

Preparation and graft-copolymerization of hydrogenated natural rubber in latex stage

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ABSTRACT: Preparation and graft-copolymerization of hydrogenated natural rubber are performed in latex stage after removal of proteins from the rubber with urea and surfactant. Hydrogenation of deproteinized natural rubber (DPNR) latex is carried out with palladium catalyst under hydrogen atmosphere. The hydrogenated DPNR (HDPNR) is crosslinked with a peroxide followed by graft-copolymerization of styrene (Sty) and acrylonitrile (AN) in latex stage in order to prepare a graft-copolymer of crosslinked HDPNR with poly(Sty-co-AN) (HDPNR-graft-PSAN). Characterization of the products is performed by nuclear magnetic resonance spectroscopy. The conversion of hydrogenation is investigated with respect to the catalyst feed, acidity (pH), and dry rubber content. In the resulting HDPNR-graft-PSAN, mole fraction of AN and Sty is 1.4 and 5.8 mol %, respectively. The graft-copolymer is used to improve properties of PSAN as an impact modifier. The Charpy impact strength of crosslinked HDPNR-graft-PSAN/PSAN is about eight times as high as that of PSAN. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42435.

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INTRODUCTION

The preparation of graft-copolymers of hydrogenated natural rubber (HNR) in latex stage may attract much attention as a green process, since natural rubber (NR) is obtained from *Hevea brasiliensis* as a latex. It meets our need for an establishment of the solvent free, low volatile, water process as a next generation procedure to prepare green soft materials. The graft-copolymers of HNR are anticipated to replace its synthetic homologues deriving from petroleum, for example, graft-copolymers of ethylene-propylene rubber and ethylene-propylene-diene rubber (EPDM).^{1,2} They may be useful for heavy duty applications such as the engine mounts for automotive, seals for tap water system, and coating materials for electric wire.

The preparation of graft-copolymer of HNR may be carried out by either of the following procedures: (1) graft-copolymerization of NR followed by hydrogenation or (2) hydrogenation of NR followed by graft-copolymerization. Through hydrogenation and graft-copolymerization, the modi-

fied NR may exhibit the remarkable improvement of the weather, ozone, heat resistance, and mechanical strength.^{3,4}

In the previous works, the preparation of graft-copolymer of HNR was carried out by graft-copolymerization of NR followed by hydrogenation. For instance, the hydrogenation of NR-graft-poly(methyl methacrylate), NR-graft-polystyrene have been investigated in the presence of hydrogenating agent and a catalyst.⁵⁻⁷ However, the side chains of graft-copolymer were modified after hydrogenation. In other words, not only double bonds of *cis*-1,4-isoprene units for NR chain but also those of side chains, that is, grafted polystyrene and grafted poly(methyl methacrylate) reacted with hydrogenating agent.

Hydrogenation of NR followed by graft-copolymerization in latex stage may be efficient to prepare graft-copolymer of HNR without the reaction of side chains. When HNR latex is prepared, it may be subjected to graft-copolymerization with various monomers. However, the monomer conversion and grafting efficiency of the graft-copolymerization on HNR may be low due to the contamination of catalyst and by-products after

hydrogenation and the proteins present in NR.^{8,9} In this work, we adopted the purified HNR latex as the resource to prepare the graft-copolymer in which the removal of proteins from NR was performed according to the procedure reported in our previous works.^{10,11} By using heterogeneous catalyst for hydrogenation, the catalyst can be separated from the product by the simple technique, for example, centrifugation.

In the present work, the hydrogenation of deproteinized NR (DPNR) followed by graft-copolymerization of styrene (Sty)/acrylonitrile (AN) was carried out in latex stage. The hydrogenation was performed in the presence of hydrogen gas and palladium catalyst. The optimal condition of hydrogenation was investigated in terms of the catalyst feed, acidity (pH), and dry rubber contents (DRC). The resulting hydrogenated DPNR (HDPNR) latex was crosslinked followed by graft-copolymerization with a mixture of Sty/AN monomers in order to prepare HDPNR-*graft*-poly(Sty-*co*-AN) (HDPNR-*graft*-PSAN). The resulting product was used as an impact modifier for PSAN. The characterization of the products, that is, HDPNR and HDPNR-*graft*-PSAN, was carried out through nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), and Charpy impact strength measurements.

EXPERIMENTAL

Materials and Reagents

High ammonia NR latex (HANR) (DRC ~ 60 w/w %) was purchased from Golden Hope (Malaysia). A commercially available EPDM latex (diene : ethylene : propylene = 9 : 61 : 30) (JSR, Japan) was used as a reference in this study. A commercial Sty-*co*-AN copolymer (PSAN) (70 w/w % Sty and 30 w/w % AN) (S300N, UMG ABS, Japan) was used in the compounding process.

