Novel Self-Crosslinking Film from Hydrogenated Carboxylated Nitrile Rubber Latex

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ABSTRACT: A new type of self-crosslinking latex film was prepared from hydrogenated carboxylated nitrile-butadiene rubber (HXNBR) latex by diimide reduction. The properties of the HXNBR rubber, including film surface morphology, physical properties, thermal stability and ageing properties, were investigated. FTIR spectroscopy was used to confirm the HXNBR structure, from which the degree of hydrogenation can be obtained. The morphology of the film surface was monitored by atomic force microscopy, which confirmed that HXNBR latex can form a continuous film with good cohesive properties from self-crosslinking latex particles. The self-crosslinking provided the latex film with excellent tensile strength. The thermal stability was improved after hydrogenation, as indicated by thermogravimetric methods. The activation energy for degradation was determined by Coats-Redfern plots. Hot air oven thermal ageing confirmed that the oxidation resistance increased as the degree of hydrogenation increased. All these results showed that HXNBR latex can form a self-crosslinking film with better mechanical properties, and heat and oxidation resistance than those of XNBR latex film in a wide range of film applications. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2013**, *000*, 39865

INTRODUCTION

The hydrogenation of diene-based rubber is expected to improve the physical properties as well as the oxidative stability of the rubber by replacing the radical-susceptive C=C double bonds with saturated hydrocarbon bonds.[1] As a potential alternative to the conventional hydrogenation technology based on hydrogen/transition-metal catalysts, the diimide hydrogenation method has received increasing attention in the hydrogenation of polybutadiene-based rubbers in latex form.[2] All of the expensive transition-metal catalysts, gaseous hydrogen, organic solvents, and 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. Compared with nitrile butadiene rubber (NBR), hydrogenated NBR (HNBR) exhibits improved thermal and oxidative stability and unique resistance to heat, oil, and aggressive chemicals. Many investigations on hydrogenating NBR latex by diimide hydrogenation have been reported.[3–11] However, HNBR latex can self-crosslink, resulting in a large amount of gel, and HNBR dry rubbers prepared by the coagula-

tion of HNBR latex are fully crosslinking and have poor mechanical properties. Various techniques have been used to overcome gel formation,[12,13] but they are not successful in eliminating the crosslinking completely. Therefore, up to now, there has been no report on the successful application of HNBR latex.

However, it is possible to apply HNBR latex in latex form directly. Carboxylated NBR (XNBR) latex has been employed extensively in the manufacture of water-based adhesives, paints, coatings, and dipped products. It is well known that emulsion polymers are mainly used for applications that require the formation of a continuous film of latex particles with good cohesive properties.[14,15] Particularly, dipped goods are generally prepared from prevulcanized latex. Prevulcanization, generally performed by using sulfur, peroxide, or γ-radiation, is a crosslinking process in which chemical crosslinking takes place inside particles.[16,17] The unvulcanized latex film is soft and cannot be used as a raw material in the manufacture of thin-film products. In various fields of application, latex films have to be crosslinked in order to reach a satisfactory level of performance and optimum physical properties such as hardness and tensile strength.

Gel makes HXNBR latex a kind of crosslinked latex. From the effect of crosslink on the XNBR latex, we can infer that even if crosslink adversely prevents HXNBR latex to prepare dry rubbers by coagulation, HXNBR latex still has the potential to replace XNBR latex to use, especially for dipped products such as gloves and catheters. Based on the above, we suppose there is the possibility that the gel in HXNBR latex could be made use of to prepare self-crosslinking HXNBR latex films. The purpose of this study was to answer two questions, firstly whether gel in HXNBR latex could be used to prepare HXNBR self-crosslinked latex films, and further more whether the prepared HXNBR film has good performance and physical properties. So far, there has been no relevant information available in literatures regarding this issue. In this study, HXNBR latex was obtained by means of diimide hydrogenation, self-crosslinking HXNBR latex films were prepared, and the properties of the films were investigated.

