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Contributed Paper

Chlorohydration of Natural Rubber Latex using N-chlorosuccinimide for Fuel-resistant Materials

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ABSTRACT

Natural rubber (NR) cannot be effectively used to store or make contact with hydrophobic substances as it will become swollen and lose its shape. In this work, we developed a simple method for synthesizing chlorohydrated NR from latex using N-chlorosuccinimide (NCS) as a new chlorohydrating agent for NR latex, in the presence of thiourea and ammonium hydroxide as the catalyst and stabilizer, respectively. A chlorohydrin content as high as 70% was obtained. The swelling resistance of chlorohydrated NR with 41% chlorohydrin in toluene was improved nearly ten times, compared with that of the unmodified NR. The chlorohydrated NR also demonstrated excellent resistance against diesel fuel, while the pristine NR was totally degraded. The chlorohydrated NR thus provides an attractive fuel-resistant material. The thermal and mechanical properties and ozone resistance of the chlorohydrated NR were characterized. The merits of the method include low cost of raw materials, simpler production processes, and the ability to scale up production. The chlorohydrated NR produced can be used in a wide range of applications.

Keywords: natural rubber, chlorohydration, N-chlorosuccinimide

1. INTRODUCTION

Natural rubber (NR) is a renewable, widely used elastomeric material derived from latex, a milky colloid produced by *Hevea brasiliensis*. NR offers high elasticity and fatigue resistance. However, NR is easily degraded upon continuous exposure to sunlight, oxygen, heat, and ozone, as it contains *cis*-polyisoprene, an unsaturated polymeric material [1-2]. Moreover, as *cis*-polyisoprene is a hydrocarbon polymer, NR is unsuitable for applications that make contact with oils,

organic solvents, or hydrocarbon substances. Upon exposure to these hydrophobic compounds, the NR becomes swollen and loses its shape and functionality [3-4]. Hence, improving the hydrophilicity of NR will improve its resistance to hydrophobic substances and expand the range of applications of NR-based materials.

Several addition-based reactions have been used to increase the hydrophilicity of NR, including grafting with monomers,

epoxidation, and chlorination [5-9]. A variety of hydrophilic monomers, such as dimethyl aminoethyl methacrylate [10], glycidyl methacrylate [11], 2-hydroxyethyl methacrylate [12-13], vinyl alcohol [14], and maleic anhydride [15-16], have been grafted onto *cis*-polyisoprene. However, grafting efficiency is low, especially when carried out in the latex. NR latex is an aqueous based system consisting of colloidal particles with *cis*-polyisoprene as the hydrophobic core. Hydrophilic monomers thus stay mostly in the aqueous phase and form homopolymers, rather than reacting with the *cis*-polyisoprene in the core [17]. Epoxidation of natural rubber is a relatively simple method for improving the hydrophilicity, but epoxidized natural rubber is susceptible to attack by hydrogen-donor molecules, leading to ring-opening and crosslinking as side reactions [18]. Chlorination is an alternative method for increasing hydrophilicity, film-forming, flame retardancy, abrasive and corrosive resistance, and insulation properties of the NR, while reducing tackiness and frictional resistance [19-23]. Chlorinated NR has been widely used as a raw material in paints, coatings, adhesives, and inks [24]. Traditionally, chlorination of NR latex was carried out using the gaseous chlorine in trichloromethane or tetrachloromethane and chlorinating organic compounds such as chlorolamine and trichloroisocyanuric acid [19, 21, 25-26]. These methods, however, are considered toxic and inconvenient and are prohibited in many countries. Tetrachloromethane, for example, was banned after being implicated in the thinning of the atmospheric ozone layer [20]. In addition, the use of reactive gaseous chlorine or these chlorinating agents leads to the formation of several by-products through undesirable side reactions, including cyclization and chain

scission [21, 26]. Therefore, simpler and safer methods of preparing chlorinated NR and producing purer products are highly desirable.

