

# Synthesis and Mechanical Properties of Diimide-Hydrogenated Natural Rubber Vulcanizates

Wanvimon Arayapranee,<sup>1</sup> Garry L. Rempel<sup>2</sup>

<sup>1</sup>Department of Chemical and Material Engineering, Rangsit University, Phatum Thani 12000, Thailand

<sup>2</sup>Department of Chemical Engineering, University of Waterloo, Ontario N2L 3G1, Canada

Received 18 March 2009; accepted 6 July 2009

DOI 10.1002/app.31132

Published online 19 August 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Hydrogenated natural rubber (HNR), providing an ethylene-propylene alternating copolymer, was prepared by the chemical modification of natural rubber latex (NRL) using diimide generated from hydrazine ( $N_2H_4$ ) and hydrogen peroxide ( $H_2O_2$ ), with copper sulfate ( $CuSO_4$ ) as catalyst.  $^1H$ -NMR analysis indicated that 48% hydrogenation was performed with a mole ratio of  $N_2H_4$ /double bonds = 4 and  $H_2O_2/N_2H_4$  = 1.5 at 50°C for 7 h. The obtained HNR was subjected to a sulfur cure by using a conventional milling process. The cure characteristics, mechanical properties before and after heat aging, and abrasion and ozone resistances of HNR vulcanizate were examined and compared with those of natural rubber (NR), ethylene propylene diene terpolymer (EPDM) and 50 : 50 NR/EPDM vulcanizates. The results indicated that the cure rate of 48% HNR showed no significant change

when compare to both NR and 50 : 50 NR/EPDM blends, and offered a better processing advantage over EPDM. The mechanical properties and abrasion resistance of a 48% HNR vulcanizate were comparable to those of a NR vulcanizate. Additionally, its heat and ozone resistances were better than those of NR vulcanizate, due to a reduction in the amount of double bonds in the backbone chain. Thus, hydrogenation of NR can lead to a type of rubber that has improved heat and ozone resistances while still maintaining its good mechanical properties. Consequently, it improves the properties of NR for a wide range of applications. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 4066–4075, 2009

**Key words:** hydrogenated natural rubber; EPDM; mechanical properties; heat and ozone resistances

## INTRODUCTION

Natural rubber latex (NRL) obtained from *Hevea brasiliensis* is a versatile elastomer and finds application in a variety of products. Because there is an increased consciousness about environmental preservation and an increased emphasis on the use of renewable resources, a considerable amount of research has been involved with the improvement of the properties of natural rubber, a sustainable resource, thus enabling it to compete with synthetic rubbers. Application of natural rubber (NR) in rubber products gives the product very useful technical characteristics of high fatigue resistance, high resilience, low heat build-up, and building tack. However, its resistance to heat, oxygen, and ozone is not good, mainly due to its unsaturated chain structure. Hence, it is not employed in demanding applications. Blending a suitable amount of low unsaturated ethylene propylene diene terpolymer (EPDM)

obtained by polymerizing ethylene and propylene with a small amount of a nonconjugated diene, into NR has been found to improve both heat and ozone resistance.<sup>1,2</sup> However, the difference in olefin concentration of EPDM and NR resulted in a cure rate incompatible blend, resulting in both inferior static and dynamic mechanical properties in the rubber blend.<sup>3</sup>

Hydrogenation with respect to organic materials, by definition, is a reaction in which hydrogen adds across a double or triple bond. Hydrogenation of diene-based rubbers helps to improve the thermal and oxidative stability of these polymers when the radical-susceptive carbon-carbon double bonds ( $C=C$ s) are replaced by saturated hydrocarbon bonds.<sup>4,5</sup> It is possible to maintain the good mechanical properties of NR while improving the thermal and oxidative stability of the rubber material by reducing the double bonds present in NR.<sup>6</sup> Hydrogenated natural rubber (HNR) has a structure of an alternating copolymer of ethylene and propylene which can lead to improved heat and ozone resistance. The reduction in the unsaturated bonds of a diene-based polymer to a saturated one can be brought about by homogeneous and heterogeneous catalysts,<sup>7–10</sup> as well as by noncatalytic hydrogenation.<sup>4,11–13</sup>

Homogeneous hydrogenation uses a soluble catalytic complex to activate the reaction between

Correspondence to: W. Arayapranee (wanvimon@rsu.ac.th).

Contract grant sponsor: Thailand Research Fund (Small Projects on Rubber).

molecular hydrogen and the unsaturated bond whereas heterogeneous hydrogenation relies on an insoluble transition metal catalyst to promote hydrogen addition to the unsaturated bond. Generally, these methods are accompanied by the removal of catalyst at the end of the reaction and more vigorous reaction conditions are required.<sup>8</sup> Inoue and Nishio<sup>14</sup> studied NR hydrogenation catalyzed by  $\text{RhCl}(\text{PPh}_3)_3$  at 70–80°C and 100% hydrogenation was achieved within 96 h. They reported that the mechanical properties of the 100% HNR vulcanizates after aging and abrasion resistance were excellent when compared with those of NR and EPDM vulcanizates.

As an economical and environmental benign alternative to the commercial processes based on hydrogen/transition metal catalysts, the diimide hydrogenation method has been widely investigated. The oxidation of hydrazine provides the active hydrogen species in the form of diimide, which hydrogenates unsaturated double bonds which is much more attractive since precious metal catalysts are not needed for the actual hydrogenation step. Both the organic solvent and the catalyst separation problems are eliminated. Additionally, no special equipment is required to perform diimide hydrogenation because the reaction is conveniently carried out at atmospheric pressure with relatively simple apparatus and procedures. The use of diimide to saturate polymers in latex form is a relatively new idea. In 1984, Wideman<sup>15</sup> introduced the hydrogenation method to hydrogenate NBR latex using diimide generated from the hydrazine/hydrogen peroxide/cupric ion as catalyst system. He et al.<sup>16</sup> studied the mechanism and the optimum conditions for the reduction of residual double bonds in styrene-butadiene rubber latex by hydrogenating the polybutadiene in the latex form. The hydrogenation involved a copper ion (II)-catalyzed procedure in which diimide hydrogenation agent was generated in situ at the surfaces of latex particles by a hydrazine/hydrogen peroxide redox system. They compared the hydrogenation of latex with respect to different particle sizes and reported that the surface density of the copper ion on the particle surfaces was found to be a crucially important parameter in controlling the degree of hydrogenation. Xie et al.<sup>17</sup> studied hydrogenation of nitrile-butadiene rubber (NBR) latex using hydrazine and hydrogen peroxide with copper sulfate as catalyst. A hydrogenation degree (HD) of 87% was achieved after 6 h at 40°C for a mole ratio of  $\text{N}_2\text{H}_4/\text{C}=\text{C} = 2.5$ . They pointed out that the product with a HD of 87% withstood thermooxidation quite well at 150°C for 65 h, maintaining ~ 98% of its tensile strength and 96% of its ultimate elongation.