EXPERIMENTAL

Materials
XNBR latex Nippon (acrylonitrile content 26–30%) was obtained from Zeon Company (Japan). Hydrazine hydrate (80%), 30% aqueous solution of hydrogen peroxide, and boric acid were obtained from Beijing Chemical Plant (China).

Hydrogenation of XNBR Latex
Two hundred mL of the 20 wt % HXNBR/water latex was added to a 1000-mL three-necked flask and stirred for 15 min before hydrazine hydrate was added. The mole ratio of hydrazine hydrate and C=C was changed from 0.5 to 1.5 to obtain HXNBR latex with different degrees of hydrogenation. The mixture was heated to 40°C and stirred for 30 min. A solution of hydrogen peroxide and boric acid was added, and the temperature was kept constant for 24 h. The mole ratio of hydrazine hydrate and hydrogen peroxide was kept constant to 1.

Preparation of HXNBR Latex Film
Cleaned plate formers of well-controlled depth were dipped into a 25% calcium nitrate solution. Then the formers were dried in an oven at 60°C for 5 min and cooled to room temperature. The HXNBR latex, with coarse particles less than 1% removed by filtering through a sieve (opening: 250 μm), was cast on the formers and dried in air to form wet films. After they were stripped from the formers, the wet films were leached in water at 40°C for 12 h and then dried in an air-circulated oven at 60°C until they become homogeneous and transparent. The dried HXNBR latex films, with a constant thickness ranging from 0.9 to 1.2 mm, were stored in a desiccator before testing.

Characterization of HXNBR Latex Film
The final conversion of double bonds (C=C) to single bonds (C-C) in the hydrogenated rubber latex was determined by attenuated total reflection Fourier transform infrared spectrometry (ATR-FTIR). ATR-FTIR spectra of the film–air interface were recorded on a single-beam spectrometer (Tensor 27, BRUKER OPTIK GMBH, Germany) with a single reflection ATR accessory (MIRacle, PIKE Technologies, Italy). The signal-to-noise ratio was controlled at higher than 5000 to obtain distinctive bands. Samples were placed on the Ge crystal plate. Horizontal

ATR spectra were obtained at an incident beam angle of 45°, and 32 scans at 4 cm^{-1} resolution were collected.

Atomic force microscopy (AFM) was used to observe the film surface. A latex film was prepared by applying one drop of the latex on a glass microscope slide. The latex film was cast at room temperature (25°C) and allowed to dry for 3 days in a desiccator before AFM imaging. The AFM experiments were performed at ambient conditions (ca. 25°C, relative humidity of 30–40%) by using a Nanoscope IIIa microscope from Digital Instruments. The height and phase images were obtained simultaneously with the instrument in the intermittent contact mode. Images were taken at the Si cantilever's the fundamental resonance frequency of 340 kHz. The digital resolution of all images was 256 × 256 points.

The crosslink density was measured by volume swelling measurements. About 0.4 g of accurately weighed film was immersed in toluene at room temperature for 72 h to reach equilibrium swelling. Then the swollen sample was taken out of toluene, wiped with a filter paper, and weighed. Finally, the swollen film was dried at 70°C in a vacuum oven to constant weight and then weighed accurately. The crosslink density was evaluated by using the Flory–Huggins equations.

Tensile tests of the latex film specimens were carried out on a CMT4101 testing machine (Shenzhen SANS Testing Machine, China) at a crosshead speed of 200 mm·min^{-1} according to Chinese standard GB/T 528. The films were cut into dumbbell-shaped pieces. Each measured value was taken as the average value of four replicate tests.
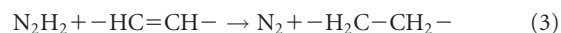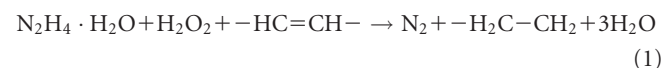
The thermal stability was evaluated by thermogravimetric analysis (TGA) using a TGA/DSC1 STARe system (Mettler Toledo). The sample (ca. 10 mg) was placed in a platinum pan and heated up to 800°C from room temperature under nitrogen atmosphere at a heating rate of 10°C·min^{-1}. The initial decomposition temperature (T_{id}) and the temperature at the maximum mass loss rate (T_{max}) were recorded

Tensile specimens were aged at 100°C for 72 h in an air-circulating aging oven. The tensile properties of the aged samples were determined according to Chinese standard GB/T 3512 to estimate aging resistance.

