Synthesis and Properties of Hydrogenated Natural Rubber

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ABSTRACT: A series of hydrogenated natural rubbers, HNRs, were prepared by homogenous hydrogenation using H_2 gas with a rhodium catalyst (chlorotris(triphenylphosphine)rhodium) in toluene. The HNRs were linear polymers with molecular weights greater than 800,000. These rubbers were vulcanized using sulfur and peroxide compounds. Vulcanized 100% HNR has a low glass transition temperature ($T_g = -43°C$) and excellent abrasion resistance, and is resistant to oxidation and ozonolysis ageing. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3957–3963, 2007

Key words: homogeneous hydrogenation; linear polymer; hydrogenated natural rubber (HNR); vulcanized 100% HNR

INTRODUCTION

People are becoming increasingly interested in the purification of the global environment. One of the issues is global worming, which is believed to be caused in part by carbon dioxide in the atmosphere. Thus, a reduction in the release of carbon dioxide is now considered to be necessary. In the rubber and plastics industries, synthetic rubbers are now mainly used, which are prepared from the petroleum. When synthetic rubber components are scrapped, the environment becomes further polluted by the generation of carbon dioxide. Recently, there has been a movement towards the use of industrial materials derived from natural products.[1–3] Meanwhile, the temperatures that are encountered in the engine compartments of cars have been rising, driven upwards by the more economical use of fuel and the control of exhaust gases. Rubber products that are used in the engine compartment now operate in high-temperature conditions. Therefore, improved heat resistance is becoming an important requirement for these rubber products.[4,5]

To realize these goals, attention has turned towards natural polyisoprenoids. This is a genetic name for polymers derived from plants such as trees and mushroom and are made up of isoprene unit (C_5H_8).[6] The natural rubber (NR) extracted from hevea brasiliensis is a typical example. Now the natural polyisoprenoids other than NR are routinely used in industry, since none have a formal steric structure when compared with NR, none have high molecular weights, and none can be produced in high yields. On the other hand, NR does have a formal steric structure, has a high molecular weight, and is readily available.[7–9] The NR used for vehicle tire and for various other rubber products is mostly ''mainframe'' rubber material. NR exhibits good elasticity and mechanical strength but has poor heat resistance and low resistance to weathering and chemical reagents. Therefore, although NR is a good eco-material, its overall use is restricted since it cannot be used for high performance and high functional materials.

There are already some examples of the hydrogenation of rubbers, such as SBR, NBR, and SBS, to improve their weather-resistance and heat-resistance.[10–12] Although the hydrogenation of NR has been reported, there has been no information concerning its physical properties.[13,14]

There has been considerable interest in improving various properties of NR that are prone to degeneration. One such example is the preparation of a perfect ethylene–propylene alternating copolymer by homogeneous catalytic hydrogenation. It is possible to produce rubber that has excellent mechanical and physical properties by reducing those factors that trigger degradation while still maintaining the high molecular weight and large molecular distribution of natural rubber.

This article reports on our experimental results for the catalytic hydrogenation of 100% HNR and mea-

surements of the properties of the products that we obtained.

EXPERIMENTAL

Materials

In this work we used natural rubber (SHR-CV60), which is an export product from Malaysia. Chlorotris-(triphenylphosphine) rhodium (I) (Nacalai Tesque) was used without further purification. Toluene (Nacalai Tesque) was kept over a 4 Å molecular sieve. Methanol was supplied by the Toyota Chemical Industry.

Measurements

^{1}H NMR (300 MHz) spectra were recorded on a Varian Unity *Plus*-300 spectrometer using tetramethyl-silane in chloroform-*d* (CDCl$_3$-*d*) at room temperature as an internal standard. The tensile properties of the rubber were investigated using a Shimazu autograph AGS-G, and JIS 3-dumbels were used for the standard samples. The measurement conditions for the tensile tests were as follows: Crosshead speed = 500 mm/min at room temperature. Heat aging tests were conducted using a Shimazu autograph AGS-G once again, and JIS 3-dumbels were used for the standard samples. The samples were heated for 96 h at 100°C using a Toyoseiki Gear oven GO-02, after which the measurements were carried out. The measurement conditions for the heat ageing tests were as follows: Crosshead speed = 500 mm/min at room temperature. Hardness was measured using a Koubunshi Keiki Durometer hardness tester (Type A). SET tests were carried out using oven for 24 h at 70°C. Ozonolysis aging tests were carried out using Sugashikenki ozone weather meter. JIS 1-dumbeles (oblong card state) were used for the standard samples. The samples were fixed to special holder with 50% stretch, and were then treated for 96 h at 40°C in ozone gas (50 pphm). Wear tests were conducted using an Ueshimaseisakusho Pico-wear apparatus

