

Preparation and Characterization of Deproteinized Natural Rubber Grafted with 4-Vinylpyridine as pH Responsive Materials

Chanon Sansuk, Sopitcha Phetrong and Peerasak Paoprasert

Abstract— Natural rubber is one of the renewable materials with excellent properties, including high elasticity and fatigue resistance. This work reports a method to introduce a pH-responsive function to natural rubber. 4-vinylpyridine was functionalized onto deproteinized natural rubber latex via graft copolymerization in the water medium. The grafted copolymer (4VP-g-DPNR) was characterized using Fourier-transform infrared spectroscopy, nuclear magnetic resonance spectrometer, and X-ray photoelectron spectroscopy. The pH-responsiveness of the functionalized materials was studied in aqueous solutions via water swelling experiment. It was found that the 4VP-g-DPNR sample became swollen under acidic conditions whereas the unmodified rubber did not change in any pH solutions. Based on these results, this work thus demonstrated a method to add the pH responsive function to natural rubber. The introduction of pH responsiveness into natural rubber will lead to new responsive rubber-based materials and widen their applications.

Keywords— Grafting, pH-responsive material, Natural rubber, Deproteinization, 4-vinylpyridine

I. INTRODUCTION

Natural rubber (NR) from *Hevea brasiliensis* is one of the most valuable renewable resources. It has attracted significant interest in many fields, including the automobile, consumer, and medical sectors, mainly due to its outstanding elasticity and good mechanical properties [1]. Thailand is the largest producer and exporter in the world [2].

The graft copolymerization of a vinyl monomer onto NR is one of the most interesting and widely studied fields of research into adding value and function to NR. Graft copolymerization of NR is usually carried out via free

radical method, which can be initiated by chemical initiator, high energy radiation, or UV illumination, under various conditions [3]. Several types of monomer have been reported producing a range of new rubber-based materials [4-9]. However, among these materials, NR with responsive functions is rare. Adding responsive functions to the unique properties of NR will expand the range of applications, for example, sensing devices and smart biomedical materials. Stimuli responsive materials are unique because they can sense and respond to changes in ambient conditions, such as pH, temperature, light, ionic strength, electric field, and magnetic field [10-12]. Changes in environmental conditions can trigger a change in the physical and chemical properties of stimuli-responsive materials, such as their size, shape, hydrophobicity/hydrophilicity, and degradation rate. The stimuli-responsive materials have numerous potential applications.

4-Vinylpyridine (4VP)-based polymers are known as pH-responsive materials that can potentially be used in many sensing and biomedical applications, such as in drug delivery and biosensors [13]. In addition, 4-vinylpyridine is a good ligand for the formation of complexes with metal ions, thereby allowing P4VP-based polymers to be used as metal absorbents [14, 15].

Therefore, in this work, a method for functionalizing 4-vinylpyridine (4VP) onto deproteinized natural rubber latex (DPNR) was demonstrated. 4VP was grafted onto DPNR via emulsion polymerization in the presence of potassium persulfate (KPS) as initiator and sodium dodecyl sulfate (SDS) as emulsifier. Thus, integration of 4VP and DPNR will expand the range of applications of rubber-based materials.

II. MATERIALS AND METHOD

A. Materials

High-ammonia NR latex (60% dry rubber content) was purchased from Department of Agriculture, Thailand. All chemicals were purchased from Sigma-Aldrich. 4-vinylpyridine monomer (4VP) (95%, Acros) was purified by passing through silica gel columns prior to use.

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Deionized (DI) water was used throughout all experiments.

B. Preparation of Deproteinized Natural Rubber Latex

The deproteinized natural rubber latex (DPNR) was firstly prepared by incubation of the high-ammonia NR latex (60% dry rubber content) with 0.1% w/w urea in the presence of 1% w/w sodium dodecyl sulfate (SDS) for 30 min. Then, the incubated urea natural rubber latex was centrifuged at 10,000 rpm for 60 min. The recovered cream fraction (top layer) was re-dispersed in 1% w/w SDS to further wash the rubber particles. The washing process was repeated twice and then the recovered cream was re-dispersed in 1% w/w SDS to make DPNR latex [16].