In this work, a novel method for increasing the hydrophilicity of NR was investigated. N-chlorosuccinimide (NCS) was used as the novel chlorinating agent to prepare chlorohydrinated NR from latex. The thermal and mechanical properties of the chlorohydrinated NR were characterized. The swelling resistance of the modified NR in toluene and diesel fuel was found to be much greater than that of the unmodified NR. Both grafting and chlorohydration were carried out in one pot to demonstrate the versatility of our method. We demonstrated a chemical method for the preparation of hydrophilic NR that will expand the range of applications for NR-based materials.

2. MATERIALS AND METHODS

2.1 Materials

All chemicals were purchased from Sigma-Aldrich unless otherwise noted. High-ammonia NR latex (60 wt% dry rubber content) was obtained from the Department of Agriculture, Thailand. Stearic acid, zinc oxide, N-cyclohexyl-2-benzothiazole sulfonamide, and sulfur were supplied by the Research and Development Centre for the Thai Rubber Industry. Diesel was purchased from a local gas station. Methyl methacrylate (MMA) was purified by passing through a column of silica gel prior to use. Deionized (DI) water was used throughout.

2.2 Synthesis of Chlorohydrinated NR (CNR)

The NR latex was placed in a round-bottom flask. Triton X-100 as surfactant and NH_4OH solution (1.5 wt%) were then added to the reaction mixture. A predetermined amount of NCS and thiourea were dissolved

in DI water. After that, a solution of NCS and thiourea were added to the latex mixture. The chlorohydration reaction was conducted for 6 h at room temperature. After that, acetone was added to precipitate the rubber. The solid rubber was filtered, washed with plenty of water, and dried in an oven at 45 °C overnight. The crude rubber was purified by soxhlet extraction in acetone for 24 h. The purified rubber was then dried in the oven at 45 °C overnight, yielding a pale yellow solid.

The chlorohydrin content of CNR can be calculated using equation (1).

$$\text{Chlorohydrin content (\%)} = \frac{I_{3.7}}{I_{5.1} + I_{3.7}} \times 100 \quad (1)$$

where $I_{3.7}$ is the integrated signal area of CH-Cl and $I_{5.1}$ is the integrated signal area of the methine proton from the $^1\text{H-NMR}$ spectrum.

2.3 Fuel-swelling Experiment

The NR samples were cut into approximately $0.5 \times 0.5 \times 0.5 \text{ cm}^3$ pieces. The samples were then immersed in toluene or diesel fuel at 30 °C for 2 h. The weight of the swollen samples was determined after removing the surface liquid gently with tissue paper. The swelling ratio was calculated from equation (2).

$$\text{Swelling ratio (\%)} = \frac{W_{\text{after}} - W_{\text{before}}}{W_{\text{before}}} \times 100, \quad (2)$$

where w_{after} is the weight of the sample after immersion and w_{before} is the weight of the sample before immersion.

2.4 Grafting Method

The NR latex (10 g), potassium hydroxide (1.67 part per hundred of rubber, phr), and DI water (100 mL) were placed in a 250-mL round-bottom flask. Sodium

lauryl sulfate (1 phr) as an emulsifier was added while stirring. After 15 min, *i*-propanol as a stabilizer (1 phr) was added to the reaction mixture. After 15 min stirring, methyl methacrylate (MMA) (100 phr) was added continuously and stirred for an additional 1 h. The mixture was heated to 50 °C. Cumene hydroperoxide (CHPO) as an initiator (0.75 phr) was then added. After 15 min of mixing, tetraethylenepentamine (TEPA) (0.75 phr) was added. The reaction was allowed to proceed for 6 h. Triton X-100 was then added to the reaction mixture. After 10 min stirring, a solution of N-chlorosuccinimide (NCS) and thiourea was added to the latex mixture. The chlorination reaction was conducted for an additional 6 h at room temperature. After that, acetone was added to precipitate the rubber. The solid rubber was filtered, washed with plenty of water, and dried in an oven at 45 °C overnight. The crude rubber was purified by soxhlet extraction in acetone for 24 h. The purified rubber was then dried in the oven at 45 °C overnight yielding a pale yellow solid.