TABLE II
Hydrogenation Reaction of NR at Various Temperatures[a]

Reaction temperature (°C)	Rate of hydrogenation (%)
70–80	18
80–85	18
85–90	—[b]
90–110	—[b]

Catalyst used was chlorotris-(triphenylphosphine) rhodium (I) (RhCl((PPh3)3:2g). Solvent was toluene.
[a] Hydrogenation reaction was carried out for 24 h at 7.1 MPa.
[b] Polymer was gelated.

AB-4510. The measurement conditions for the wear tests were as follows: 44 N load, 60 rpm, both sides 20 times × 2 at room temperature. Dynamic mechanical analysis was performed on a Seiko Instruments DMS6100 at a heating rate of 5.0°C/min between 100 and 100°C and at a frequency of 20 Hz. Differential scanning calorimetry (DSC) measurements were performed on a Seiko Instruments DSC6200 at a heating rate of 5.0°C/min over the range 100 to 100°C under nitrogen gas (flow rate, 50 mL/min.). The average molecular weight and molecular distributions were investigated using a Shimazu Gel Per Chromatography (GPC) LC10AT equipped with a Refracting Interval meter (RI). The measurement conditions for GPC were as follows: Sample, 0.1 wt % THF solution; Solvent, THF; Column, Showa Denko SHODEX KF-802, -804, and -806*M*; Quantum, polystyrene transformation method. SEM measurements were performed on a HITACHI S-2460N operated at an acceleration voltage of 20 kV. After the wear test, the abrasion faces of the samples were then gold-sputter coated and scanned in an SEM.

Hydrogenation

A 2 wt % NR/toluene solution was prepared from NR and toluene. The resulting solution (10 L) and the (chorotris(triphenylphosphine) rhodium (I)) catalyst were added in a 20 L auto-cleave, and then the

TABLE I
Recipe of Vulcanized Hydrogenated Rubber

	S cure[a]	PO cure[b]
Polymer	100	100
Stearic acid	1	1
ZnO	5	5
CB (N220)	20	20
CZ	2.5	0
PO	0	3
S	1	0

[a] Sulfur is used for vulcanized reagent.
[b] Peroxide is used for vulcanized reagent.

TABLE III
Effect of Catalyst on Hydrogenation Reaction[a]

Catalyst (g)	Rate of hydrogenation (%)	Molecular weight (10^4)
8	70	100
9	90	114
18	100	80
20	100	80

Hydrogen pressure was 7.1 MPa. Catalyst used was chlorotris(triphenylphosphine) rodium (I).
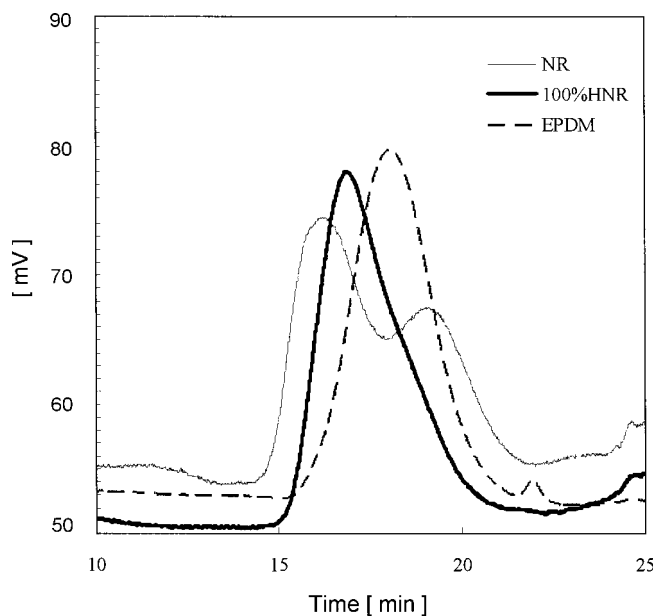[a] Hydrogenation reaction was carried out for 96 h at 70–80°C.