RESULT AND DISCUSSION

Structural Aspects of HXNBR Characterization
The overall hydrogenation reaction with diimide [eq. (1)] is realized by two steps: (1) the reaction between hydrazine and hydrogen peroxide to produce diimide [eq. (2)] and (2) the reaction between diimide and carbon–carbon doubles bonds to form hydrogenated polymer [eq. (3)], as follows:

$$N_2H_4 \cdot H_2O + H_2O_2 + -HC{=}CH- \rightarrow N_2 + -H_2C-CH_2 + 3H_2O \tag{1}$$

$$N_2H_4 \cdot H_2O + H_2O_2 \rightarrow N_2H_2 + 3H_2O \tag{2}$$

$$N_2H_2 + -HC{=}CH- \rightarrow N_2 + -H_2C-CH_2- \tag{3}$$

The extent of unsaturation for C=C in HXNBR has to be calculated first. As HXNBR latex films cannot be dissolved in organic solvents, ATR-FTIR spectroscopy was chosen to
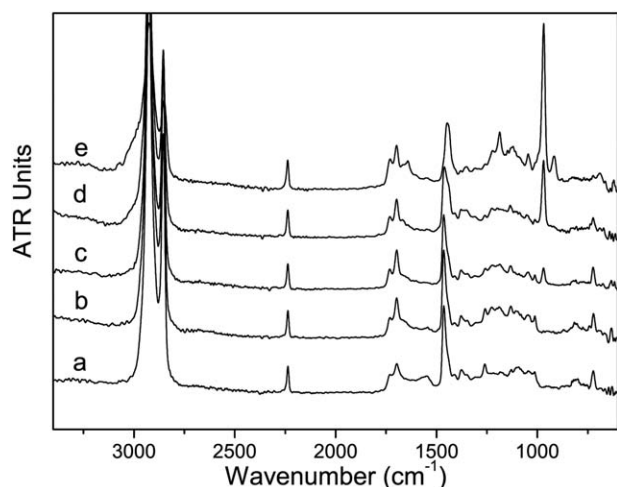
Figure 1. ATR-FTIR spectra of: (a) HXNBR-99, (b) HXNBR-90, (c) HXNBR-75, (d) HXNBR-35, and (e) XNBR latex films.

characterize the extent of C=C unsaturation according to international standard ISO14558: 2000. HXNBR latex films with different degrees of saturation or hydrogenation were designated as HXNBR-x, where x denotes the degree of saturation. The ATR-FTIR spectra of HXNBR-99, HXNBR-90, HXNBR-75, HXNBR-35, and XNBR film are shown in Figure 1. Spectral intensity changes are detected at 2237, 967, 917, and 740 cm^{-1}, corresponding to C-N stretching, 1, 4 trans butadiene unit stretching, 1, 2 vinyl stretching, and 1, 4 cis butadiene unit stretching, respectively. As the extent of C=C unsaturation decreases, the peaks as a result of butadiene units decrease in height and a new peak at 722 cm^{-1} as a result of –CH$_2$– rocking vibrations [(–CH$_2$–)$_{n > 4}$] is observed. The intensity of the absorption peak at 2237 cm^{-1} shows no change, reflecting the stability of the nitrile groups towards diimide reduction. The C=O peak is split into three absorption bands, one at the original 1697 cm^{-1} position and the other two at 1730 and 1642 cm^{-1}. A similar phenomenon was reported for the hydrogenation of carboxylated styrene-butadiene rubber latex.[18] The content of residual double bonds was estimated from the intensity ratio of the signals at 2236, 973, and 723 cm^{-1} according to an equation given in Marshall et al.[19]

Swelling Properties and Gel Fraction

A latex has to be crosslinked in order to reach a satisfactory level of performance in various fields of application. In some cases external crosslinking agents are needed to prepare a prevulcanized latex.[16,17] For HXNBR latex, crosslinking occurs during hydrogenation; i.e., HXNBR latex is a self-crosslinking latex without the need for any external crosslinking agent.