For the first part of the present work, an investigation was directed toward the synthesis of the HNR by the diimide hydrogenation process using hydra-

zine and hydrogen peroxide with copper sulfate as a catalyst. The redox reaction between hydrazine and hydrogen peroxide was used as the hydrogen source. Diimide was generated and the addition of the hydrogen molecule from diimide onto unsaturation bonds of *cis*-1,4-polyisoprene units of NR gave HNR. Subsequently, the obtained HNR was subjected to the sulfur curing by using a conventional milling and molding processes. The cure characteristics, mechanical properties before and after heat aging, abrasion and ozone resistances, and morphology of the tensile fracture surfaces of vulcanized HNR compared to those of the NR, 50 : 50 NR/EDPM, and EDPM vulcanizates were investigated.

## EXPERIMENTAL

### Materials

The commercial high-ammonia NRL was comprised almost entirely of *cis*-polyisoprene, having 60% by weight dry rubber content and was produced by Yala Latex Industry, (Yala, Thailand). Hydrazine hydrate (purity ~ 98.0%, Carlo Erba, Rodano, Milan, Italy), aqueous hydrogen peroxide (purity ~ 30 wt %, Univar, Auckland 6, New Zealand), cupric sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , purity ~ 99.5%, Carlo Erba, Rodano, Milan, Italy), sodium dodecyl sulfate (SDS, purity ~ 90%, BHD, England), and silicone oil (Labchem, Auckland 6, New Zealand) were used as received. Deionized water was used throughout the work.

EPDM rubber used in the study was DuPont's Nordel® IP 4570 (DuPont Dow Elastomers L.L.C., Wilmington, DE, USA) having an ethylene/propylene ratio of 50/45. Sulfur (commercial, Chemmin, Thailand), paraffin oil (Exxon, Thailand), *N*-cyclohexyl-2-benzothiazole-2-sulphenamide (CBS, Flexsys, Germany), tetramethylthiuram bisulfide (TMTD, Flexsys, Germany), mercaptobenzothiazole disulfide (MBTS, Flexsys, Belgium), zinc oxide (activator, Gradmann, Thailand), stearic acid (activator, P. T. Cisadaneraya Chemical, Indonesia), poly(ethylene glycol) (PEG 3350, Brand, Thailand), and silica (Hi-Sil 255, PPG-Siam Silica, Thailand) were of commercial grade and used as received.

### Preparation of hydrogenated natural rubber

158.7 g of the 15 wt % NR/water emulsion was put into a 2-L, four-neck round-bottom flask, in which an over-head agitator was mounted. 0.0125 g of sodium dodecyl sulfate (SDS)/g dried rubber was used to ensure the stability of the latex. After stirring for 15 min, 1.4 mole of hydrazine hydrate (4 mole ratio to  $\text{C}=\text{C}$ ) and 0.0018 mmol  $\text{CuSO}_4$ /g of dried rubber was added into the flask. A water bath was used to maintain the temperature at 50°C. 2.1 mole

**TABLE I**  
**Formulations of the Vulcanized Rubbers**

Ingredient	phr <sup>a</sup>
Rubbers (NR, 48% HNR, 50 : 50 NR/EPDM, and EDPM)	100
Paraffin oil	4.0
Zinc oxide	5.0
Stearic acid	2.0
CBS	1.5
TMTD	0.5
MBTS	1.0
Sulfur	1.2
Silica	20
PEG	1.0

<sup>a</sup> phr, parts per hundred of rubber

of hydrogen peroxide (1.5 mole ratio to N<sub>2</sub>H<sub>4</sub>), which was supplied as a 30 wt % aqueous hydrogen peroxide solution, was added dropwise with a pump over 6 h. During addition of hydrogen peroxide, if too many bubbles were formed, 2–3 drops of mineral oil was added to reduce foaming. The latex was aged for an additional period of an hour after the last addition of H<sub>2</sub>O<sub>2</sub>. The product latex was discharged into boiling water containing 5% formic acid and the polymer product was precipitated. The product was washed with deionized water. The gross polymer was recovered and dried to constant mass in a vacuum oven at 40°C. The HD was determined by <sup>1</sup>H-NMR-spectroscopy.

### Preparation of vulcanizates

The formulations for mixing are provided in Table I. The mix was prepared via conventional vulcanization using a laboratory-sized two-roll mill (Kodaira Seisakusho, Tokyo, Japan). First, each rubber was initially masticated for 3 min, followed by addition of the plasticizer (paraffin oil), activators (ZnO and stearic acid), filler, PEG, and accelerators (CBS, MBTS, and TMTD). Second, mixing was completed by the addition of sulfur at 70°C for 3 min. In advance of the processing, the optimum cure time, T<sub>90</sub> was determined on the basis of the results of curing characteristics using a rheometer (TECH-PRO, Cuyahoga Falls, OH) according to ISO 3414 for 30 min at 150°C. Each rubber compound was compression molded at 150°C with a force of 17.5 MPa using a hydraulic press according to their respective cure time, t<sub>90</sub>, determined with a TECH-PRO. Vulcanizates were conditioned for 24 h before testing.

### Mechanical properties

Tensile properties were determined on an Instron universal testing machine (model 4466; Instron Corp., Canton, MA) using C-type Dumbbell-speci-

men, according to ASTM D412. Hardness measurement of samples was done according to ASTM D2240 (Shore A) using a Bajeiss Serial DTE 5205/03 instrument (MEGA Advance, Berlin, Germany). An abrasion test was carried out according to B.S. 903 Part A9 on a Wallace Test Equipment (England).

### Ozone ageing

Ozone aging studies under static conditions were conducted according to ISO 1431/1-1980 (E) in a Hampden (Model 1008-AH, Northampton, England) ozone test chamber at 40°C. Ozone concentration in the chamber was adjusted to 50 parts per hundred million (pphm). The ozonised oxygen generated in the ozoniser by a UV quartz lamp was collected in a separate chamber where the sample was exposed.