Figure 1 GPC chromatography of 100% HNR.

Figure 3 ^{1}H NMR spectrum of 100% HNR.

air in auto-cleave was replaced by H_2 gas. The pressure of the H_2 gas was maintained at 7.1 MPa, and the solution was stirred slowly (120 rpm) and heated at 70°C for 72 h. Before all of the rubber was completely deposited, methanol (about 10 mL) was added little-by-little to the reaction solution. The result-
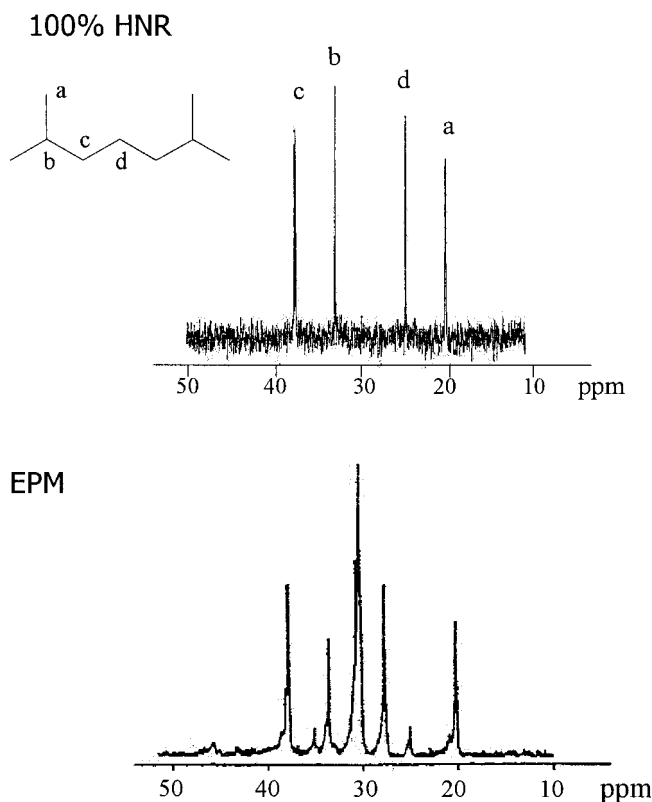
ing hydrogenated NR (HNR) was filtrated and then washed 3 or 4 times with methanol until the color of the catalyst had disappeared. The HNR that was obtained was dried at 60°C for 24 h under reduced pressure (2.7–4.0 MPa).

It was conformed by ^{1}H NMR that the hydrogenation rate was 100%. Also, it was possible to yield various HNRs by controlling the reaction times.

Vulcanization

The 100% HNR was kneaded 40 rpm at 150°C for 3 min with a variety of other reagents, such as stearic acid, ZnO, carbon black (N220), and Cz, in a sealed kneading machine, after which the HNR product was kneaded further by open rolling at 80°C with
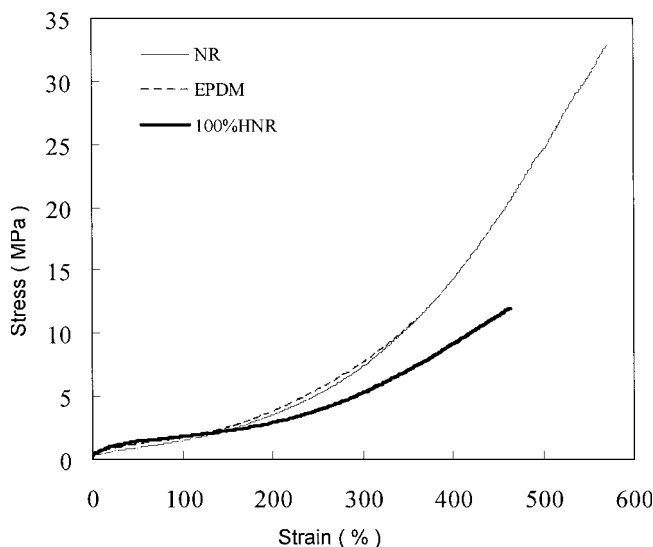

Figure 2 ^{13}C NMR spectra of 100% HNR and EPM.