In previous studies on diimide hydrogenation[4,5] only the gel content was used to characterize the extent of crosslinking. But the crosslinking density from equilibrium swelling is often a more accurate parameter to characterize the extent of crosslinking for crosslinked rubber. The crosslinking density of HXNBR latex films is a useful parameter for studying their properties. For the determination of crosslinking density, the molecular

weight between crosslinkings (M_c) was estimated from the equilibrium swelling data by using the Flory–Rehner equation:

$$M_c = \frac{-\rho_p V_s [\varphi_p^{1/3} - \varphi_p^{1/2}]}{\ln(1 - \varphi_p) + \varphi_p + \chi \varphi_p^2} \quad (4)$$

where V_s is the molar volume of the solvent toluene (105.9 g cm^{-1}) and φ_p is the volume fraction of the polymer in the swollen state. The value of φ_p was calculated by the following equation:

$$\varphi_p = \left[1 + \frac{\rho_p W_2}{\rho_s W_1} - \frac{\rho_p}{\rho_s} \right]^{-1} \quad (5)$$

where W_1 is the initial weight of the film, W_2 is the weight of swollen film, ρ_s is the solvent density (toluene, 0.87 g/cm^3), and ρ_p is the density of the HXNBR (0.98 g/cm^3). The interaction parameter χ was calculated from the following equation:

$$\chi = \beta + \frac{V_s}{RT(\delta_s - \delta_p)^2} \quad (6)$$

where β is the lattice constant (0.34 for elastomer–solvent systems), R is the universal gas constant, T is the absolute temperature, and δ_s and δ_p are the solubility parameters of HXNBR (9.64) and toluene (8.91), respectively. After calculating, the Flory–Huggins interaction parameter χ value used was 0.42. The crosslink density (v) was calculated by the following equation:

$$v = 1/2M_c \quad (7)$$

The gel fraction (Gel) was calculated by the following equation:

$$\text{Gel} = \frac{W_3}{W_1} \times 100\% \quad (8)$$

where W_3 is the weight of the dried swollen film.

Plots of M_c and gel fraction for HXNBR-99, HXNBR-90, HXNBR-75, and HXNBR-35 are shown in Figure 2. The gel fraction is above 95% and about the same for latex films at different degrees of hydrogenation but the M_c value decreases rapidly as the degree of hydrogenation increases. These results indicate that hydrogenation and crosslinking took place at the same time. The increases in both the degree of hydrogenation and the crosslink density are believed to
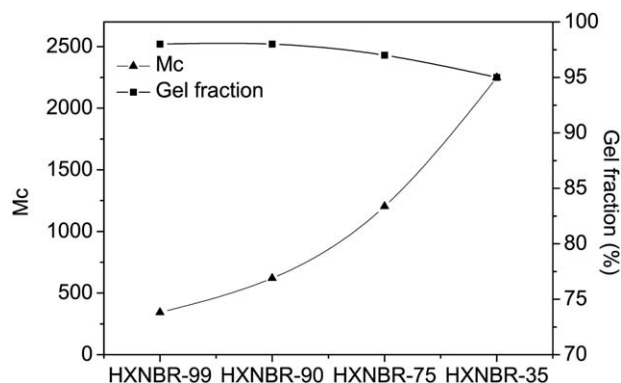