Urea, palladium chloride, hydrogen peroxide, hydrochloric acid, sodium hydroxide, and potassium hydroxide were provided by Nacalai Tesque (Japan). Dimethylglyoxime, Sty and AN monomer were products of Tokyo Chemical Industry (Japan). Sodium dodecyl sulfate (SDS), perbutyl PV, tetraethylene pentamine (TEPA), and *tert*-butyl hydroperoxide (TBHPO) were purchased from Kishida Chemical (Japan). The reagents were used without further purification in this study.

Deproteinization of HANR Latex

HANR latex was adjusted to DRC 30 w/w % by distilled water. The latex was incubated with urea 0.1 w/w % in the presence of SDS 1 w/w % for 1 h at room temperature, followed by centrifugation at 9000 g at 15°C for 30 min. The washing process of resulting cream fraction was carried out by redispersing cream in the SDS solution 0.5 w/w % and centrifuging at 9000 g at 15°C for 30 min. After washing twice, the cream fraction was redispersed in the SDS solution 0.1 w/w % to obtain the DPNR latex.

Hydrogenation of DPNR Latex

HDPNR was prepared with palladium catalyst under hydrogen atmosphere in latex stage. The experimental procedure is illustrated in Figure 1. DPNR latex was charged into the flask containing SDS solution. A solution of PdCl₂ in HCl was dropped into the DPNR latex. Thereafter, NaOH solution was added to

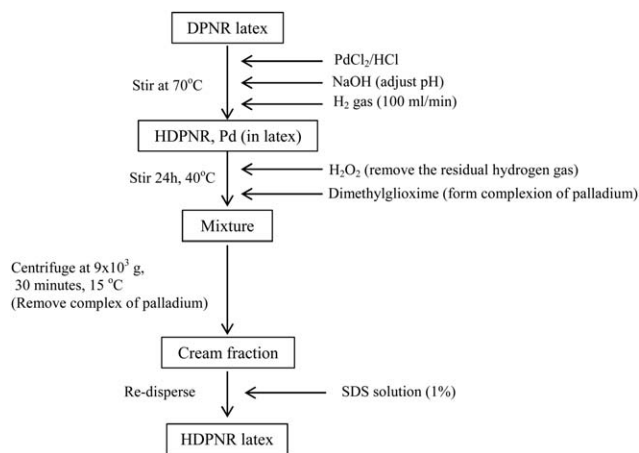


Figure 1. Hydrogenation of NR in latex stage.

the latex to adjust pH in three ranges 5–6, 6–7, and 7–8. The hydrogenation of the rubber latex was performed by continuously bubbling hydrogen gas at the agitation rate of 50 rpm at 70°C for 6 h. The flow rate of gas was 100 mL/min. After the hydrogenation reaction, because hydrogen gas may be still present as stabilized bubbles,¹² hydrogen peroxide was poured into the flask in order to remove residual hydrogen gas in the latex, according to the reaction: $\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O}$. The reaction was carried out for 2 h at 40°C in continuously stirring. Thereafter, dimethylglyoxime was added into the latex to form complex with palladium for 24 h at 40°C. The resulting latex was subjected to the centrifugation at 9000 g at 15°C for 30 min in order to collect the cream fraction. The cream was redispersed in SDS solution 1 w/w % followed by filtering through a mesh (pore size 200 micron) to obtain HDPNR latex.

Graft-Copolymerization of HDPNR

HDPNR (preserved in SDS 1%) was crosslinked by the treatment with perbutyl PV/divinylbenzene in latex stage at 80°C for 3 h. After curing, pH of the crosslinked HDPNR latex was adjusted to 12.5 with KOH solution.

The resulting crosslinked HDPNR latex was graft-copolymerized with the mixture of Sty/AN (1 : 1 mol) in the presence of TBHPO/TEPA as the initiator under nitrogen atmosphere for 3 h. After reaction, the unreacted monomers were removed by using a rotary evaporator under reduced pressure. The procedure of graft-copolymerization is illustrated in Figure 2. The resulting graft copolymer HDPNR-*graft*-PSAN was dried under reduced pressure at 50°C.

The graft-copolymerization of Sty and AN onto crosslinked EPDM was carried out in latex stage by the same procedure (Figure 2). The resulting sample is EPDM-*graft*-PSAN.

Compounding Process

The graft-copolymers were mixed with PSAN (ratio 1 : 1), followed by kneaded at 230°C with a PCM-30 twin-screw extruder (Ikegai). The resulting compounds, that is, HDPNR-*graft*-PSAN/PSAN and EPDM-*graft*-PSAN/PSAN resin, were obtained in the pellet form.

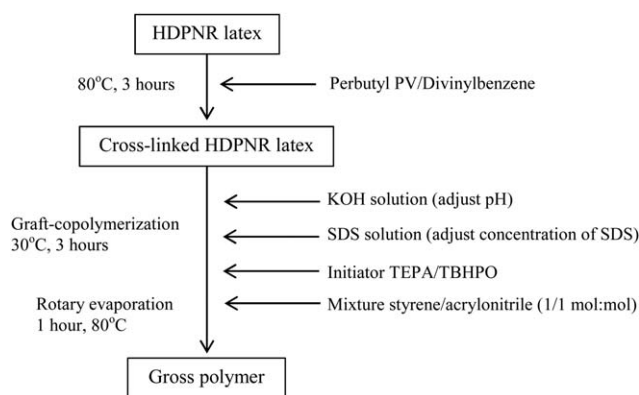


Figure 2. Graft-copolymerization of HDPNR in latex stage.