2.5 Preparation of Rubber Vulcanizates

To measure the mechanical properties, the rubbers were vulcanized via conventional vulcanization. The vulcanized rubber was prepared using a two-roll mixing mill. First, 70 g of rubber (100 phr) was masticated for 3 min at 70 °C and mixed with stearic acid (2 phr), zinc oxide (1 phr), and N-cyclohexyl-2-benzothiazole sulfonamide (1 phr) followed by mastication for an additional 3 min. Sulfur (1.5 phr) was then added and the mixture was allowed to stand for 3 min. Prior to the processing step, the curing time (T_{90}) was determined on the basis of the curing characteristics measured by a moving die rheometer (TECHPRO, rheotech MD+) following ASTM D5289,

at a temperature 150 °C. The rubber compound was compression molded into a sheet of 2 mm thickness at 150 °C under a force of 1800 psi, using a hydraulic press and a cure time of T_{90} . Rubber vulcanizates were conditioned for 24 h at room temperature before testing.

2.6 Characterization

^1H (400 MHz) nuclear magnetic resonance (NMR) spectra was obtained on an AVANCE Bruker NMR Spectrometer using chloroform- d as the solvent. The Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using a Perkin Elmer FT-IR (Spectrum 2000 model) and NaCl salt windows. Thermogravimetric analysis (TGA) of the polymers was carried out using a Perkin Elmer TGA7 analyzer. The samples were heated at a rate of 20 °C/min from 25 °C to 600 °C under a nitrogen atmosphere. The glass transition temperatures of the polymers were obtained using a Mettler Toledo DSC1 differential scanning calorimeter. The samples were heated at a rate of 10 °C/min under a nitrogen atmosphere. The surface elements of the sample surface were investigated using an X-ray photoelectron spectrometer (XPS; AXIS ULTRA^{DLD}, Kratos analytical, Manchester UK.) The chemical composition of the samples was measured using a PANalytical PW-2404 X-ray fluorescent spectrometer in semi-quantitative analysis mode. Water contact angles were measured using a ram-hart goniometer (model 100-00-220). At least five positions on each sample were measured and the volume of each water droplet used was 1 μL . The tensile properties of the unmodified and modified NR samples were investigated. The specimens

were cut into a dumbbell shape using a die C following ASTM D412. The tensile properties of all vulcanized rubber samples were determined on a universal testing machine (INSTRON 3366). The average of three specimens was used as the representative value. The ozone resistance of the rubber samples was measured following ISO 1431-1 using an ozone aging tester (TOYOSEIKI) with the following test conditions: ozone concentration: 500 ppb, temperature: 40 °C, exposure time: 20 h, strain: 20%, and shape of test piece: strip.

3. RESULTS AND DISCUSSION

3.1 Analysis of CNR

A chlorohydration reaction of NR latex was carried out using NCS. NCS has been used as a chlorinating agent for several alkenes under aqueous conditions with product yields up to 69% [27]. A chlorohydrinated NR was obtained because the reaction was carried out under aqueous conditions (Figure 1a). Thiourea was added as a catalyst to facilitate the transfer of chlorine atoms via hydrogen bonding with the NCS (Figure 1b). The ^1H NMR spectra of the UNR (unmodified NR) and CNR were obtained (Figure 2). The ^1H NMR spectra of UNR showed signals at 1.7, 2.1, and 5.2 ppm, which are attributed to $-\text{CH}_3$, $-\text{CH}_2-$, and olefinic protons, respectively. The ^1H -NMR spectrum of CNR showed additional signals at 3.7 and 4.4 ppm, corresponding to protons in the CH-Cl and $-\text{OH}$, respectively. These results agree with a previous study [28], indicating the formation of a chlorohydrinated product of modified *cis*-polyisoprene using NCS/thiourea under aqueous conditions.