Photographs were taken using an optical microscope Carl Zeiss Stemi 2000 C (Werk Göttingen, Germany) with magnification of 50.

### Accelerated thermal ageing test

Tensile specimens were aged at 100°C for 72 h in an air-circulating aging oven and the tensile properties of the aged samples were determined according to ASTM D573 (1994). Tensile test (ASTM D412-99) was carried out on a tensile dumbbell test specimen after aging to estimate aging resistance.

### Scanning electron microscopy

Scanning electron microscopic studies of the compounds' tensile fracture surfaces were carried out on gold-coated samples using a Joel Microscope (model JSM 5600 LV; Tokyo, Japan) at a magnification of 3,000.

## RESULTS AND DISCUSSION

The cure characteristics and mechanical properties of the rubber compounds are presented in Table II. From these results, it can be seen that the cure characteristic and mechanical properties, depend on the amount of unsaturation levels which are subsequently discussed in detail.

### Hydrogenated natural rubber characterization

The diimide hydrogenation reaction is achieved by two steps: (1) the reaction between hydrazine and hydrogen peroxide to produce diimide [eq. (1) in Fig. 1] and (2) the reaction between diimide and carbon-carbon double bonds to form HNR [eq. (2) in Fig. 1].

The microstructure of HNR can be investigated by <sup>1</sup>H-NMR as the signal adjacent to the double bond

TABLE II  
The Cure Characteristics and Mechanical Properties of Rubber Compounds Cured at 150°C

	NR	HNR	50 : 50 NR/EPDM	EPDM
Optimum cure time (min)	3.38	3.71	3.79	17.79
Tensile strength before thermal aging (MPa)	28.10 (0.57) <sup>a</sup>	26.67 (0.43)	7.43 (0.41)	6.30 (0.52)
Tensile strength after thermal aging (MPa)	16.42 (0.53)	18.75 (0.41)	7.01 (0.44)	6.05 (0.51)
Modulus at 100% before thermal aging (MPa)	1.66 (0.04)	2.00 (0.01)	2.08 (0.01)	2.21 (0.04)
Modulus at 100% after thermal aging (MPa)	1.84 (0.02)	2.16 (0.04)	2.26 (0.03)	2.39 (0.07)
Hardness (shore A)	56.97 (0.38)	59.29 (0.21)	64.43 (0.34)	65.35 (0.24)
Volume loss (cm <sup>3</sup> /1000)	126	171	217	248

<sup>a</sup> The standard deviation is in a parenthesis.

decreases as the hydrogenation proceeds. Figure 2 shows the <sup>1</sup>H-NMR spectra of natural rubber and HNR, containing 48% of HD, respectively. The <sup>1</sup>H-NMR spectra of NR shows signals at 1.75, 2.12, and 5.25 ppm [Fig. 2(a)] which are attributed to -CH<sub>3</sub>, -CH<sub>2</sub>-, and olefinic protons, respectively. It can be seen that after hydrogenation, the peak at 5.25 ppm decreases and new peaks appear at 0.8 and 1.2 ppm [Fig. 2(b)] attributed to -CH<sub>3</sub>, -CH<sub>2</sub>-, and -CH of the product, which confirms the hydrogenation reaction. The integrated areas of the signal at 5.12 and the summation of the area between 0.84 and 2.12 ppm, corresponding to the olefinic unit and methyl proton of the saturated unit, respectively, were used for the determination of the degree of hydrogenation. For this work, diimide hydrogenation was carried out using hydrazine/hydrogen peroxide/Cu<sup>2+</sup> (as catalyst) under the following conditions: 0.0018 mmol of CuSO<sub>4</sub> as catalyst /g of dried rubber, mole ratio of N<sub>2</sub>H<sub>4</sub>/C=C at 4, mole ratio of H<sub>2</sub>O<sub>2</sub>/N<sub>2</sub>H<sub>4</sub> at 1.5, hydrogenation temperature at 50°C, and hydrogenation time at 7 h, providing hydrogenated NR with a HD of 48%.

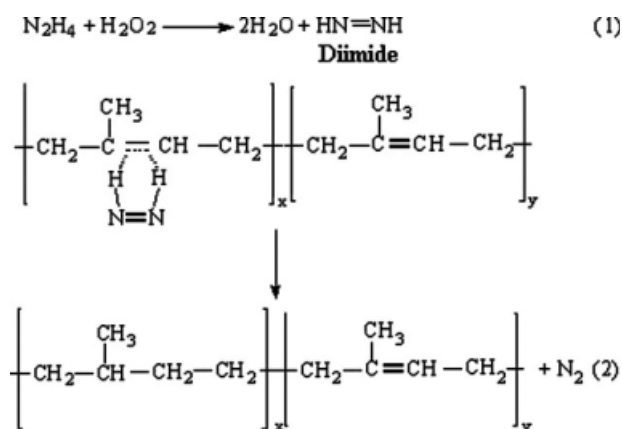


Figure 1 Hydrogenation of the polyisoprene unit using hydrazine and hydrogen peroxide: (1) reaction of hydrazine and hydrogen peroxide and (2) reaction of diimide and the polyisoprene unit.

### Cure characteristics

The cure curves for the rubber compounds are shown in Figure 3. The initial decrease in torque was due to the softening of the matrix. Torque then increased due to the formation of cross linking between the macromolecular chains. The results from the rheographs indicated that the EPDM compound showed a marching increase in rheometer torque and the compounds containing NR showed a plateau torque with an increase in cure time. The vulcanization reaction of NR as can be seen from the rheograph, was faster than that with EPDM. This has been attributed to the low level of unsaturation in EPDM, as reflected in the cure curves of pure NR and the compounds containing NR.