Characterization

NMR measurements for samples were carried out using an ECA-400 FT-NMR spectrometer (JEOL). ^{13}C -NMR measurements were made for DPNR and HDPNR in the latex state operating at 100 MHz at 30°C with pulse repetition times of 5 s and 1000 accumulations. ^{13}C -NMR and DEPT measurements were made for HDPNR-graft-PSAN in CDCl_3 (Wako 99.8 v/v %) operating at 100 MHz at 30°C and 20,000 accumulations.

The particle size distributions of the NR latex before and after hydrogenation were determined with a Coulter LS 230 instrument (Beckman Coulter). DPNR and HDPNR latex were dispersed in the solution SDS 0.1 w/w % by an ultrasonic bath to obtain the latexes with DRC \sim 3 w/w %. The measurements for the latexes were made through dynamic light scattering technique at room temperature.

DSC measurements for the samples were performed with a DSC 7020 (SII NanoTechnology). The sample packed into an aluminum pan was heated from -120 to 150°C at a heating rate of $10^\circ\text{C}/\text{min}$.

Charpy impact test for the compounds of crosslinked HDPNR-graft-PSAN/PSAN, crosslinked EPDM-graft-PSAN/PSAN, HDPNR was carried out with a Charpy impact tester (TOYO-SEIKI). The measurements were performed at 23 and -30°C according to JIS 7111-1.

RESULTS AND DISCUSSION

Hydrogenation of NR Latex

Figure 3 shows the particle size distribution of DPNR latex and HDPNR latex. The size distribution of DPNR latex was identical to that of HDPNR latex. This may be explained that there was no change in the particle size during hydrogenation of DPNR latex and HANR latex; in other words, the agglomeration of the particles did not occur during hydrogenation.

Figure 4 shows the ^{13}C -NMR spectra for (a) DPNR latex, (b) partially HDPNR latex (conversion: 59.5 mol %) and (c) HDPNR latex (conversion: 99.3 mol %). As is clearly seen in the spectrum for DPNR, five characteristic signals appeared at 134.9, 125.1, 32.8, 26.5, and 23.3 ppm, which were assigned to unsaturated carbon (I2), unsaturated methine (I3), methylene (I1), methylene (I4), and methyl (I5) of the *cis*-1,4-isoprene unit, respectively. In the spectrum of partially HDPNR latex,

the signals of unsaturated carbons (I2 and I3) decreased, whereas some new signals appeared which may be assigned to hydrogenated *cis*-isoprene unit. In the ^{13}C -NMR spectrum for HDPNR [Figure 4(c)], the characteristic signals of *cis*-1,4-isoprene units disappeared. Four major signals at 37.7, 33.0, 24.6, and 20.0 ppm were assigned to methylene (H1 and H3), methine (H2), methylene (H4), and methyl (H5) of the hydrogenated isoprene units, respectively. The conversion of hydrogenation (C_h) was estimated from an intensity ratio of the signals, as follows:

$$\text{Hydrogenation conversion [mol]} = \frac{\frac{2I_s - 3}{2I_u + 2}}{I_u} \times 100(\%) \quad (1)$$

where I_s is the sum of intensity of the signals at 20.0, 24.6, 32.8, and 37.7 ppm and I_u is the sum of intensity of the unsaturated signals at 125.1 and 134.9 ppm. The estimated values of C_h in various conditions of hydrogenation procedure were shown in Table I.

Effect of pH

The conversion of hydrogenation was found to be significantly affected by pH. The values of C_h were low, that is, less than 65 mol %, when the reaction was carried out in the range of pH from 5 to 6, as shown in Table I. The conversions attained were the highest values in the range of pH from 6 to 7 and went down in the range of pH from 7 to 8 as the hydrogenation was carried out with the same DRC and catalyst feed. For instance, the plots of pH versus conversion of hydrogenation carried out at DRC 6 w/w % and various feeds of catalyst are shown in Figure 5. The locus of the conversion versus DRC was convex. The obtained conversion was the maximum value in the range of pH from 6 to 7. Therefore, the range of pH from 6 to 7 is the most suitable for the hydrogenation of DPNR in latex