Figure 4 Stress–strain curve of 100% HNR.

	100% HNR	NR	EPDM
Before aging			
TS[a] (MPa)	12	32.6	11
EL[b] (%)	460	570	360
Hardness	64	56	63
After aging			
ΔTS[a] (Mpa)	−1	−57	11
ΔEL[b] (%)	2	−19	−6
Δhardness	1	−9	−1

[a] Tensile strength at breaking point.
[b] Elongation at breaking point.

vulcanizing reagents (peroxide or sulfur). The vulcanized sheets were then pressed for 1 h at 160°C. The recipe is indicated in Table I.

RESULTS AND DISCUSSION

Hydrogenation

The effect of reaction temperature was examined by holding different samples for 24 h at various temperatures, and the results are shown in Table II. When the reaction was carried out at 70°C, the molecular weight of the product (HNR) fell a little. When the reaction temperature was over 80°C, the molecular weight of the resulting HNR fell markedly. It was further conformed that gelation of the polymer occurred when the reaction temperature was above 90°C. When the quantity of catalyst was increased, the reaction time was decreased quite noticeably (Table III). However, it was also conformed that there was a tendency for the molecular weight of the HNR to fall. The hydrogenation rate of HNR was determined by ^{1}H NMR.
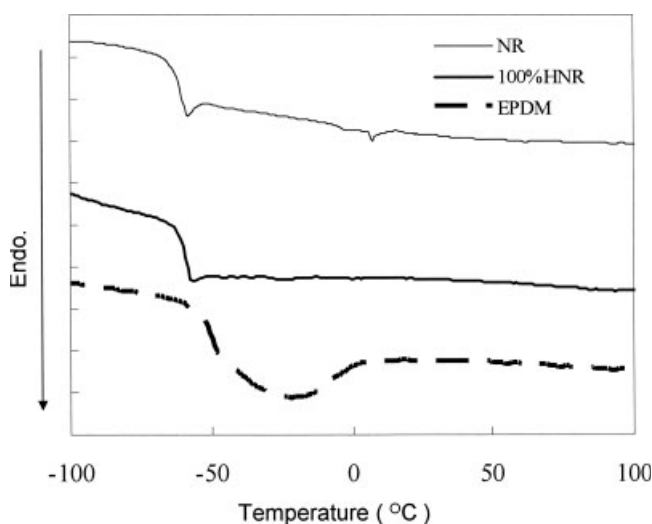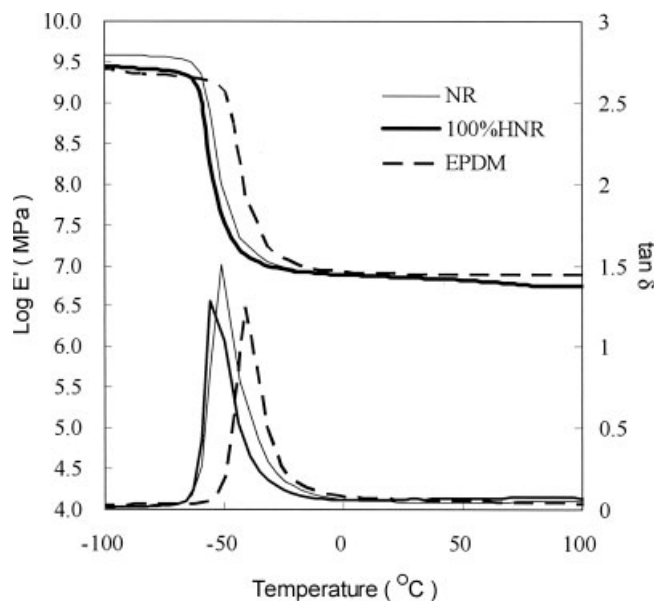

Figure 5 DSC thermogram of 100% HNR.

