

Hydrogenated Natural Rubber from Different Types of Preserved Latex

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One of the major disadvantages of natural rubber (NR) is poor ozone and ageing resistance besides poor oil and chemical resistance. These weaknesses are partly caused by the double bonds present in the rubber molecules. However the number of double bonds can be reduced by hydrogenation. This paper discusses the effect of preservation systems of NR latex used as the starting materials and also the effect of hydrogen peroxide on the efficiency of the hydrogenation reaction. The hydrogenated NR was prepared by reacting NR latex with hydrazine hydrate and hydrogen peroxide. The rubber was characterised by using proton Nuclear Magnetic Resonance (NMR). The results showed that the hydrogenation level is significantly affected by the different preservation systems and the concentration of hydrogen peroxide. The optimum level of hydrogen peroxide concentration was found to be in the range of 20-30% for all types of preservation systems. The use of field latex as a starting material achieved a much higher hydrogenation level (67%) compared to other types of preserved latex examined.

Keywords: Natural rubber; hydrogenation; field latex

Chemical modification of natural rubber is carried out in order to improve the chemical and mechanical properties of NR or to introduce desirable functional groups in NR. Hydrogenated NR (HNR) has been shown to have improved thermal and ozone resistance¹. There has been limited interest in the past to produce HNR because the process was complex and uneconomical². Recently, there have been attempts by researchers to improve the quality of natural rubber such that it can withstand extreme conditions of thermal oxidation and ozone degradation by using a simple hydrogenation method³.

A successful hydrogenation process saturates the double bonds in the polyisoprene molecules. The molecular modification of the polymer can be characterised by NMR spectroscopy. In this study, HNR was prepared by the diimide reaction whereby hydrazine hydrate was reacted with hydrogen peroxide^{4,5}. Latexes with different stabilisation systems such as low ammonia-tetramethyl thiuram disulphide/zinc oxide preserved latex (LATZ), high ammonia (HA), deproteinised natural rubber latex (DPNRL) and field natural rubber latex were used as the starting materials.

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EXPERIMENTAL

Materials

The LATZ and HA latices were obtained from the Malaysian Rubber Development Corporation (MARDEC) while the field latex came from the Malaysian Rubber Board plantation. Hydrogen peroxide (50%) was supplied by CCM Chemicals Sdn Bhd (Industrial Grade), hydrazine hydrate (99%) by BDH Chemical, Alcalase (100%) by Science Teknik and sodium dodecyl sulfate (technical grade) by Distech Enterprise.

Hydrogenating Method

Latex and sodium dodecyl sulfate (10% solution) were added together in a 2L round bottom flask and the mixture diluted to 30% dry rubber content with distilled water. Hydrazine hydrate and hydrogen peroxide were added to the latex simultaneously drop wise. The latex was kept at a constant temperature of 70°C and continuously stirred until all the chemicals were added. The slow rate of addition of hydrazine hydrate and hydrogen peroxide was to control foaming and the high temperature exotherm.

Deprotenised Natural Rubber Latex (DPNRL) Preparation

DPNRL was prepared using field latex. Field latex, sodium dodecyl sulfate (10% solution) and Alcalase (10% solution) were added together in a 5L beaker and the mixture diluted to 25% DRC. It was incubated for 72 hours at ambient temperature and then centrifuged to give DPNRL 1 and a portion of DPNRL 1 was then diluted to 25% DRC and recentrifuged to give DPNRL 2.

Spectral Analysis

Proton NMR spectra of HNR cast film samples were obtained using a Bruker AMX 400 Wide Bore NMR Spectrometer (^1H = 400 MHz) with tetramethylsilane (TMS, δ = 0.0 p.p.m.) as the internal standard. Deuterated chloroform solvent, CDCl_3 (Aldrich 99.8%) was used as solvent. TGA analysis was carried out using TGA 7, Perkin Elmer.

Gel Content

About 0.2 g finely cut sample was weighed in a stoppered bottle, 100 mL of toluene (AR Grade) was added and kept for 48 h with occasional shaking. The content was then sieved through 100 mesh cone-shape steel gauze. The residue contained wet macro gel whilst the filtrate contained sol and micro gel. The wet weight of the residue together with the sieve was measured and dried in an air circulated oven at 100°C for 16–24 h to a constant weight. The weight of the dry rubber over weight of the sample times hundred gives the percentage macro gel.