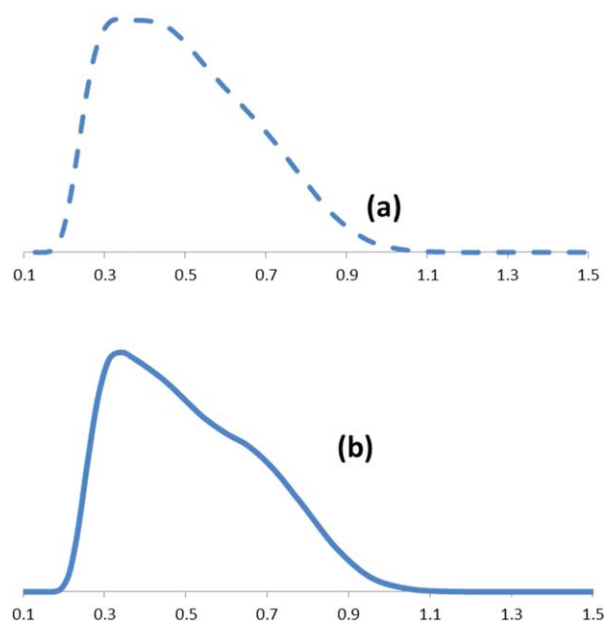


Figure 3. Particle size distribution of (a) DPNR latex and (b) HDPNR latex. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

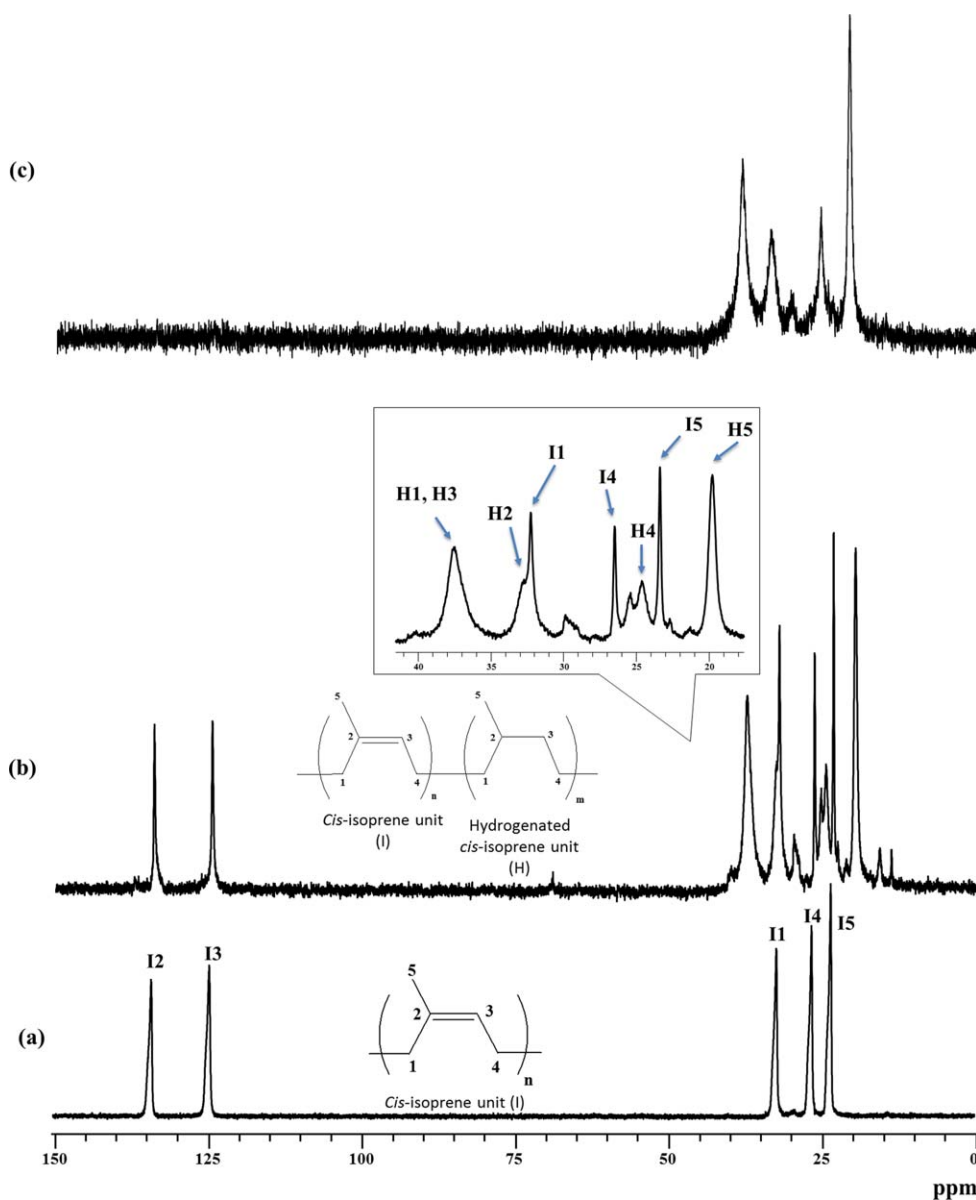


Figure 4. ^{13}C -NMR spectrum for (a) DPNR (b) HDPNR (conversion 59.5 mol %) and (c) HDPNR (conversion approximate 100 mol %) (recorded with 1000 accumulations at room temperature). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stage in the presence of palladium catalyst. It may be explained that the range of pH from 6 to 7 is suitable to convert palladium chloride to palladium-nanoparticles,¹³ which efficiently catalyzes the hydrogenation of DPNR in latex stage.