C. Grafting of 4VP on DPNR

The DPNR latex (5 g) was firstly placed into a 250 mL two-neck round-bottom flask equipped with a mechanical stirrer and reflux condenser, followed by dilution with DI water (5mL). A solution of potassium hydroxide (0.1 g) to maintain pH of the system and sodium dodecyl sulfate (0.1 g) as an emulsifier was then added. The 4VP (150 phr with respect to dry rubber content) monomer was then gradually dropped. The reaction mixture was continuously stirred for 30 min to allow rubber particles to swell with 4VP monomer and become homogeneous. After that, the reaction was heated to approximately 70 oC and a solution of potassium persulfate (10 phr with respect to dry rubber content) in distilled water was added. The reactions were allowed to proceed under agitation at 90 oC for 3 hours and then the reactor was discharged. The grafted latex was coagulated with 5 wt% acetic acid, washed several times with distilled water, and dried up in an oven at 60 oC for an overnight. The obtained product was purified by soxhlet extraction in acetone for 24 hours to remove the residue free monomer, homopolymer, and any contaminants, followed by dry at 60 oC for 24 hours.

The grafting ratio was calculated from the following equation:

$$\text{Grafting efficiency (\%)} = \frac{I_{4.4}}{I_{5.1}} \times 100, \quad (1)$$

where I_{8.5} and I_{5.1} are the integrated signal area of the proton of pyridine ring of 4VP unit and the unsaturated methyne proton of polyisoprene, respectively.

D. Water swelling experiment

The P4VP-NR and dry NR were cut into small pieces (1x1 cm²). The samples were immersed in aqueous solutions with pH ranging from 2 to 12 for 24 hours at room temperature. The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH deionized water. After removing the surface liquid gently with tissue paper, the weight of materials was measured and the swelling percentage was according to the following equation:

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

where W₁ and W₂ was the weight of the material before and after immersion, respectively.

E. Characterization

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 CHN analyzer was obtained using Perkin-Elmer 2400 series CHNS/O Analyzer. 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 Kα_{1,2} radiation at 1.4 keV.

III. RESULTS AND DISCUSSIONS

A. Analysis of grafted material

In this work, the graft copolymerization of 4VP onto natural rubber latex (NR) was prepared by emulsion polymerization. Prior to grafting reaction, NR was deproteinized to remove surface proteins in order to increase grafting efficiency. The DPNR was prepared using urea as surfactant. From CHN analyzer, the total nitrogen content in the as-prepared DPNR was reported as shown in Table 1. It was found that total nitrogen content of the as-prepared DPNR decreased, compared with untreated NR. Thus, in this work, urea and SDS were able to remove protein from NR, consistent with previous reports [17-19].

TABLE I:
C, H, AND N DATA OF NR AND DPNR..

Sample Name	Composition (%w/w)		
	Carbon	Hydrogen	Nitrogen
NR	84.79	12.68	0.76
DPNR	84.19	12.88	0.43

The graft copolymerization of 4VP and DPNR in water medium was carried out in the presence of potassium persulfate (KPS) as initiator and sodium dodecyl sulfate (SDS) as emulsifier. It is well-known that KPS thermally dissociates to generate free radicals as shown in Figure 1. Those free-radicals reacted with DPNR at the "α" - methylenic hydrogen atom via hydrogen abstraction processes to give polyisoprene radicals [6, 16]. The polyisoprene radicals then react with 4VP monomer during propagation to obtain 4VP-g-DPNR (Figure 2a). After the

graft copolymerization and purification process, the photograph of the obtained 4VP-g-DPNR was taken, showing a yellowing solid rubber (Figure 2b).

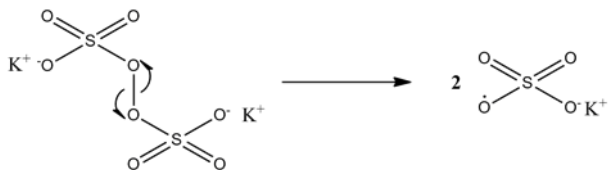


Fig. 1: Thermal decomposition of potassium persulfate.