Figure 4 shows the variation in the cure properties of a NR, 48% HNR, 50 : 50 NR/EPDM, and EPDM. The elastomers were vulcanized for their optimum cure time. For the optimum cure time, it can be

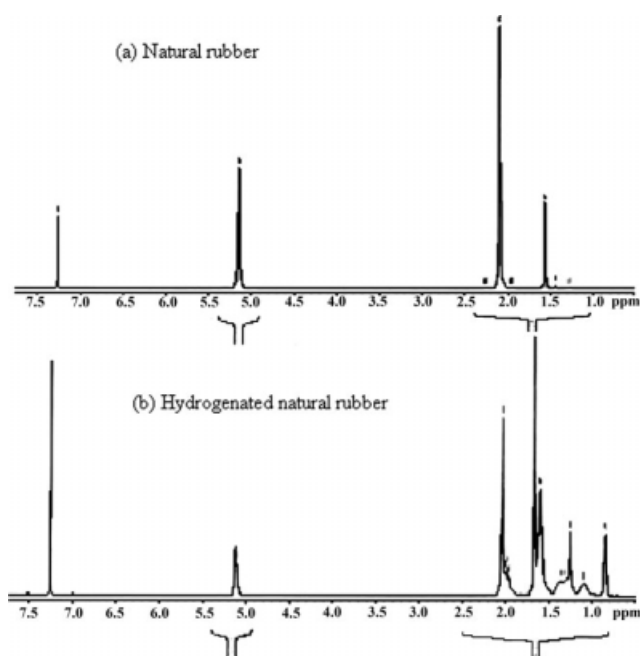
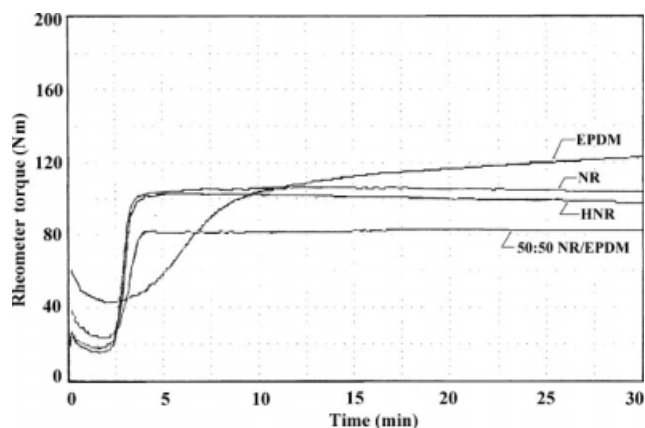
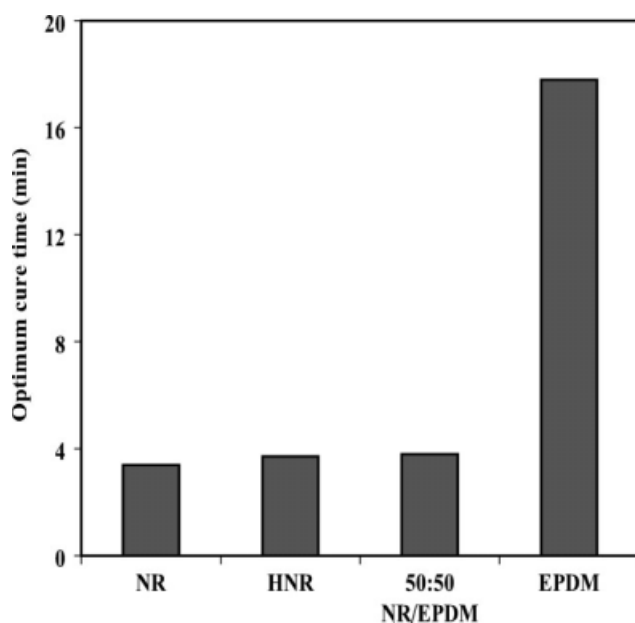


Figure 2 <sup>1</sup>H-NMR spectra of: (a) NR and (b) 48% hydrogenated natural rubber.



**Figure 3** Rheographs of NR, 48% HNR, 50 : 50 NR/EPDM blend, and EPDM at 150°C.

observed that NR exhibited the shortest  $t_{90}$  followed by 48% HNR, 50 : 50 NR/EPDM, and EPDM respectively. The results indicated that the cure rate of 48% HNR showed no significant change when compared to both NR and 50 : 50 NR/EPDM blends whereas the cure rate of the EPDM vulcanizate, as can be seen from the cure time, was much slower than that of the NR products. This has been attributed to the low efficiency of EPDM being vulcanized with the sulfur system, since EPDM has comparatively much lower diene content. Concerning the cure rate, vulcanizates prepared with NR showed a slightly lower cure rate than those of 48% HNR. For a vulcanizate prepared with 48% HNR, the lower amount of diene content, retarded the cure rate and increased the optimum cure time. The cure time values of 48% HNR vulcanizate showed no change as compared to



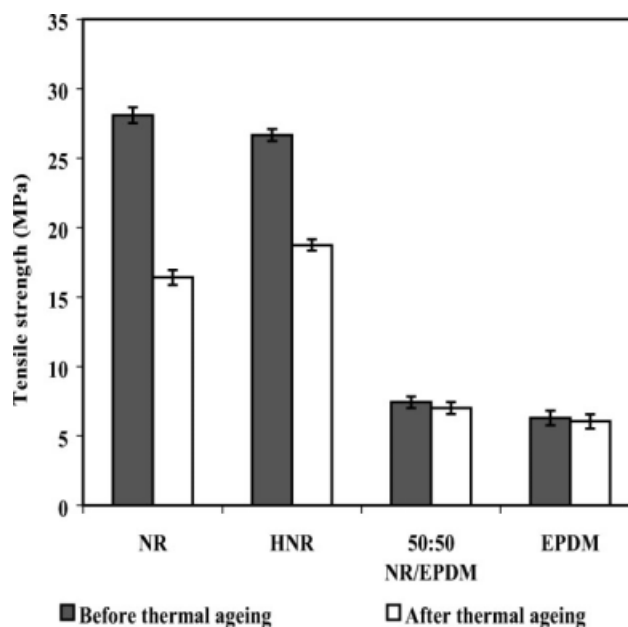
**Figure 4** Optimum cure time of NR, 48% HNR, 50 : 50 NR/EPDM blend, and EPDM.

50 : 50 NR/EPDM vulcanizate due to the same amount of unsaturation level.