Effect of Catalyst Feed

At catalyst feed of 1.35 mg-Pd/g-rubber, the hydrogenation conversion was quite low. For instance, the values of C_h at catalyst feed of 1.35 mg-Pd/g-rubber and pH from 6 to 7 were 42.3, 59.5, and 48.0 mol % at DRC 3, 6, and 10 w/w %, respectively. Thus, it was considered that the catalyst feed of 1.35 mg-Pd/g-rubber was insufficient for hydrogenation of NR in latex stage. When the catalyst feed increased, the conversion of hydrogenation increased; for instance, the value of the C_h was 94.6 mol % at the catalyst feed of 2.7 mg-Pd/g-rubber at DRC 3 w/w %. When the feed of catalyst used was double, that is, 5.4 mg-Pd/

g-rubber, the C_h raised to 98.5 mol %. The value of the C_h increased at the other values of DRC, as the catalyst feed increased. Therefore, the catalyst feed of 5.4 mg-Pd/g-rubber was found to be suitable for the hydrogenation of DPNR latex.

Effect of DRC

The DRC of DPNR latex made the significant influence on C_h . The value of C_h was found to be dependent upon DRC. The highest value of C_h was achieved at DRC of 6 w/w %, when the reaction was carried out with the same feed of catalyst and pH. The low value of C_h at low DRC may be associated with less probability of collision between the rubber particles and Pd catalyst due to heterogeneous reaction in nature.¹⁴ In contrast, the low value of C_h at high DRC may be explained to be due to the reduced stability of the latex, since the coagulation occurred as the DRC was higher than 10 w/w %. At 10 w/w % DRC,

Table I. Condition and Conversion of Hydrogenation of DPNR in Latex Stage

| No. | DRC (w/w %) | Feed of catalyst (mg-Pd/g-rubber) | pH | Conversion (mol %) |
|-----|-------------|-----------------------------------|------|--------------------|
| 1. | 3 | 1.35 | 5.33 | 24.2 |
| 2. | 3 | 1.35 | 6.34 | 42.3 |
| 3. | 3 | 1.35 | 7.29 | 40.2 |
| 4. | 3 | 2.70 | 5.48 | 37.1 |
| 5. | 3 | 2.70 | 6.18 | 94.6 |
| 6. | 3 | 2.70 | 7.50 | 78.9 |
| 7. | 3 | 5.40 | 5.12 | 65.2 |
| 8. | 3 | 5.40 | 6.50 | 98.5 |
| 9. | 3 | 5.40 | 7.10 | 72.8 |
| 10. | 6 | 1.35 | 5.30 | 23.0 |
| 11. | 6 | 1.35 | 6.40 | 59.5 |
| 12. | 6 | 1.35 | 7.46 | 50.3 |
| 13. | 6 | 2.70 | 5.79 | 45.2 |
| 14. | 6 | 2.70 | 6.22 | 95.5 |
| 15. | 6 | 2.70 | 7.09 | 85.1 |
| 16. | 6 | 5.40 | 5.54 | 52.9 |
| 17. | 6 | 5.40 | 6.52 | 99.3 |
| 18. | 6 | 5.40 | 7.29 | 90.4 |
| 19. | 10 | 1.35 | 5.56 | 11.5 |
| 20. | 10 | 1.35 | 6.15 | 48.0 |
| 21. | 10 | 1.35 | 7.47 | 16.7 |
| 22. | 10 | 2.70 | 5.63 | 51.2 |
| 23. | 10 | 2.70 | 6.24 | 89.9 |
| 24. | 10 | 2.70 | 7.78 | 80.9 |
| 25. | 10 | 5.40 | 5.45 | 49.2 |
| 26. | 10 | 5.40 | 6.20 | 96.5 |
| 27. | 10 | 5.40 | 7.36 | 88.3 |

Flow rate of H₂ gas 100 mL/min, stirring rate 50 rpm, reaction time 6 h.

flocculation may somewhat take place to reduce the probability of collision between the rubber particles and Pd catalyst. As can be seen from the results, the highest conversion of the hydrogenation, that is, 99.3 mol %, was achieved at the optimal condition (pH 6–7, DRC 6 w/w %, and feed of catalyst 5.4 mg-Pd/g-rubber).

Graft-Copolymerization

Figure 6 shows ¹³C-NMR spectrum for HDPNR, HDPNR-graft-PSAN, and DEPT135 for HDPNR-graft-PSAN. The assignment of signals in the ¹³C-NMR spectrum for HDPNR was made, based on DEPT measurements and the references.^{15–17} Values of chemical shifts of ¹³C were tabulated in Table II.

