The signal at 1442 cm^{-1} corresponded to C=C stretching of the polyisoprene. The FT-IR results are consistent with those in previous work [28].

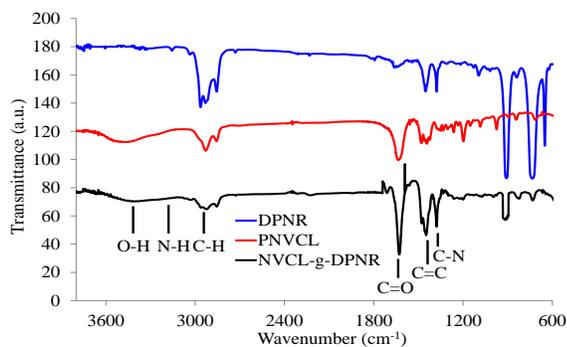


Fig. 2: FT-IR spectra of DPNR, PNVCCL, and NVCL-g-DPNR.

$^1\text{H-NMR}$ spectrum of DPNR showed signals at 5.2, 2.1 and 1.7 ppm, corresponding to C-H, CH_2 , and CH_3 respectively (Figure 3), consistent with previous report [29]. The $^1\text{H-NMR}$ spectrum of the PNVCCL showed signals at 4.4, 3.3, 2.5, and 1.8 ppm, corresponding to CH-NH, CH_2 -NH, CH_2 -CO, and CH_2 respectively. The $^1\text{H-NMR}$ spectrum of NVCL-g-DPNR showed signals corresponding to both DPNR and PNVCCL. The signal at 4.4 ppm corresponded to CH-NH of the PNVCCL, whereas the signal at 5.2 ppm corresponded to C-H of the isoprene units. These signals were used to calculate grafting efficiency, which was found to be 25%.

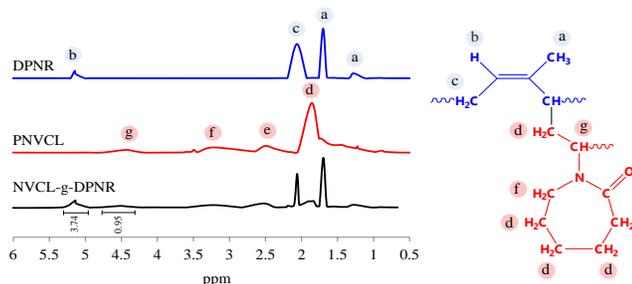


Fig. 3: $^1\text{H-NMR}$ spectra of DPNR, PNVCCL, and NVCL-g-DPNR. In addition, only the XPS spectrum of NVCL-g-DPNR

showed strong N1s signal at 400 eV, which was not observed in the DPNR sample due to the presence of amide group of NVCL units in grafted-rubber (Figure 4).

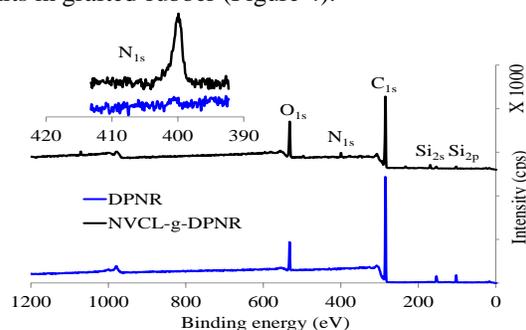


Fig. 4: XPS spectra of DPNR and NVCL-g-DPNR. The inset is the high-resolution spectra in the N1s region.

To further confirm the formation of grafted copolymer, a blend sample between DPNR latex and PNVCCL was prepared in water solution and dried by placing on glass plate as a thin film. After that, the film was peeled off and purified via stirring in acetone twice and dried in an oven at 60 °C overnight. It was found that PNVCCL was not detected in $^1\text{H-NMR}$ spectrum as it was soluble in acetone. Therefore, the presence of both PNVCCL and DPNR in the NVCL-g-DPNR sample must be due to the formation of a grafted structure inseparable by stirring in acetone. This result also confirmed that stirring in acetone twice effectively removed unbound PNVCCL homopolymer.

B. Temperature-responsive studies

The temperature responsiveness of DPNR and NVCL-g-DPNR in water were characterized at a temperature range of 28–38 °C. At 28 °C, NVCL-g-DPNR swelled by 15% of its original weight and about 8 times more than the DPNR, due to the presence of hydrophilic NVCL units. The NVCL-g-DPNR can be thus considered as a hydrogel-like material. As the temperature was increased, the percentage of swelling of the DPNR did not change, whereas that of the NVCL-g-DPNR started to decrease when the temperature of water exceeded 30 °C and became constant above 34 °C (Figure 5).

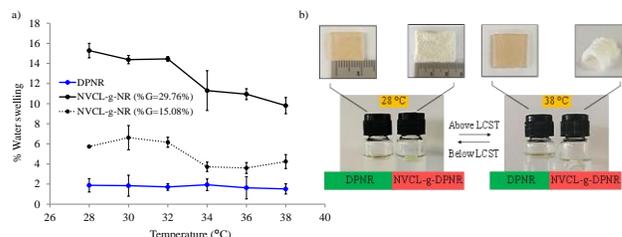


Fig. 5: a) water swelling percentage of DPNR and NVCL-g-DPNR in aqueous solutions at different temperatures and b) schematic illustration of water swelling studies of DPNR and NVCL-g-DPNR in aqueous solutions at below and above LCST.

The LCST of NVCL-g-DPNR was therefore determined to fall in the range of 32–34 °C, which is similar to the coil-to-globule transition temperature of PNVCCL. These results suggest that the presence of DPNR and grafted structure in the NVCL-g-DPNR did not significantly affect the LCST of the PNVCCL. This finding is consistent with other reports on

temperature-responsive crosslinked materials [30, 31].

IV. CONCLUSIONS

In this work, the grafted copolymers between NVCL and DPNR were successfully prepared via grafting reaction in emulsion using AIBN as an initiator. The characterizations were performed by FT-IR, ¹H-NMR and XPS techniques. The FT-IR and ¹H-NMR spectra were showed both DPNR and PNVCCL signals which were strongly confirmed that the NVCL units were introduced onto DPNR backbone. Furthermore, the XPS spectra of the grafted materials showed a significant increase in N1s signal at 400 eV, that confirm the amide group of NVCL units in grafted materials whereas this signal was not observed in DPNR. The temperature responsiveness of NVCL-g-DPNR was studied by water swelling experiment that showed an LCST around 32-34 °C, which was close to the phase transition of PNVCCL. These temperature-responsive rubbers will be useful for a variety of biomedical applications. Potential consumer products include, smart bandages and facial masks with the ability to efficiently release medicine or healing ingredients upon contact with human skins.

ACKNOWLEDGMENT

This work is financially supported by the Thailand Research Fund (TRF) and the Faculty of Science and Technology, Thammasat University (TRG5880199). The authors acknowledge the Central Scientific Instrument Center (CSIC), Department of Chemistry, Faculty of Science and Technology, and Thammasat University. In addition, the authors gratefully acknowledge the financial support provided by Thammasat University under the TU Research Scholar (2017).

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