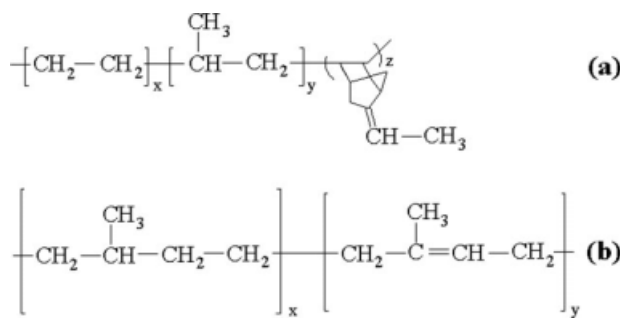
### Mechanical properties

#### Tensile properties before and after heat aging

Tensile strength is an important characteristic of polymeric materials because it indicates the limit of final stress in most applications. Tensile strength of the NR, 48% HNR, 50 : 50 NR/EPDM, and EPDM are shown in Figure 5. For the tensile strength, it can be observed that NR vulcanizate exhibits the highest tensile strength followed by 48% HNR, 50 : 50 NR/EPDM, and EPDM vulcanizates. It is clear that the NR vulcanizate possessed the highest tensile strength as expected, due to the NR crystallinity exhibited upon stretching. The lowest tensile strength was shown by a EPDM vulcanizate, and the reason can be explained on the basis of its chemical structure. This may be attributed to the ethylene and propylene units present in EPDM [Fig. 6(a)] which inhibits the crystallization upon stretching. It is found that the 48% HNR vulcanizate had a higher tensile strength as compared to the vulcanizates containing EPDM. This may be attributed to the alternating ethylene-propylene segments in 48% HNR [Fig. 6(b)] which are assumed to be very flexible and result in a higher stress, but the alternating ethylene-propylene segments in 48% HNR are not long enough for crystallization, but afford interaction between the chains to result in a little lower tensile strength in comparison with the NR vulcanizate.



**Figure 5** Tensile strength of NR, 48% HNR, 50 : 50 NR/EPDM blend, and EPDM vulcanizates.



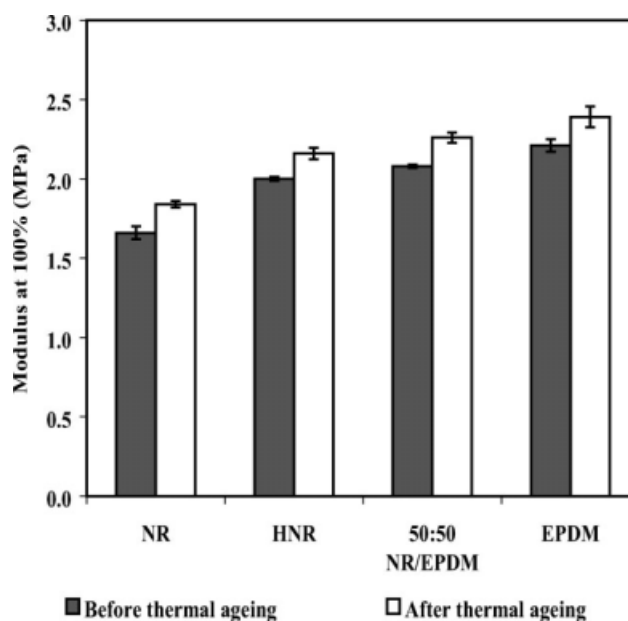
**Figure 6** Schematic representation of the structure of: (a) EPDM and (b) 48% HNR.

Figure 5 also shows that all of the vulcanizates after aging showed a reduction in tensile strength, as compared to before aging, indicating thermal degradation of the matrix during the vulcanizates. The superiority of vulcanizates containing low diene contents over the NR vulcanizate, with respect to tensile strength was obvious. The aging resistance is also found to be superior for vulcanizates containing EPDM. It is apparent that a change in tensile strength on aging was minimal, due to the low unsaturation levels and absence of any unsaturation in the backbone chain, whereas the tensile strength of the NR vulcanizate greatly decreased upon thermal aging. The tensile strength after aging was reduced to a greater extent with the 48% HNR vulcanizate than with the EPDM or 50 : 50 NR/EPDM vulcanizates, due to the presence of some unsaturation in the backbone chain of the 48% HNR. However, the tensile strength after aging of the 48% HNR vulcanizate was excellent when compared with that of EPDM or a 50 : 50 NR/EPDM vulcanizate. This is due to the crystalline domains formed by the alternating ethylene-propylene segments which are produced from the hydrogenation of *cis*-1,4-polyisoprene units in the NR rubber. Obviously, the 48% HNR vulcanizate was more resistant to thermal aging than NR, as shown in Figure 5. After the thermal aging test, the HNR sample with 48% HD maintained  $\sim 70\%$  of its original tensile strength. Since hydrogenation can convert the weak  $\pi$  bond within NR to the stronger C–H  $\sigma$  bond, thermal stability can be regarded as the ability to maintain the required properties of materials at a high temperature. These results are in agreement with those reported by Inoue and Nishio<sup>14</sup> for their studies concerning HNR materials. They reported that the mechanical properties of the HNR vulcanizate after aging were higher than for the NR vulcanizate because of a reduction in the number of the C=Cs in the backbone chain.

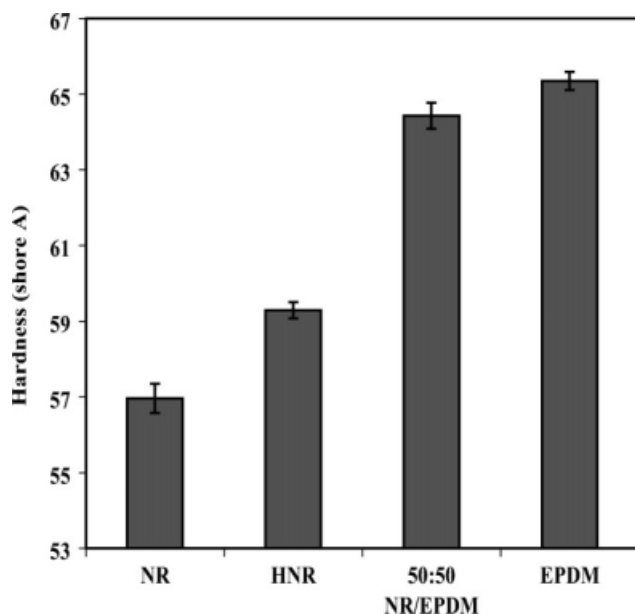
Figure 7 shows the effect of various rubber materials on the modulus at 100% elongation of the rubber vulcanizates, which is an indication of material stiff-

ness. It was believed that the reduction of elasticity is due to the lower amount of unsaturation in the backbone chain. Because of the large amount of unsaturation in the NR structure, the NR vulcanizate (Fig. 7) showed the lowest 100% modulus. In the case of the EPDM vulcanizate, the modulus value obtained in the experiments was highest because of the absence of any unsaturation in the backbone, resulting in lower elasticity and a higher rigid property. The results from both NR and EPDM vulcanizates indicated that the 100% modulus increased as the unsaturation content in the backbone chain decreased. The following trend of modulus has been observed among all vulcanizates: EPDM > 50 : 50 NR/EPDM > 48% HNR > NR.