In the ¹³C-NMR spectrum for HDPNR-graft-PSAN, the worthy of note is the presence of the signals at 145.2, 128.0, 127.5, 125.7, and 40.5 ppm. These signals were attributed to Sty and AN unit HDPNR-graft-PSAN according to literature.^{18,19} The assignment was tabulated in Table III.

The mole fractions of AN and Sty in HDPNR-graft-PSAN were estimated based on the intensities of signals at 128.0, 127.5 ppm

(characteristic signals of Sty), 40.5 ppm (characteristic signals of Sty and AN), 23.5 and 19.8 ppm (characteristic signals of rubber) by the following equations:

$$\text{Mole fraction of AN and Sty [mol\%]} (M_{12}) = \frac{I_{40.5}}{I_{40.5} + I_{23.5} + I_{19.8}} \times 100 \quad (2)$$

$$\text{Mole fraction of Sty [mol\%]} (M_1) = \frac{(I_{128.0} + I_{127.5})}{I_{40.5} + I_{23.5} + I_{19.8}} \times 100 \quad (3)$$

$$\text{Mole fraction of AN [mol\%]} (M_2) = M_{12} - M_1 \quad (4)$$

where *I* is the intensity of the signals, the subscript number represents chemical shift (ppm).

It was shown that the values of the mole fractions of AN and Sty in HDPNR-graft-PSAN were 1.4 and 5.8 mol %, respectively, as HDPNR contained 15 mol % C=C double bond (i.e., *C_h* = 85 mol %). These values were quite similar to those for graft-copolymerization of AN and Sty on EPDM. Therefore, HDPNR with 15 mol % content of C=C double bonds (*C_h* = 85 mol %) was used for the measurements of properties.

Glass Transition Temperature

Figure 7 shows the DSC thermograms for DPNR, HDPNR (*C_h* = 85 mol %) and HDPNR-graft-PSAN. The glass transition temperatures (*T_g*) of the specimens were determined to be the reflection point of the DSC thermograms. They were tabulated in Table IV. DSC thermogram for DPNR and HDPNR exhibits only one value of *T_g* at –67.0 and –65.8°C, respectively. In DSC thermogram of HDPNR-graft-PSAN, there are two reflection points at –62.5 and 108.2°C, which may confirm the presence of two phases in the resulting graft-copolymer. The reflection point at 108.2°C may be attributed to *T_g* of plastic-rich phase (PSAN) in HDPNR-graft-PSAN, according to literature.^{20,21} The reflection point at –62.5°C may be attributed to *T_g* of rubber-rich phase (HDPNR) in the graft-copolymer. *T_g* of rubber-rich phase in HDPNR-graft-PSAN was found to be higher than those of DPNR and HDPNR. It may indicate that

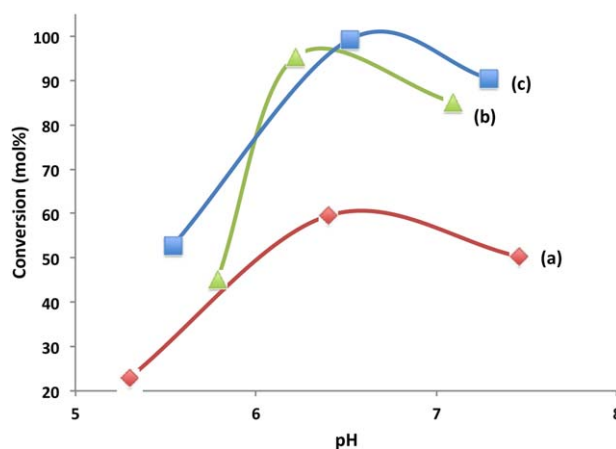


Figure 5. The plots of pH versus conversion of hydrogenation carried out at various conditions: (a) DRC 6 w/w %, catalyst feed 1.35 mg/g-rubber; (b) DRC 6 w/w %, catalyst feed 2.7 mg/g-rubber; (c) DRC 6 w/w %, catalyst feed 5.4 mg/g-rubber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