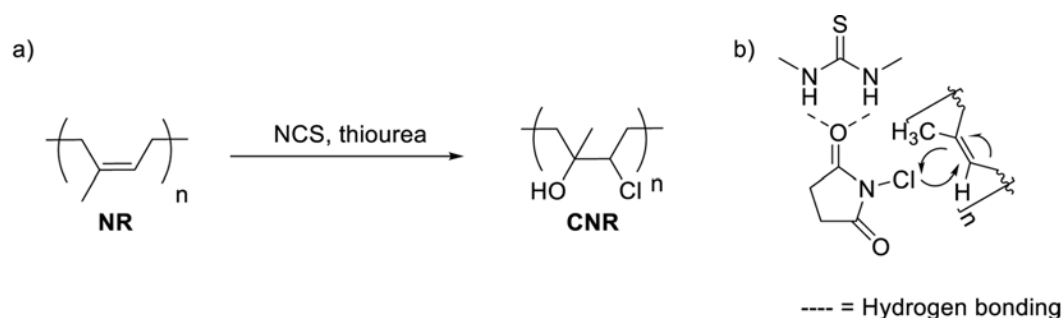


Figure 1. a) Chlorohydrin reaction of NR and b) catalytic mechanism of thiourea and NCS.

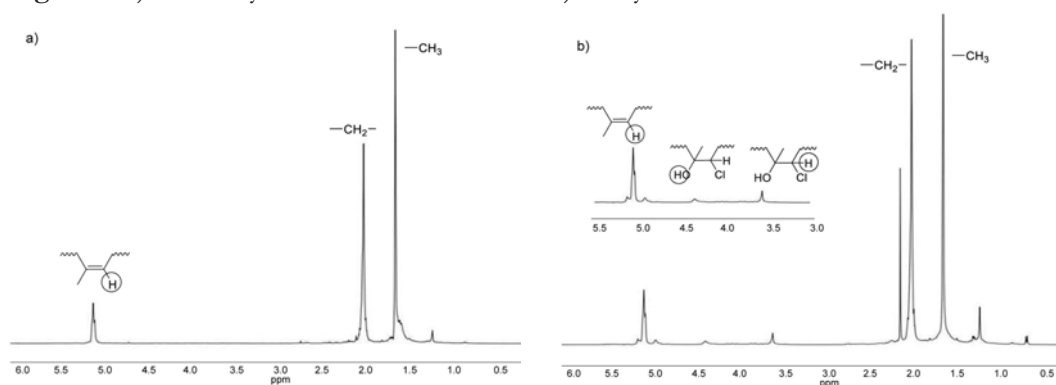


Figure 2. ¹H-NMR spectra of a) UNR and b) CNR.

The UNR and CNR were characterized using FT-IR (Figure 3). The FT-IR spectra showed signature signals of *cis*-polyisoprene as follows: a C-H stretching vibration at around 2900-3000 cm^{-1} and a C=C stretching vibration at 1457 cm^{-1} . The FT-IR spectra of the CNR showed C-Cl stretching peaks at 918 and 741 cm^{-1} . This confirmed the successful formation of chlorohydrinated natural rubber, as these two signals were not present in the spectra of the UNR.

XPS is a surface specific technique routinely used to probe surface elements. The XPS spectrum of the CNR showed the appearance of Cl_{2p} peaks at 200 eV, confirming the presence of chlorine atoms in the CNR (Figure 4), whereas no Cl_{2p} signals were observed in the UNR sample. The results from the FT-IR, NMR, and XPS characterizations thus indicate that the chlorination method using NCS developed in

this work produces only the chlorohydrinated product. The XRF technique was used to quantify the chlorohydrin content of the solid CNR sample. The chlorohydrin content obtained from the chosen sample was found to be ~23%, which is close to the 28% chlorohydrin content calculated from the NMR spectrum.

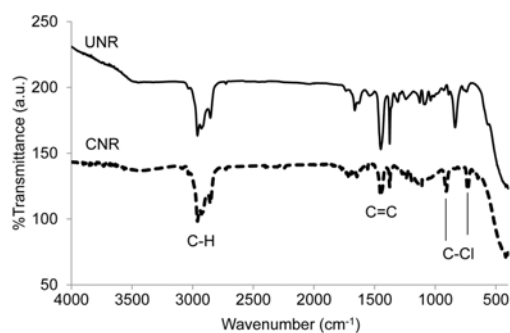


Figure 3. FT-IR spectra of UNR (solid line) and CNR (dotted line).