Figure 2. Gel fraction and molecular weight between crosslinks of HXBNR films with different degrees of hydrogenation.
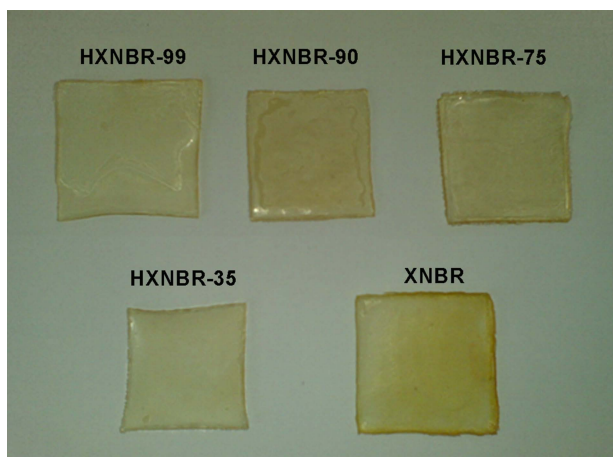
Figure 3. Photo images of HXNBR-99, HXNBR-90, HXNBR-75, HXNBR-35, and the XNBR films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

result from the increase of the amount of reaction agents, namely hydrazine hydrate, hydrogen peroxide, and boric acid.
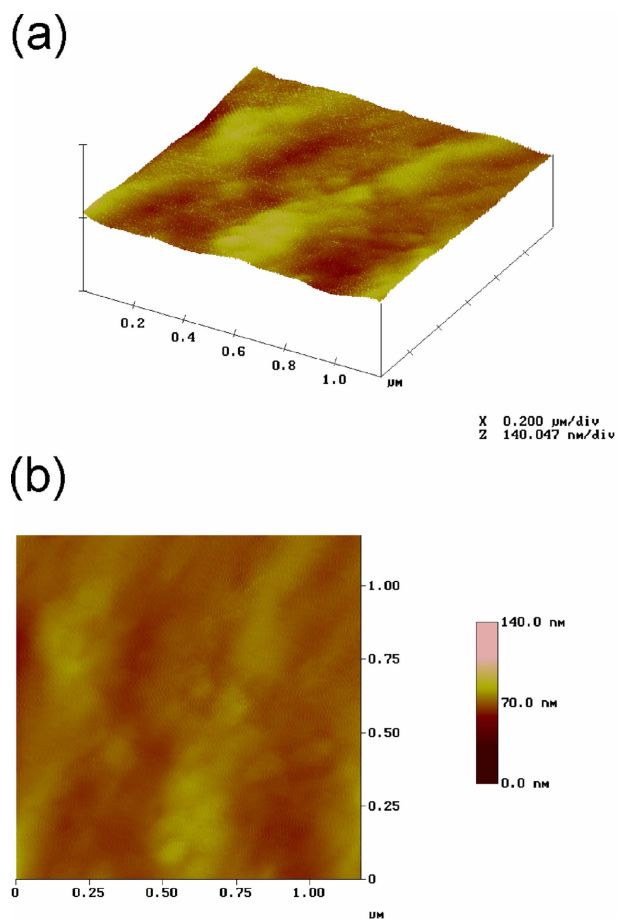

Figure 4. Three-dimensional AFM (a) surface images and (b) height image of HXNBR-99 latex film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Surface Morphology of HXNBR Latex Films

Photo images of HXNBR-99, HXNBR-90, HXNBR-75, HXNBR-35, and the XNBR film are shown in Figure 3. A well-formed continuous film is a prerequisite for the HXNBR latex film to function as a barrier material in the manufacture of dipped goods and to improve the mechanical strength. The formation of latex film can be regarded as a three-stage process: packing, deformation, and gradual coalescence of the latex particles.[20,21] Atomic force microscopy (AFM) has become a very powerful tool in the study of latex film morphology because it can provide high-resolution three-dimensional (3-D) images of the film surface without any sample pretreatment. If the latex particles are over-crosslinked then interdiffusion and the formation of interparticular entanglements would be impossible in the latex film.[22–24] In that case the film surface would be greatly uneven. A small area of 1.174 μm $\times$ 1.174 μm was scanned to observe the HXNBR-99 film surface by AFM. Figure 4(a) shows the 3-D AFM surface image. It can be seen that the film surface is relatively smooth, and the maximum height of the roughness (R_y) value is 140 nm. Figure 4(b) illustrates a tapping-mode AFM height image of a HXNBR latex film, and showing a flat surface. This type of morphology is observed in HXNBR latex film for the first time. Unlike its XNBR counterpart, HXNBR latex is crosslinked. Although the crosslinking of polymer chains is expected to increase the internal friction between the particles, leading to a slower rate of flattening of the film, the film surface becomes flattened eventually. The film surface remains even, an indication that the crosslinking of the latex particles is not excessive. The deformation of the particles, the diffusion of the rubber molecules, and the gradual coalescence of the latex film still occur to form a flat film.