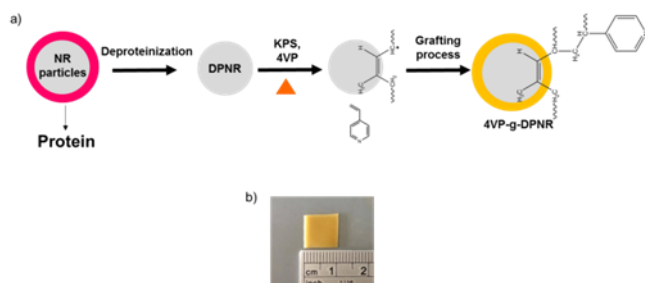


Fig. 2: Schematic representation of (a) grafting reaction between 4VP and DPNR using KPS and (b) photograph of DPNR-grafted 4VP. Sample size is approximately 1x1 cm²

The FT-IR spectrum of the DPNR in Figure 3. exhibited the vibration bands of C=C stretching and bending at 1662 cm⁻¹ and 841 cm⁻¹, CH₃ stretching at 2961 cm⁻¹, CH₂ stretching at 2916 cm⁻¹, CH₂ bending at 1451 cm⁻¹, CH₃ bending at 1376 cm⁻¹, and =C-H bending at 835 cm⁻¹. [20] After the graft copolymerization and soxhlet extraction by acetone, the 4VP-g-DPNR showed the signatures of both P4VP and DPNR. The important characteristic bands for the grafted materials appeared at 1604 cm⁻¹, 1420 cm⁻¹, and 1000 cm⁻¹, corresponding to C=N, C=C, and pyridine ring deformation, respectively, [13], whereas the signal at 1451 cm⁻¹ corresponded to CH₂ bending of the polyisoprene, suggesting the occurrence of grafting process of 4VP onto DPNR.

The confirmation of the chemical structure was then investigated using ¹H-NMR. Figure 4. shows ¹H-NMR spectrum of 4VP-g-DPNR. The signal characteristic peak of DPNR appeared at 1.7, 2.0 and 5.1 ppm, which were assigned to methyl (-CH₃), methylene (-CH₂-), and unsaturated methane (=C-H-) protons of isoprene units, respectively. Moreover, broad signals around 6.5 and 8.5 ppm were attributed to the aromatic protons of the pyridine rings [21, 22]. These confirmed that 4VP was grafted onto DPNR. The grafting efficiency determined from the ¹H-NMR spectrum was 45%.

In addition, the chemical composition at the surface of the graft copolymer using an XPS technique is shown in Figure 5. Signals of O1s, C1s, Si2s, and Si2p were observed on DPNR sample at binding energies of 532 eV, 285 eV, 153 eV, and 102 eV, respectively. It can be seen

that the chemical composition of the DPNR sample mainly consisted of carbon atoms and the presence of the small oxygen content may resulted from the impurities in the rubber latex [23]. Moreover, the silicon signals arose from the silicon substrate used for the measurement. Unlike the DPNR sample, only the 4VP-g-DPNR sample showed a nitrogen signal at 399 eV, which owing to the presence of nitrogen atom of pyridine ring in the grafted material [24]. Hence, in this work, the results from FT-IR, ¹H-NMR, and XPS on 4VP-g-DPNR sample indicated the successful graft copolymerization of 4VP on DPNR via using emulsion polymerization.

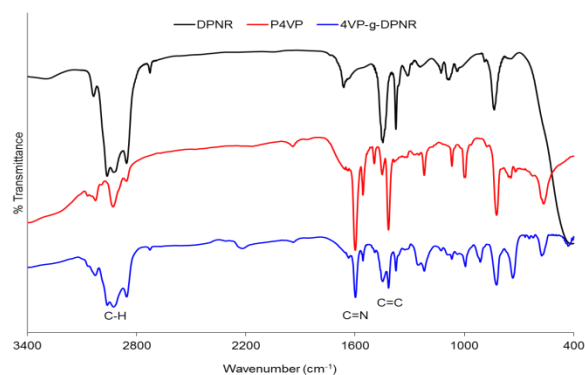


Fig. 3: FTIR spectra of DPNR, P4VP and 4VP-g-DPNR.