Figure 6 Temperature dependence of storage modulus (E') and tan δ of 100% HNR.

Characterization of 100% HNR

The M_w of NR is between 100×10^4 and 200×10^4 consisting of two components, the high weight fraction and the low weight fraction while M_w/M_n is wide.[15]

The molecular weight and the molecular weight distribution of 100% HNR were measured and the results are shown in Figure 1. In Figure 1, it is con-
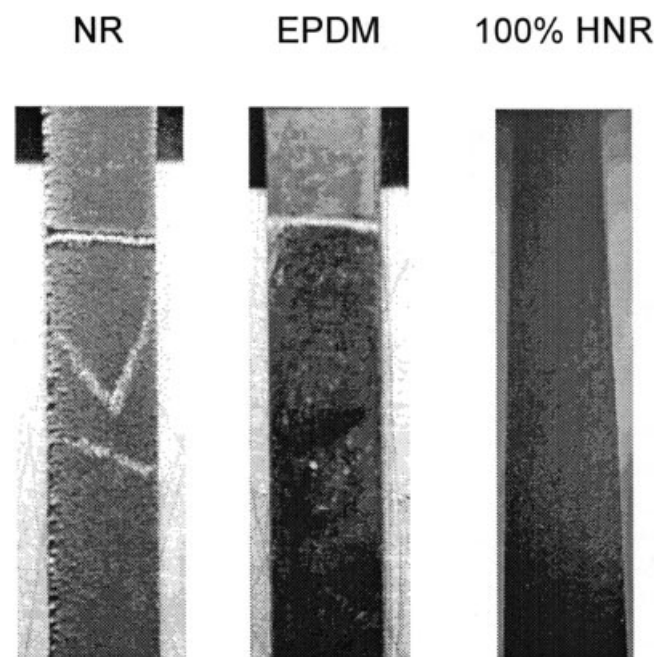

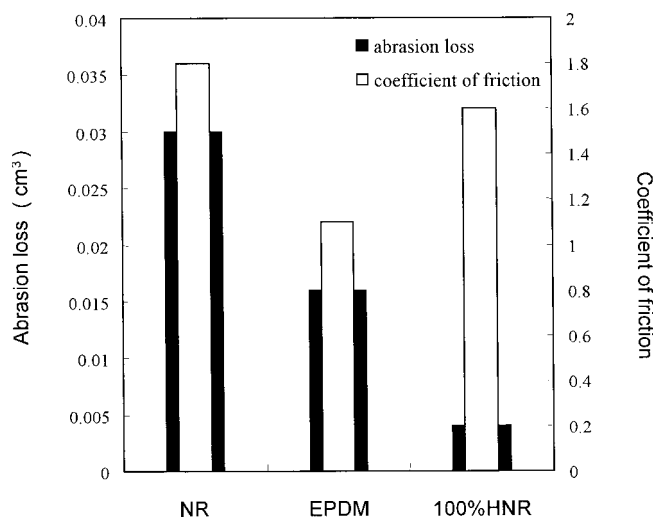**Figure 7** Picture of ozone cracking tested face of 100% HNR.

Figure 8 Abrasion loss and coefficient of friction of 100% HNR.

formed that molecular chains from the high molecular weight portion in the NR are cut in preference to those of low molecular weight ($M_w = 83 \times 10^4$), and that the molecular weight distribution is narrow ($M_w/M_n = 2.7$) in comparison with NR ($M_w = 120 \times 10^4$; $M_w/M_n = 5.7$). Also, in comparison with EPDM ($M_w = 28 \times 104$; $M_w/M_n = 2.5$), the molecular weight is high and the molecular weight distribution is the same.

^{13}C NMR spectra of 100% HNR and of ethylene–propylene copolymer (EPM)[16] are illustrated in Figure 2. In Figure 2, four peaks for the carbon (Ca) in the side chain methyl groups and the α(Cb), β(Cc), and γ(Cd) carbons in the normal chain methylene groups in 100% HNR can be identified and it is very simple to compare this with EPM, which has ethylene–ethylene bonds and propylene–propylene bonds.