Mechanical Properties of Self-Crosslinking HXNBR Latex Films

The tensile stress–strain curves of the HXNBR films are shown in Figure 5, and some tensile parameters are listed in Table I. For comparison, a compression-molded XNBR film was also studied. It can be seen that HXNBR-90 has better mechanical properties than the other films. With the increase of degree of hydrogenation, the tensile strength first increases and then decreases, the stress at 100% strain increases, and the elongation
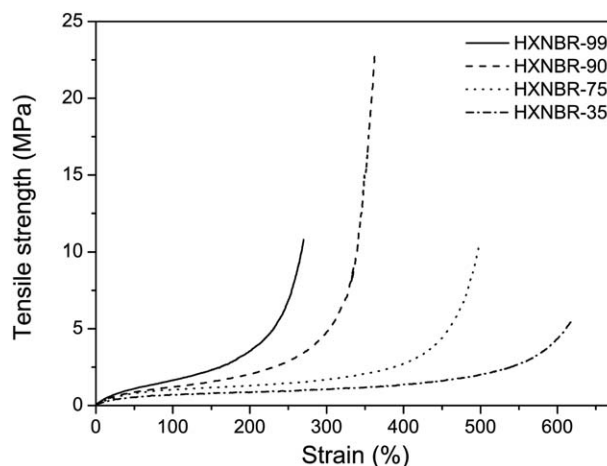

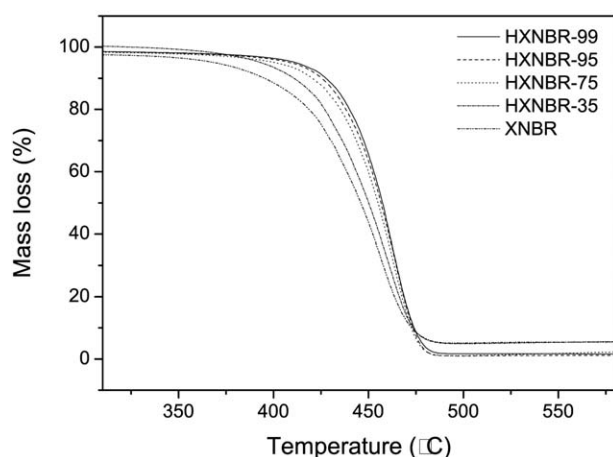**Figure 5.** Tensile stress–strain curves of HXNBR latex films.

Table I. Mechanical Properties of HXNBR Films with Different Degrees of Hydrogenation

Sample designation	Tensile strength (MPa)	Elongation at break (%)	Stress at 100% elongation (MPa)	Stress at 300% elongation (MPa)	Crosslink density (mmol/cm^3)
HXNBR-99	10.7	270	1.64	–	1.46
HXNBR-90	22.4	362	1.21	4.8	0.80
HXNBR-75	10.56	498	1.03	1.69	0.41
HXNBR-35	5.6	619	0.71	1.06	0.22
XNBR	13.0	305	2.85	9.34	0.94

at break decreases. Table I shows that the degree of hydrogenation and crosslinking density increase (or decrease) simultaneously because the crosslinking and hydrogenation of the rubber molecules take place at the same time. It is crosslinking that offers the latex films the excellent physical performance. During the gradual coalescence of the particles, the mechanical strength of the film is determined by the interdiffusion of chain ends and segments and the formation of entanglements across the particle boundaries. The observed reduction of elongation at break is because of the fact that the molecular chain activity is restrained as the crosslink density increases. If the extent of crosslinking is too high, such as in HXNBR-99, the coalescence would be disrupted, leading to low tensile strength. On the contrary, if the extent of crosslinking is too low such as in HXNBR-35, the film will not have good mechanical properties. HXNBR-90 has the optimum crosslink density and therefore the best mechanical properties of the HXNBR films. Furthermore, HXNBR-90 shows higher tensile strength and elongation at break than those of the XNBR compression-molded film at about the same crosslink density.