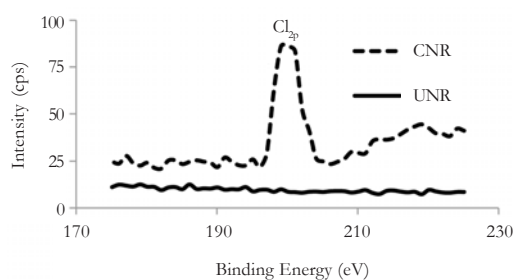


Figure 4. XPS spectra of CNR and UNR.

The effects of NCS and thiourea concentration on chlorohydrin content were investigated. The chlorohydrin content was calculated using the ratio between

the methine protons and CH-Cl protons in the $^1\text{H-NMR}$ spectra. It was found that the chlorohydrin content increased from 13% to 70% when the amount of NCS was increased from 133 phr to 600 phr (Figure 5a). However, when the amount of thiourea was increased from 11 phr to 45 phr, the chlorohydrin content decreased from 62% to 28% (Figure 5b). Increasing the amount of thiourea might increase the steric effect around the NCS, thereby reducing the product yield, consistent with a previous report [27].

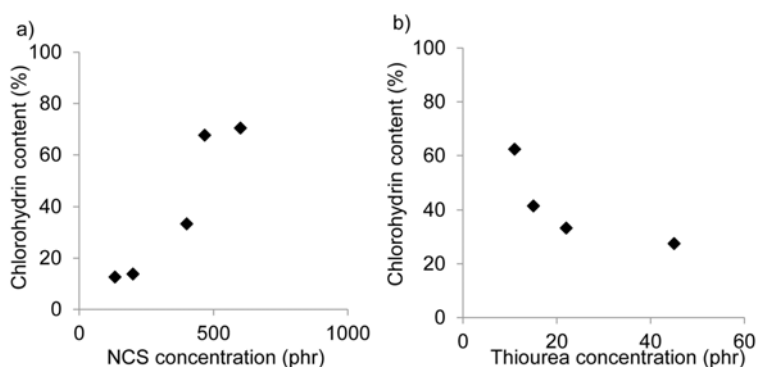


Figure 5. Chlorohydrin content as a function of a) NCS and b) thiourea concentration.

3.2 Thermal Properties

The thermal properties of the UNR and CNR samples were characterized using TGA and DSC (Figure 6a). From the DSC analysis, the glass transition temperature of CNR was found to be $-41.9\text{ }^\circ\text{C}$, which was approximately $20\text{ }^\circ\text{C}$ higher than that of the UNR. The decomposition temperatures of UNR and CNR were characterized using thermogravimetric analysis (TGA) (Figure 6b). It was found that the onset

decomposition temperature of UNR was $342\text{ }^\circ\text{C}$. The weight loss of CNR occurred in two steps. The CNR showed an initial weight loss of 23% at $228\text{ }^\circ\text{C}$, which can be attributed to removal of the chlorohydrin units from the CNR. This weight loss is close the chlorohydrin content of the CNR (28%), suggesting that the weight loss was due to the loss of Cl and OH groups from the CNR.

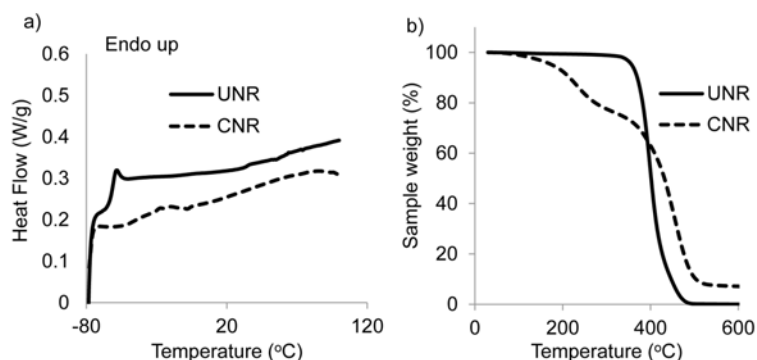


Figure 6. a) DSC and b) TGA thermograms of UNR and CNR (28% chlorohydrin content).