These results suggested that 100% HNR has a formal structure and is probably a perfect alternating copolymer of ethylene and propylene. The ^{1}H NMR spectrum of 100% HNR is shown in Figure 3. In Figure 3, the peaks that are characteristic of the methyl group could only be detected as the doublet at 0.86 ppm. No peaks that had been shifted by tacticity were conformed, which supports the results of the ^{13}C NMR analysis.

The initial thermal decomposition temperatures and specific gravities of HNR samples that were formed at different hydrogenation rates were measured. When the hydrogenation rate increased, the thermal decomposition temperature also rose. The thermal decomposition temperature of 100% HNR was 420°C (NR = 365°C), i.e., it rose by about 50°C more than that of NR. When the hydrogenation rate increased, the specific gravity decreased. The specific gravity of 100% HNR was 0.84 which is no lower than EPM.

Physical properties of vulcanized materials

Figure 4 shows the tensile property of 100% HNR. Table IV shows the tensile strength (TS) and elongation (EL) and hardness of 100% HNR. The hardness of 100% HNR was higher than that of NR (and is the same as EPDM). In the case of the tensile properties, the values of TS and EL at the breaking point of 100% HNR are low prior to ageing. Also, after aging, these values remained virtually unchanged for 100% HNR, whereas the values for NR and EPDM had changed, with the change for NR being particularly wide. The result of DSC analyses for 100% HNR is shown in Figure 5. The transition (T_g) appearing below 0°C is attributed to the relaxation of the rubber. The value of T_g for 100% HNR is the same as
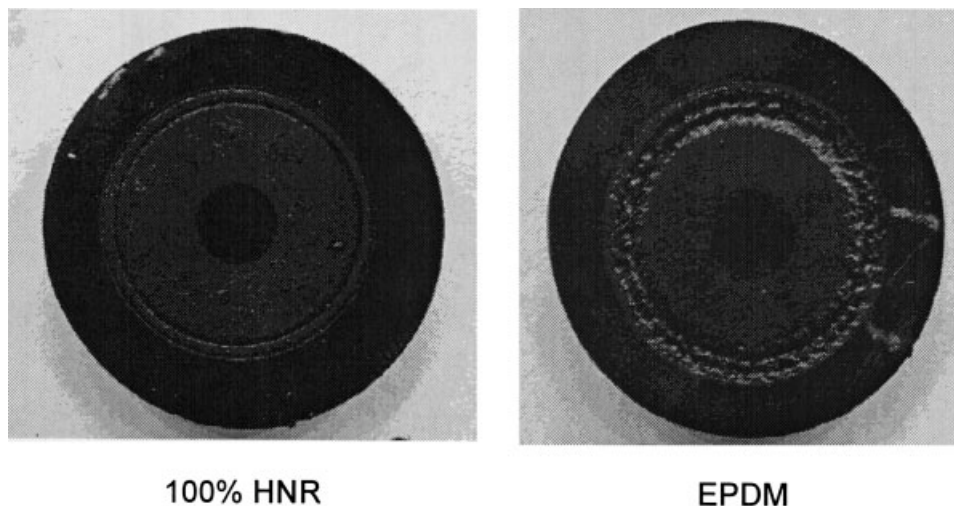