Thermogravimetric Analysis

The objective of the hydrogenation of diene elastomers is to improve their thermal and oxidative stability. The decomposition temperature obtained by TGA is a measure of the thermal stability. The TGA thermograms of HXNBR at various hydrogenation levels are shown in Figure 6, which indicates that the

degradation occurs in one step for all the samples. The initial decomposition temperature (T_{id}) is determined from the intersection of two tangents at the onset of the decomposition temperature. The maximum decomposition temperature (T_{max}) is obtained from the peaks of the DTG curves. With the decrease in the number of carbon–carbon double bonds, T_{id} and T_{max} of each HXNBR sample increase. This result indicates that hydrogenation can improve the thermal stability of XNBR by converting the weak π bonds in XNBR to stronger C–H σ bonds in HXNBR.

Activation Energy of Degradation

The activation energy of degradation of a latex film was determined by applying the Coats–Redfern equation:

$$\log\left[-\frac{\log(1-\alpha)}{T^2}\right]=\log\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{2.303RT} \quad (9)$$

where α is the fractional mass loss at time t, T is the absolute temperature, A is the pre-exponential factor, R is the universal gas constant, β is the heating rate, and E is the activation energy. A plot of $\log[-\log(1-\alpha)/T^2]$ vs $1/T$ gives a straight line with the slope equal to $-E/(2.303R)$ and the y-intercept equal to $\log[AR/(\beta E)(1-2RT/E)]$. The kinetics of the thermal decomposition of rubber from latex has been extensively studied by Stephen et al.[25] using the Coats–Redfern equation.

The Coats–Redfern plots for HXNBR-99, HXNBR-90, HXNBR-75, HXNBR-35, and the XNBR films are given in Figure 7. The
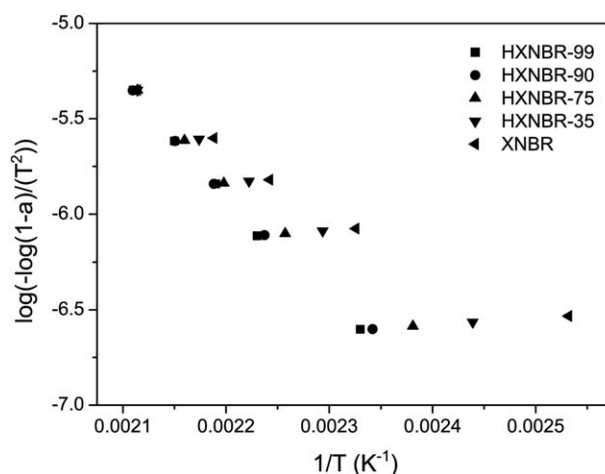

Figure 6. TGA thermograms of HXNBR latex films with different degrees of hydrogenation.

Figure 7. Coats-Redfern plot for HXNBR latex films with different degrees of hydrogenation.

Table II. Degradation Temperature and Activation Energy for Degradation (Obtained from Coats-Redfern Equation) of HXNBR Latex Films

Sample	Degradation temperature (°C)					Activation energy (kJ/mol)
	$T_{10\%}$	$T_{30\%}$	$T_{50\%}$	$T_{70\%}$	$T_{90\%}$	
HXNBR-99	428	449	457	465	473	107.0
HXNBR-90	427	447	457	465	474	102.2
HXNBR-75	420	443	455	463	473	87.6
HXNBR-35	410	436	450	460	473	71.2
XNBR	395	430	446	457	473	53.8

Figure 8. Thermal stability of HXNBR films with different degrees of hydrogenation.

activation energy of degradation was calculated from the slope of the Coats–Redfern plot, and the results are given in Table II. HXNBR-99 shows the highest activation energy of degradation of all the samples. The C–C bonds formed during hydrogenation and crosslinking are less flexible and have higher bond energy than C=C. As the C=C content decreases, the activation energy increases because of the higher thermal stability of HXNBR.