The effect of heat aging on Young's modulus is illustrated in Figure 7. After the thermal aging test, the rubber samples became brittle. Young's modulus for all of the vulcanizates shifted to a higher value after aging. These increases are generally attributed to an increase in the stiffness of the rubber matrix brought about by a reduction in the number of double bonds. On comparing these results, it is observed that the EPDM vulcanizate showed the highest 100% Young modulus after heat aging, followed by 50 : 50 NR/EPDM and 48% HNR, with the lowest modulus being observed for the NR vulcanizate. As mentioned earlier, the elasticity of the rubber chains is reduced with a reduction in the number of double bonds, thus enhancing stiffness properties. Similar results were also reported by Ikada et al.<sup>18</sup>



**Figure 7** Modulus at 100% elongation of NR, 48% HNR, 50 : 50 NR/EPDM blend, and EPDM vulcanizates.



**Figure 8** Hardness of NR, 48% HNR, 50: 50 NR/EPDM blend, and EPDM vulcanizates.

### Hardness

Hardness, a measure of the modulus of elasticity at low strain, showed a similar trend in Young's modulus. Figure 8 shows the hardness of vulcanized rubber materials. It can be seen that the hardness of 48% HNR was higher than that of NR. This is simply due to the fact that the presence of a small amount of unsaturation in 48% HNR reduced the elasticity of the rubber chains leading to more rigid rubber materials. As expected, EPDM and 50 : 50 NR/EPDM vulcanizates had higher hardness than did the corresponding 48% HNR vulcanizate. The following trend of hardness has been observed among all vulcanizates: NR < 48% HNR < 50 : 50 NR/EPDM < EPDM. This may be caused by differences in the amount of unsaturations in the backbone chain.

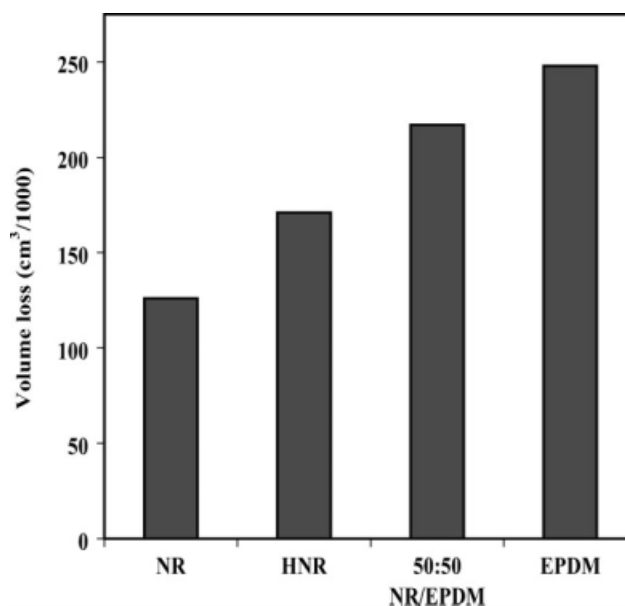
### Abrasion resistance

The abrasion resistance of a solid body is defined as its ability to withstand the progressive removal of material from its surface, as the result of mechanical action of rubbing, scraping, or of an erosive nature. The abrasion resistance of all vulcanizates is shown in Figure 9. The trend of the abrasion resistance of vulcanizates can be arranged in a descending order, as follows: NR > 48% HNR > 50 : 50 NR/EPDM > EPDM. The highest abrasion resistance of the NR vulcanizate could be attributed to high unsaturated structure, as evident from its highest tensile strength compared to other vulcanizates. The abrasion loss of

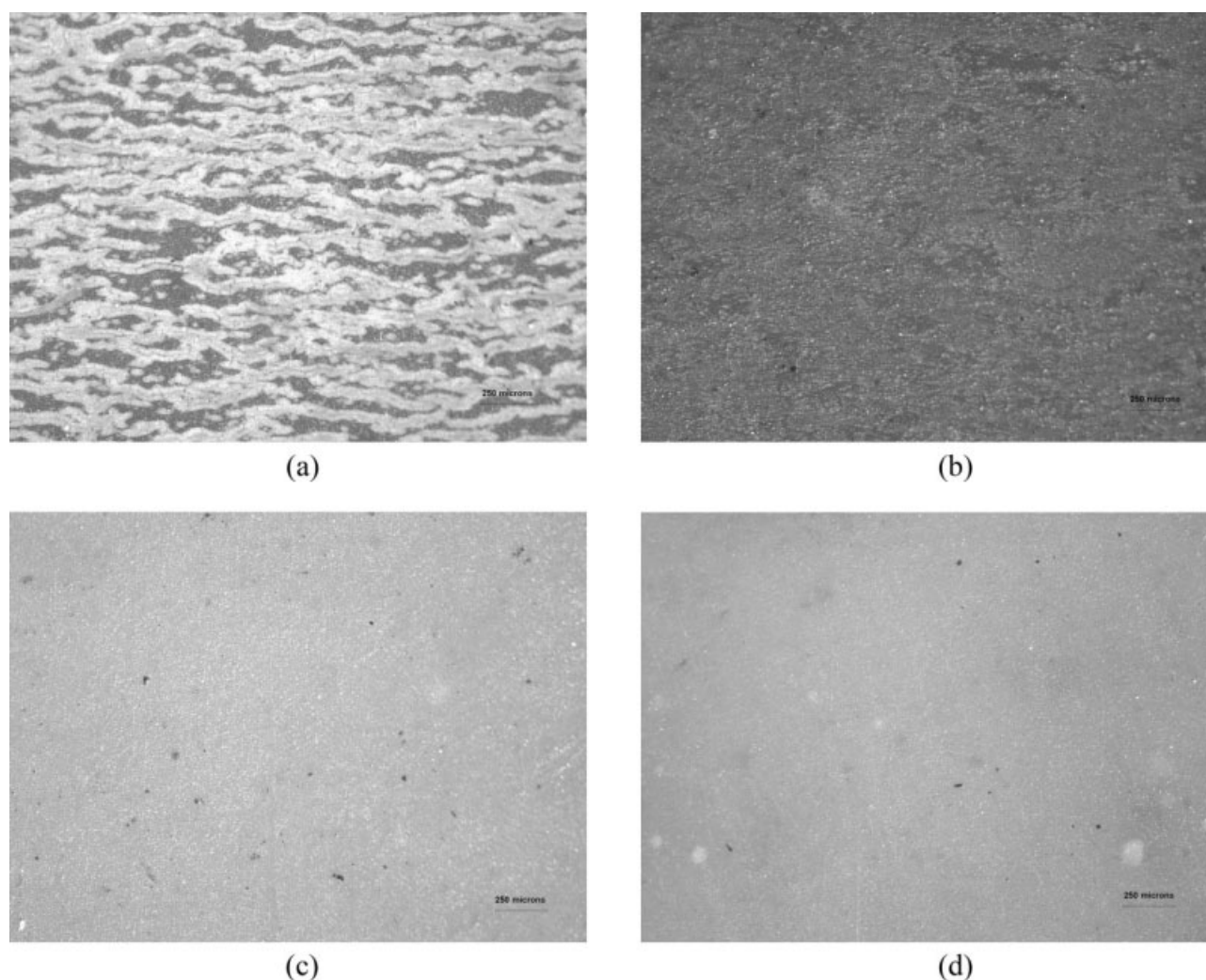
48% HNR is higher than that of the NR vulcanizate, due to a reduction in the number of the double bonds. This suggests that abrasion resistance is heavily dependent on the unsaturation content in the backbone chain.