3.3 Mechanical Properties

The mechanical properties of the UNR and the UNR/CNR blend were measured. The blend was prepared because pure CNR could not be processed into dumbbell shapes. A blend ratio of 2:1 UNR/CNR was used. It was found that the tensile strength,

elongation, and modulus of the UNR were slightly higher than those of the UNR/CNR blend (Table 1). This indicates that UNR is only slightly stronger and more elastic than CNR. Thus, CNR can be potentially used as an alternative to UNR.

Table 1. Mechanical properties of UNR and UNR/CNR blend.

Parameter	UNR	UNR/CNR blend
Tensile strength (MPa)	13.6 ± 0.8	7.5 ± 0.3
Elongation at break (%)	489 ± 14	367 ± 11
300% Modulus (MPa)	6.4 ± 0.1	6.0 ± 0.1

Chlorohydrin content of 8%

3.4 Ozone Aging

Ozone resistance is an important property of materials to be used in outdoor applications (Figure 7). It is known that NR is prone to ozone degradation. The ozone aging of UNR and UNR/CNR blend were characterized. After ozone treatment, it was found that the UNR sample showed more and deeper cracks than the UNR/CNR blend sample. This result indicates that the presence of chlorohydrinated NR confers better ozone resistance, and that CNR is a better candidate for outdoor applications than pristine NR.



Figure 7. Ozone resistance of a) UNR and b) CNR (9x magnification).

3.5 Swelling Test

The fuel resistance of the UNR and CNR were studied. Toluene and diesel fuel were used and the swelling ratios of the samples were recorded. The swelling ratios in toluene

of CNR with 41% and 3.6% chlorohydrin contents were lower by almost tenfold and fourfold, respectively, compared with the UNR (Figure 8a). The UNR lost its shape in diesel fuel and its weight could not be measured, indicating that UNR has no resistance to diesel fuel at all. The CNR samples, however, showed resistance against diesel fuel with swell ratios of approximately

360% and 260% for samples with 41% and 3.6% chlorohydrin contents, respectively (Figure 8b). This much improved fuel resistance is due to the presence of hydrophilic hydroxyl and chlorine groups in the CNR. These results indicate that the CNR developed in this work is much more resistant against hydrophobic substances than the UNR.

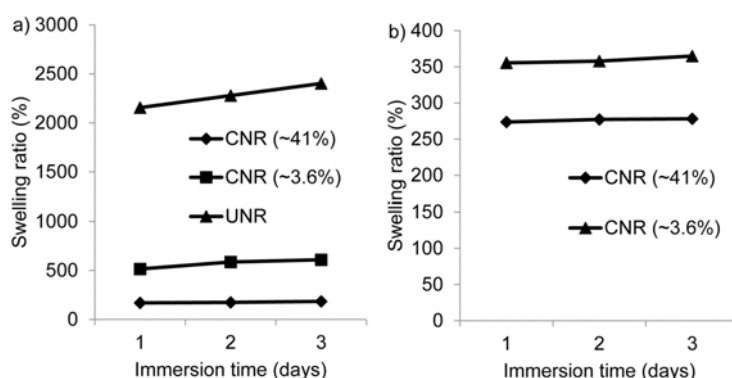


Figure 8. Swelling ratio of UNR and CNR samples in a) toluene and b) diesel.

The increased hydrophilicity of CNR compared with UNR was also confirmed by water contact angle measurement (Figure 9). The CNR sample showed a water contact angle of $70.3 \pm 2^\circ$, which is lower than that of $91.1 \pm 1^\circ$ from the UNR sample, suggesting that the CNR is more hydrophilic than the UNR.

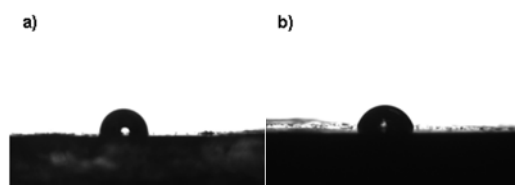


Figure 9. Water contact angles of (a) UNR and (b) CNR.