Oxidation Resistance

The thermal stability of rubber should be considered as the ability of the rubber to maintain its required properties at a desired temperature. It is important to maintain the physical properties of latex goods during service. The latex film may undergo chain scission reaction as well as crosslinking reaction during service life at elevated temperatures. Therefore, the information about the ageing characteristics of HXNBR latex films is critical for determining the service life and the application level of latex goods.

The thermal ageing results for HXNBR-99, HXNBR-90, and HXNBR-75 are listed in Table III. For comparison, the corresponding results for a XNBR compression-molded film are also included. The thermal stability in terms of the retention of properties after aging can be discussed with respect to the hydrogenation level and the crosslink density. It can be seen from Figure 8 that all of the films except HXNBR-99 show a reduction in tensile strength after aging, which indicates that thermal degradation occurred during aging. The XNBR film shows the lowest retention of tensile strength (58%) and elongation at break (66%) because of the crosslinking and main chain scission at high temperatures. In addition, the tensile strength
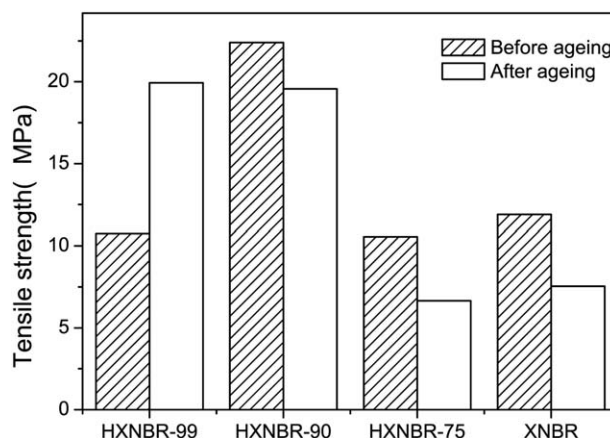
of HXNBR-99 is higher after aging than before aging, probably because the high crosslink density of HXNBR-99 was reduced to an appropriate value by main chain scission during aging. The retention of tensile strength and retention of elongation at break after thermal aging of HXNBR-90 are 87% and 85%, respectively, and higher than those of the pure XNBR sample, as hydrogenation can convert the weak π bond in XNBR to the stronger C–H σ bonds in HXNBR. Hence, this result indicates that HXNBR-90 was more resistant to heat than HXNBR-99, HXNBR-75, and the XNBR samples and confirms that HXNBR-90 has better oxidation resistance than the XNBR sample.

CONCLUSIONS

A new type of self-crosslinking HXNBR latex film with excellent physical properties and heat and oxidation resistances was prepared. During the hydrogenation, the degree of hydrogenation and crosslink density increased simultaneously. HXNBR latex could form a continuous film with good cohesive properties from self-crosslinking particles without any additional crosslinking agents. The HXNBR-90 latex film showed higher tensile strength and elongation at break than a XNBR compression-molded film. Moreover, HXNBR-90 had better heat resistance and oxidation resistance than the XNBR film because of a reduction in the amount of double bonds in the backbone chain. We think HXNBR latex, which has better processability than XNBR latex, can be utilized as latex films in applications such as gloves.

Table III. Thermal Stability of HXNBR Films at Various Degrees of Hydrogenation

Sample	Tensile strength (MPa)			Elongation at break (%)		
	Before aging	After aging	Retention[a] (%)	Before aging	After aging	Retention[a] (%)
HXNBR-99	10.7	19.94	186	270	254	94
HXNBR-90	22.4	19.57	87	362	307	85
HXNBR-75	10.56	6.65	62	498	294	59
XNBR	13.0	7.54	58	305	203	66

[a] Retention = (property after aging/property before aging) × 100.

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