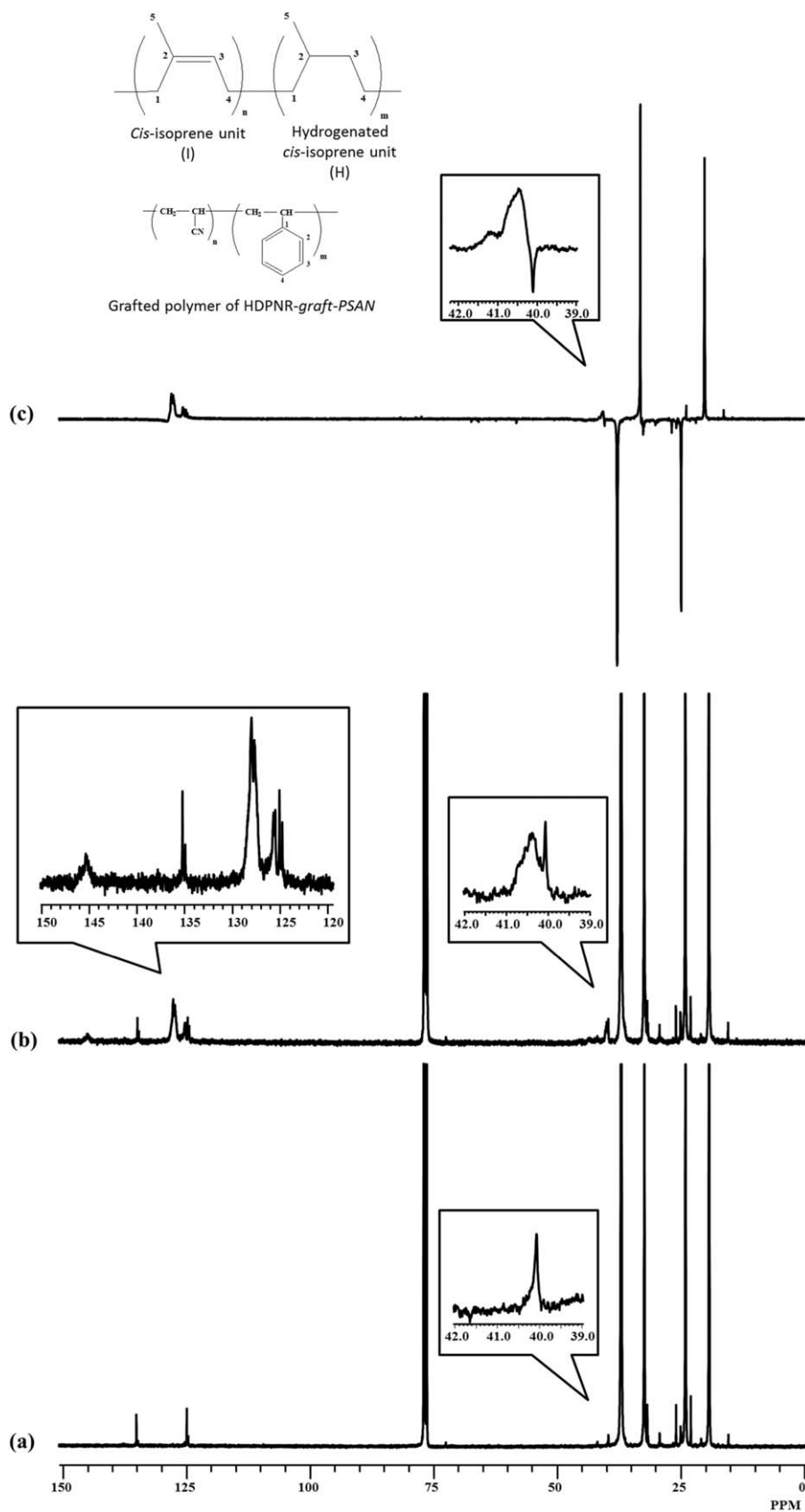


Figure 6. (a) ^{13}C -NMR spectrum for HDPNR, (b) ^{13}C -NMR spectrum for HDPNR-graft-PSAN, (c) DEPT135 spectrum for HDPNR-graft-PSAN. (Recorded in CDCl_3 with 20,000 accumulations).

Table II. Assignment of the Signals in the ^{13}C -NMR Spectrum for HDPNR

| δ for ^{13}C (ppm) | Results from DEPT | Assignments |
|------------------------------------|-------------------|---|
| 135.1 | q | C-2 of I |
| 125.0 | t | C-3 of I |
| 40.2 | s | CH_2 of <i>trans</i> -isoprene unit |
| 37.3 | s | C-1 and C-3 of HHH |
| 33.0 | t | C-2 of HHH |
| 32.2 | s | C-1 of I |
| 29.8 | s | CH_2 of fatty acid naturally present in NR |
| 26.4 | s | C-4 of I |
| 25.5 | s | C-4 of IHH |
| 24.5 | s | C-4 of HHH |
| 23.5 | p | C-5 of I |
| 19.8 | p | C-5 of HHH |
| 15.9 | p | CH_3 of <i>trans</i> -isoprene unit |

I: *cis*-isoprene unit, H: hydrogenated *cis*-isoprene unit.

q: quaternary carbon, t: tertiary carbon, s: secondary carbon, p: primary carbon.

the rigidity of HDPNR-*graft*-PSAN is highest among three specimens. In other words, the rigidity of NR is improved by hydrogenation and graft-copolymerization of the mixture Sty/AN. The increase in rigidity of HDPNR-*graft*-PSAN may be explained to be due to chain stiffening causing by the presence of Sty and AN units.²²

Charpy Impact Resistance

The crosslinked HDPNR-*graft*-PSAN was used as the impact modifier for PSAN. The Charpy impact resistance of crosslinked HDPNR-*graft*-PSAN/PSAN blend was compared with that of the crosslinked EPDM-*graft*-PSAN/PSAN blend.