3.6 Synthesis of MMA-grafted, Chlorohydrinated NR

In this work, a one-pot synthesis of MMA-grafted, chlorohydrinated NR

(GCNR) was carried out to show that the chlorohydration method could be integrated with other chemical modifications in a one-pot fashion. Grafting reaction was performed prior to the chlorination because NCS and urea might interfere with the formation and reaction of free radicals with the *cis*-polyisoprene. MMA-grafted NR (GMR) was also prepared for comparison. From the NMR and FT-IR spectra, it was found that GCNR had been successfully prepared. Compared with the NMR spectrum of GMR, the GCNR showed NMR signals at 3.55 and 3.6 ppm, corresponding to the $-\text{OCH}_3$ of MMA and CH-Cl in the isoprene units, respectively (Figure 10). In addition, the FT-IR spectrum of GCNR showed signatures for both GMR and CNR at 741 cm^{-1} and 913 cm^{-1} for CNR and 1732 cm^{-1} for GMR (Figure 11). These results demonstrate that grafting and chlorination

using NCS can be combined, allowing the preparation of grafted, chlorohydrated NR in one pot. The versatility of our

chlorohydration method will lead to new rubber-based materials for use in a variety of applications.

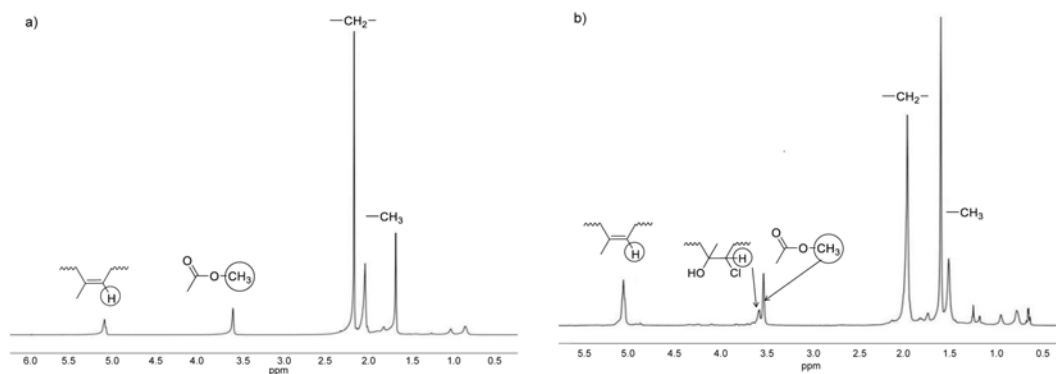


Figure 10. $^1\text{H-NMR}$ spectra of a) GNR and b) GCNR.

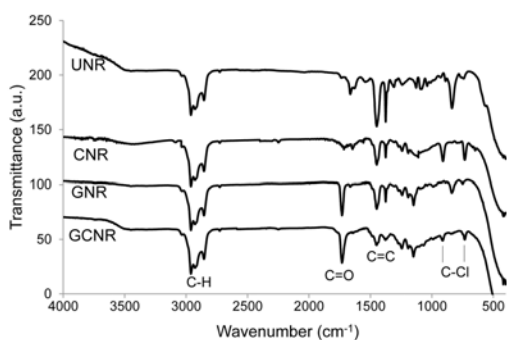


Figure 11. FT-IR spectra of UNR, CNR, GNR, and GCNR.

4. CONCLUSIONS

This work has demonstrated a simple one-step method for preparing hydrophilic NR, using N-chlorosuccinimide and thiourea as a new chlorinating agent for NR latex. After purification, a chlorohydrated product was obtained, as confirmed by NMR, FT-IR, and XPS analysis. The NCS and thiourea concentration was found to influence the chlorohydrin content of the CNR. The thermal and mechanical properties of the CNR were characterized. The fuel and ozone resistance of the CNR was much better than that of the unmodified NR. The versatility of the chlorination method

developed in this work was demonstrated by integrating it with a grafting reaction in a one-pot fashion. This strategy can be utilized to prepare multi-functional NR materials. Based on these results, the CNR prepared in this work provides an excellent alternative to NR. This will expand the range of applications, such as fuel-proof containers, hoses, and coatings.

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