### Ozone ageing

The interaction of rubber with ozone is best noted when the rubber is stressed or stretched in use. Optical photographs of the surfaces of the vulcanized rubbers of ozone exposed samples are presented in Figure 10. The nature and intensity of cracks due to ozone attack are different for various rubbers. The photograph clearly shows that the highest level of cracks were deep, wide, and continuous in NR [Fig. 10(a)]. The growth of ozone cracks were initiated in the rubber matrix and the cracks grew over the critical length for failure, resulting in brittleness and macroscopic cracks on the surface of the NR specimens. In the case of 48% HNR the crack density was less and the vulcanizate showed shorter cracks represented by the horizontal lines and rough surface [Fig. 10(b)], which confirms that the crack growths were retarded. This implies that the hydrogenation of NR which resulted in a reduction of carbon-carbon double bonds in the main chain led to less ozone cracking on the surface of the rubber specimen. When there are carbon-carbon double bonds in the backbone structure, then ozonolysis occurred. Therefore, the ozone resistance of this vulcanizate was much better than that of the NR vulcanizate. Due to the absence of any unsaturation in the main chain, EPDM showed



**Figure 9** Abrasion resistance of NR, 48% HNR, 50: 50 NR/EPDM blend, and EPDM vulcanizates.



**Figure 10** Optical photographs of ozone exposed: (a) NR, (b) 48% HNR, (c) 50 : 50 NR/EPDM blend, and (d) EPDM ( $\times 50$ ).

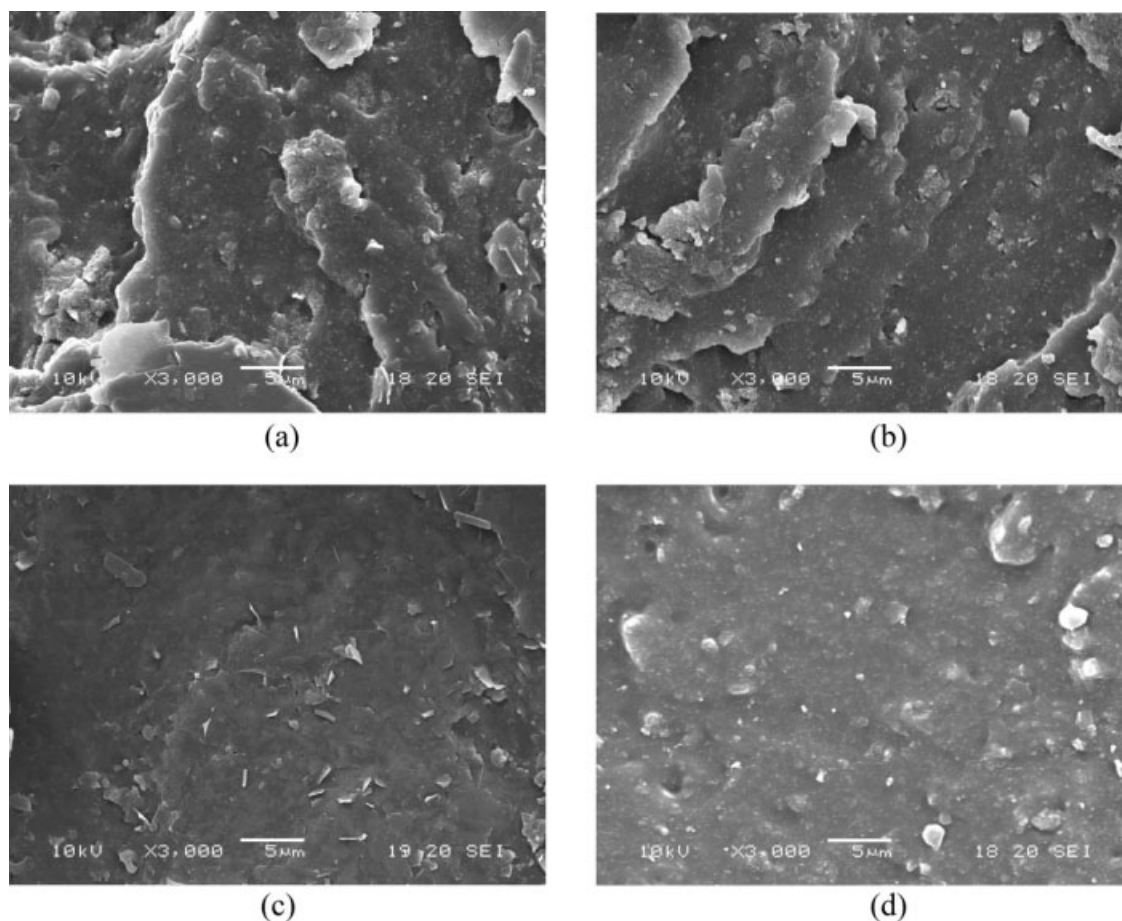
no cracks as seen in Figure 10(d), which confirms that crack growth was suppressed more effectively. Also, the optical photograph of EPDM [Fig. 10(d)] was smoother than that of the 50 : 50 NR/EPDM vulcanizate [Fig. 10(c)]. Results revealed that the ozone resistance of the vulcanizate improved more when there is a lower level of unsaturated bonds in the main chain. Therefore, the hydrogenation of NR provides a new material that has greater thermal and ozone resistance than NR.