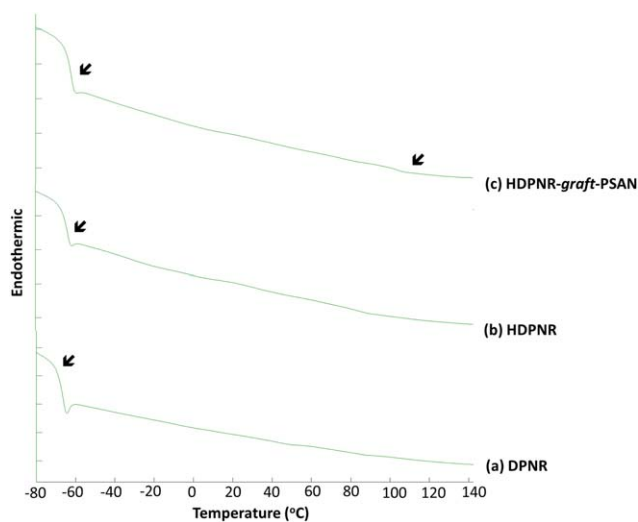
The results of Charpy impact test for the PSAN, HDPNR, the blends of HDPNR-*graft*-PSAN/PSAN, and EPDM-*graft*-PSAN/PSAN are shown in Table V.

The value of the Charpy impact of the HDPNR-*graft*-PSAN/PSAN was found to be higher than that of the HDPNR at room temperature as well as low temperature, that is, -30°C .

Table III. Assignment of the Signals of Sty and AN in the ^{13}C -NMR Spectrum for HDPNR-*graft*-PSAN

| δ for ^{13}C (ppm) | Results from DEPT | Assignments |
|------------------------------------|-------------------|---|
| 142.5 | q | C-1 of phenyl ring in Sty unit |
| 128.0 | t | C-2 of phenyl ring in Sty unit |
| 127.5 | t | C-4 of phenyl ring in Sty unit |
| 125.7 | t | C-3 of phenyl ring in Sty unit |
| 40.5 | t | Methine group (CH) the chain of AN and Sty unit |

q: quaternary carbon, t: tertiary carbon.

**Figure 7.** DSC thermograms for (a) DPNR, (b) HDPNR (conversion 85 mol %), (c) HDPNR (conversion 85 mol %)-*graft*-PSAN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

This may be explained to be due to the rubber toughened effect, which is expressed by ligament thickness.²³ Moreover, Sty and AN monomers also contribute to the improvement of mechanical properties of elastomers when they were grafted.²⁴ These results may clearly illustrate the increase of impact resistivity of HDPNR through graft copolymerization.

The Charpy impact was also examined for EPDM-*graft*-PSAN/PSAN blend at room temperature and -30°C . The result showed that Charpy impact of HDPNR-*graft*-PSAN/PSAN is lower than that of EPDM-*graft*-PSAN/PSAN at room temperature. Conversely, the compound of HDPNR-*graft*-PSAN

Table IV. Glass Transition Temperatures of the Samples

| | T_g ($^\circ\text{C}$) | |
|---------------------------|----------------------------|--------------------|
| | Rubber-rich phase | Plastic-rich phase |
| DPNR | -67.0 | - |
| HDPNR | -65.8 | - |
| HDPNR- <i>graft</i> -PSAN | -62.5 | 108.2 |

Table V. Charpy Impact Values for the Samples

| | Crosslinked EPDM- <i>graft</i> -PSAN/PSAN | Crosslinked HDPNR- <i>graft</i> -PSAN/PSAN | HDPNR | PSAN |
|--|---|--|-------|------|
| Charpy impact value (23°C) [kJ/m^2] | 30.6 | 10.7 | 7.7 | 1.3 |
| Charpy impact value (-30°C) [kJ/m^2] | 6.9 | 7.7 | 5.2 | - |

exhibited the higher Charpy impact than the compound of EPDM-*graft*-PSAN at -30°C . This implies that the fracture toughness of HDPNR-*graft*-PSAN/PSAN blend is enhanced at low temperature. It may be considered that the regularity of alternative ethylene-propylene units in HDPNR plays an important role in the Charpy impact improvement of HDPNR-*graft*-PSAN/PSAN at low temperature.²⁵ HDPNR-*graft*-PSAN, a green material, may have potential to displace EPDM-*graft*-PSAN for the applications in severe environmental conditions.

CONCLUSIONS

Hydrogenation of DPNR followed by graft-copolymerization in latex stage was performed. The optimal condition to attain the highest conversion of hydrogenation of DPNR latex was determined, that was DRC 6 w/w %, feed of catalyst 5.4 mg-Pd/g-rubber and pH 6–7. The graft-copolymer of crosslinked HDPNR and Sty/AN was prepared, in which mole fraction of AN and Sty were 1.4 and 5.8 mol %, respectively. The cross-linked HDPNR-*graft*-PSAN was exhibited the higher T_g than the parent materials. Charpy impact resistance of HDPNR-*graft*-PSAN/PSAN at low temperature was superior compared to that of EPDM-*graft*-PSAN.

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