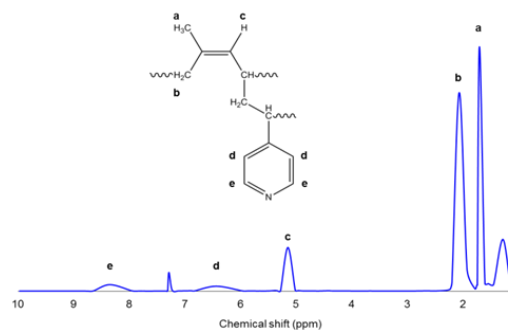


Fig. 4: ¹H-NMR spectrum of 4VP-g-DPNR.

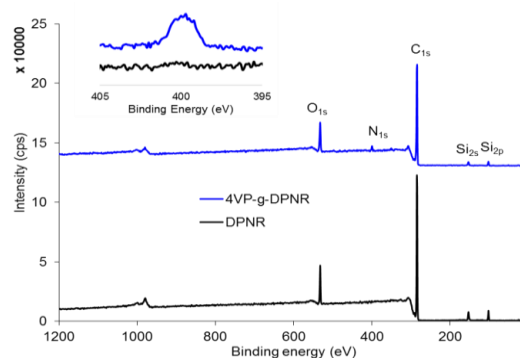


Fig. 5: XPS spectra of 4VP-g-DPNR and DPNR. The inset shows the multiplex-scan spectra in the N1s region.

B. pH Responsiveness

The pH responsiveness of DPNR and 4VP-g-DPNR samples was characterized in aqueous solutions for a pH range of 2-12. It was found that 4VP-g-DPNR sample became more swollen than the pristine DPNR sample due to the presence of hydrophilic vinylpyridine units (Figure 6). The swelling percentage of the 4VP-g-DPNR samples increased when the pH of the aqueous solution was below 4 whereas that of the DPNR sample did not change in any pH of the aqueous solution. Since, pyridine is a weak base in which the pKa of 4.7 [25]. When the pH of solution is below 4.7, pyridine is protonated and converted into pyridinium salt containing positive charges. Since the electrostatic repulsion of positive charges, the materials become swollen and absorb more water. When the pH was higher than 4, the pyridine groups were deprotonated or became neutral, leading to a lower swelling percentage. In addition, it was also found that the swelling ratio increased as the grafting ratio increased owing to the greater amount of 4VP onto the samples.

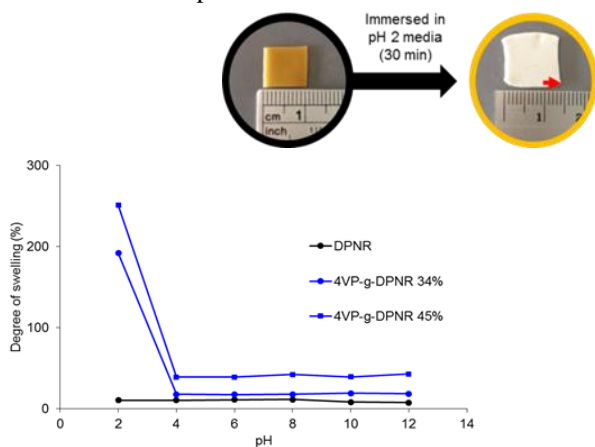


Fig. 6: Degree of swelling of DPNR and 4VP-g-DPNR (grafting ratio =34 and 45 %) in aqueous solutions with various pH values.

IV. CONCLUSIONS

In this work, 4VP-g-DPNR was successfully prepared via emulsion polymerization. The materials showed pH responsiveness in acidic conditions when pH was below 4, as confirmed by water swelling. Based on our work, it will also be possible to prepare other types of responsive or multi-stimuli-responsive rubbers through the reactions of multiple responsive materials, which will extend the properties and expand the range of applications of these rubbers.

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