Nitrogen Content Determination

Nitrogen content was determined using a semi-micro Kjeldahl procedure. The cast latex film was oxidised by heating with a catalyst and concentrated sulphuric acid, thereby converting nitrogen compounds into ammonium hydrogen sulphate. After making the solution alkaline, the ammonia was removed by steam distillation. The liberated ammonia was absorbed in boric acid solution and titrated with acid.

RESULTS AND DISCUSSION

The proton NMR spectra (*Figures 1 and 2*) show the NR and partially hydrogenated NR

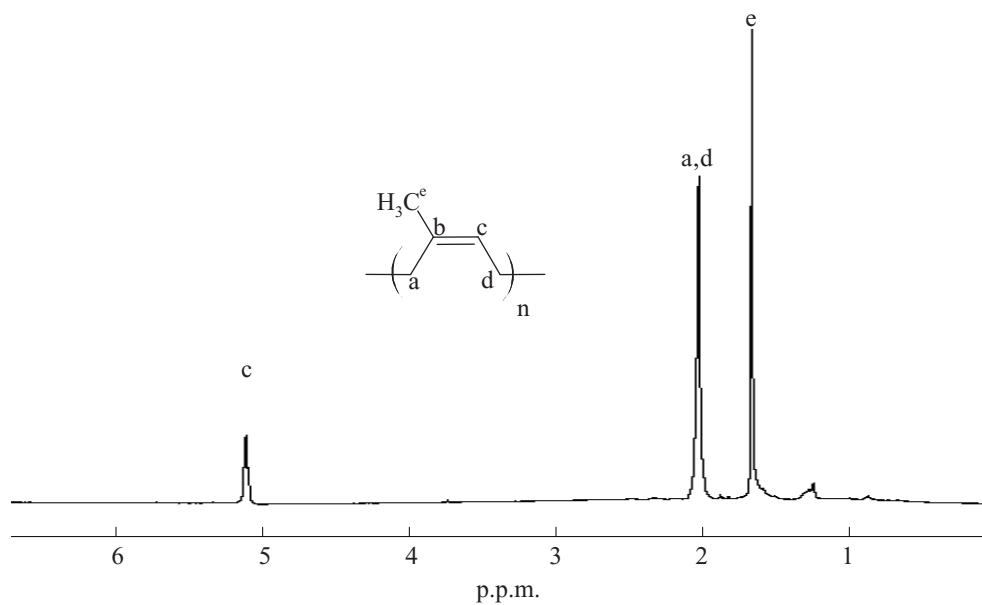


Figure 1. NMR Spectra of NR.

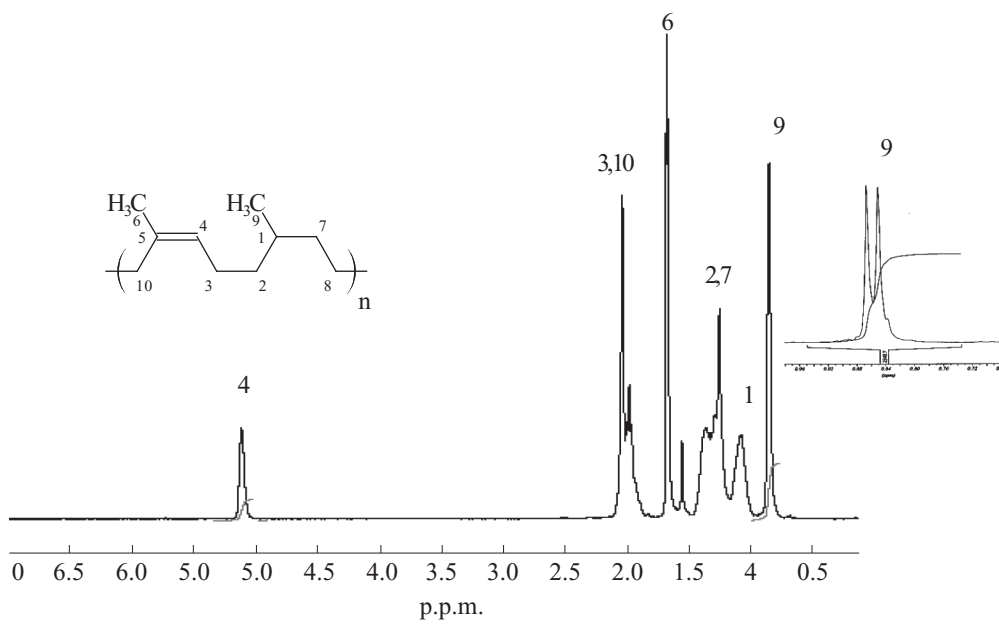


Figure 2. NMR Spectra of 45% Hydrogenated NR.