### Morphology

The morphology of all vulcanizates after tensile fracture is shown in Figure 11. NR and 48% HNR vulcanizates are shown in Figure 11(a,b); it can be seen that the fracture surface of the vulcanizates showed the rough surface with stress whitening is a typical feature of ductile failure; which indicates the higher tensile strength of the vulcanizates. From the frac-

ture surface of the 48% HNR vulcanizate in Figure 11(b) [compare to Fig. 11(a)], the rough surface with stress whitening decreased due to a reduction in unsaturation in the main chain, which resulted in the brittle failure, hence the enhancement in the stiffness. A brittle and scaly surface was observed for vulcanizates containing EPDM with the microcharacteristics typical of a rigid surface. The EPDM matrix was relatively large and smooth, suggesting brittle failure [Fig. 11(d)]. However, the fractured surfaces become relatively rough when an amount of NR was added into the EPDM vulcanizate [Fig. 11(c)]. These micrographs revealed that the extent of stress whitening is enhanced by the presence of the number of the double bonds in the main chain. Therefore, the vulcanizates containing a low diene showed lower tensile strength in comparison to vulcanizates containing high diene, but the extension of saturations in the main chain was decisive to improve the ozone and thermal aging resistance in vulcanizate.





**Figure 11** Scanning electron micrographs of tensile fractured surfaces of the vulcanizates: (a) NR, (b) 48% HNR, (c) 50: 50 NR/EPDM blend, and (d) EPDM ( $\times 3,000$ ).

## CONCLUSIONS

The hydrogenation of NRL with diimide generated by hydrazine/hydrogen peroxide/ $\text{Cu}^{2+}$  (as catalyst) is a useful method for hydrogenation. A molar ratio of  $\text{N}_2\text{H}_4/\text{C}=\text{C}$  at 4, molar ratio of  $\text{H}_2\text{O}_2/\text{N}_2\text{H}_4$  at 1.5, 0.0018 mmol  $\text{CuSO}_4$  as catalyst/g dried rubber, hydrogenation temperature at  $50^\circ\text{C}$ , and a hydrogenation time of 7 h provided 48% hydrogenation. Analyses of the  $^1\text{H-NMR}$  spectra confirmed that the 48% HNR took the form of a partial alternating copolymer of ethylene and propylene. This rubber was vulcanized using sulfur and its vulcanized properties were compared with those of NR, 50 : 50 NR/EPDM, and EPDM vulcanizates. The cure time  $t_{90}$  of the 48% HNR vulcanizate was comparable to that of both NR and 50 : 50 NR/EPDM compounds whereas EPDM showed the highest cure time. The 48% HNR vulcanizate showed a reduction in tensile strength and abrasion resistance compared with that of the NR vulcanizate, however these properties were excellent when compared with those of 50 : 50 NR/EPDM and EPDM vulcanizates. Both heat and ozone resistances of the 48% HNR vulcanizate were higher than those of the NR vulcanizate due to a

reduction in the number of double bonds in the backbone chain. These observations suggest that weather resistance of the HNR vulcanizates are better due to the hydrogenation of NR while still maintaining good mechanical properties of the parent NR. Thus, the 48% HNR synthesized from a renewable resource (NR) can provide improved rubber materials for outdoor use.

The authors thank Miss J. Jarmornsakullert and Miss S. Janjad, the Department of Science Service within Ministry of Science and Technology for the physical testing experiments, and the Rubber Research Institute of Thailand within the Department of Agriculture for the rubber processing.

## References

1. Botros, S. H. *Polym Plast Technol Eng* 2002, 41, 341.
2. Ghosh, A. K.; Debnath, S. C.; Naskar, N.; Basu, D. K. *J Appl Polym Sci* 2001, 81, 800.
3. Baranwal, K. C.; Son, P. N. *Rubber Chem Technol* 1973, 46, 88.
4. Schulz, D. N.; Turner, S. R.; Golub, M. A. *Rubber Chem Technol* 1982, 55, 809.
5. Rempel, G.; Mohammadi, N. *Macromolecules* 1987, 20, 2362.

6. Singha, N. K.; De, P. P.; Sivaram, S. J. *J Appl Polym Sci* 1997, 66, 1647.
7. Olah, G. A.; Molnar, A. *Hydrocarbon Chemistry*; 2nd ed.; Wiley: New York, 1995; 633.
8. Gan, S. N.; Subramaniam, N.; Yahya, R. *J Appl Polym Sci* 1996, 59, 63.
9. Bhattacharjee, S.; Bhowmick, A. K.; Avasthi, B. N. *Polymer* 1993, 34, 5168.
10. Schulz, G.; Worsfold, D. J. *Polym Commun* 1984, 25, 206.
11. Nakagawa, T.; Okawara, M. *J Polym Sci A-1* 1968, 6, 795.
12. Nang, T. D.; Katabe, Y.; Minoura, Y. *Polymer* 1976, 17, 117.
13. Samran, J.; Phinyocheep, P.; Daniel, P.; Kittipoom, S. *J Appl Polym Sci* 2005, 95, 16.
14. Inoue, S.; Nishio, T. *J Appl Polym Sci* 2007, 103, 3957.
15. Wideman, L. G. U.S. Pat. 4,452,950 (1984).
16. He, Y.; Daniels, E. S.; Klein, A.; El-Aasser, M. S. *J Appl Polym Sci* 1994, 64, 2047.
17. Xie, H.-Q.; Li, X.-D.; Guo, J.-S. *J Appl Polym Sci* 2003, 90, 1026.
18. Ikeda, Y.; Phinyocheep, P.; Kittipoom, S.; Ruanchaoren, J.; Kokubo, Y.; Morita, Y.; Hijikata, K.; Kohjiya, S. *Polym Adv Technol* 2008, 19, 1608.