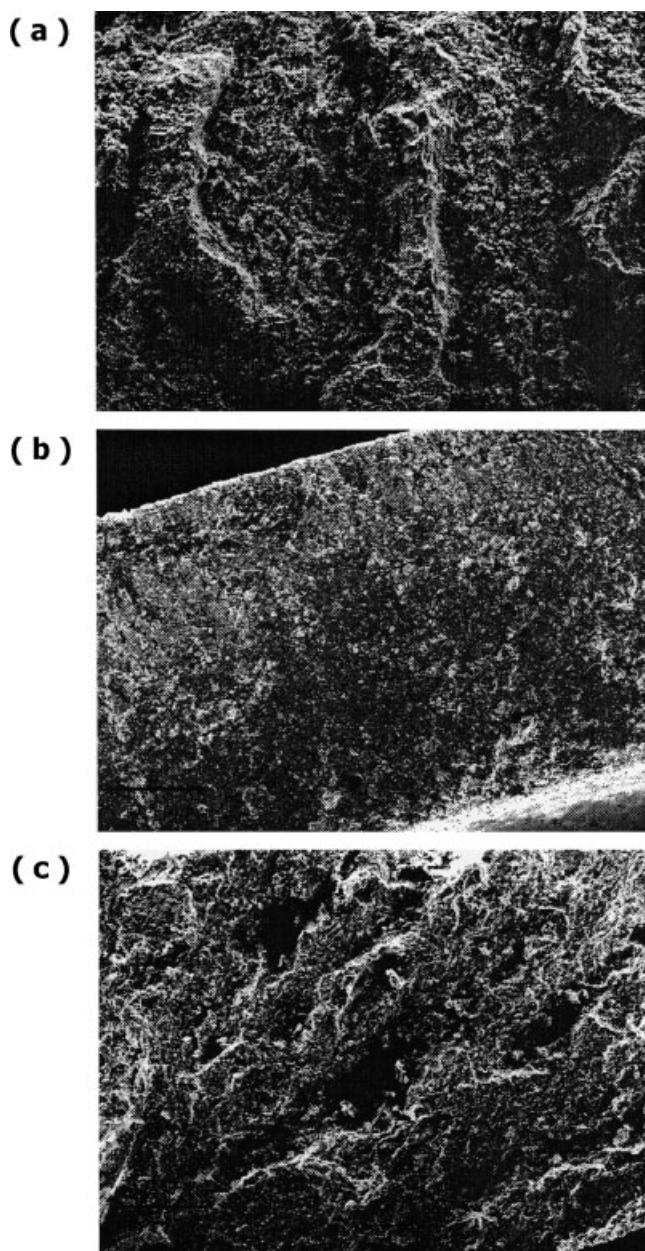**Figure 9** Picture of abrasion face of 100% HNR.

Figure 10 SEM pictures of the wear surfaces of the pico typed abrasion samples. (a) NR, (b) HNR, and (c) EPDM.

that of NR. Also, E' and tan δ are the same as NR in the rubber condition region (Fig. 6), i.e., above $-20°C$. The SET properties were improved considerably (100% HNR = 8%, NR = 30.3%, EPDM = 22.6%).

Ozonolysis aging test

A study of the ozonolysis of the material was carried out using an ozone weather meter. Figure 7 shows ozone cracking pictures for 100% HNR. By applying JIS K6259, almost no cracks grew in the 100% HNR, whereas the result for NR was C-4. These results

suggested that when there are unsaturated bonds (double bonds) in the main chain, then ozonolysis occurred.

Wear test

Generally, the abrasion-resistance of the rubber that is vulcanized using peroxide tends to rise. However, the resistance of 100% HNR rose remarkably by much more than that had been expected. The abrasion loss was not more than 1/4 of the comparable value for EPDM when vulcanized using peroxide. Although the coefficient of friction tends to decrease when the abrasion-resistance increased, it is still high in the case of 100% HNR (Fig. 8).[17,18] After the test, the abrasion face of 100% HNR is smoother than that of EPDM vulcanized by peroxide (Figs. 9 and 10), and the abrasion powder takes a rolled conformation. This suggested that 100% HNR is a polymer that has a high coefficient of friction and undergoes low stress relaxation.[19,20]

CONCLUSIONS

When the catalytic homogeneous hydrogenation of natural rubber was carried out for 96 h at 70–80°C, the 100% HNR, which has a high molecular weight and a low gel content, was successfully prepared. Analyses of the ^1H and ^{13}C NMR spectra conformed that the 100% HNR took the form of a perfect alternating copolymer of ethylene and propylene. The initial thermal decomposition temperature increased by about 50°C compared with that for NR. The molecular weight distribution was narrow.

The 100% HNR that was obtained was then vulcanized, and its physical properties were investigated. Its hardness increased, and its TS and EL at breaking point decreased. The value of T_g was low. Its weather-resistance rose due to a reduction in the number of the double bonds. Also, it was conformed that its SET properties and abrasion resistance were excellent when compared with those of NR and EPDM.

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