signals in CDCl_3 ; proton NMR $\delta = 1.6$ p.p.m. ($-\text{CH}_3$, 3H); $\delta = 2.1$ p.p.m. ($-\text{CH}_2-\text{C}=\text{C}$, 4H) and $\delta = 5.1$ p.p.m. (vinyl proton). The signal due to hydrogenation of NR was observed at $\delta = 0.8$ p.p.m. The ($-\text{CH}_3$, 3H) signals showed as duplet due to the addition of proton at the neighbouring carbon (*Figure 2*) where $\delta = 1.6$ p.p.m. ($-\text{CH}_2-\text{C}=\text{C}$, 4H) and $\delta = 1.1$ p.p.m. (tertiary C-H)³. The degree of hydrogenation for each sample was calculated from the peak area at 5.1 p.p.m. and 0.8 p.p.m. and the summation of peak areas between 1.0 p.p.m. and 2.2 p.p.m.⁶⁻⁸.

TGA results (*Figure 3*) also shows that hydrogenation has occurred and the thermal decomposition shifted from 388.15°C (NR) to 400.3°C (HNR 29%) and 405.65°C (HNR 31%).

Hydrogen peroxide concentration is very important in order to achieve high hydrogenation level of natural rubber, as shown in *Figure 4*. The efficiency of hydrogenation was observed to be dependent upon the type of latex preservation used. Too high or too low hydrogen peroxide concentration resulted in

inefficient hydrogenation reaction with a low hydrogenation level. Very high concentration of hydrogen peroxide also contributes to difficulty in control of temperature rise and hence develops degradation of rubber⁹. Whereas, low peroxide concentration will contribute to very dilute latex concentration which deter the coagulation process. *Figure 4* shows that the optimum hydrogen peroxide concentration for hydrogenation is 23% weight on rubber when using LATZ latex and 30% weight on rubber when using HA and field latex. Data obtained at zero percent hydrogen peroxide were for samples prepared using all the reagents but without the hydrogen peroxide.

Gel contents of HNR prepared from different types of preserved latices are shown in *Figure 5*. It was expected that the higher the hydrogen peroxide concentration, the higher the percentage of gel content¹⁰. This is because hydrogen peroxide can contribute to crosslinking at certain temperatures¹¹. The gel content results for HNR prepared using field latex was unexpected with a maximum gel content of 80% when using 10% w/w level of hydrogen peroxide.

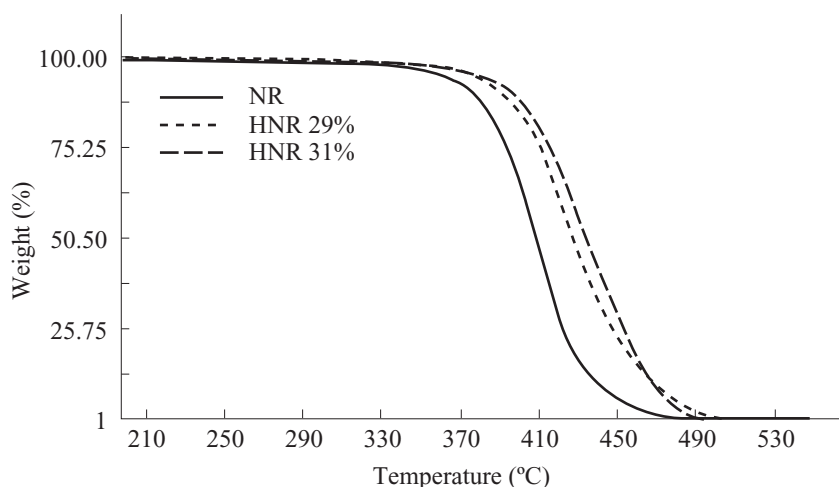


Figure 3. TGA spectra of NR and HNR.

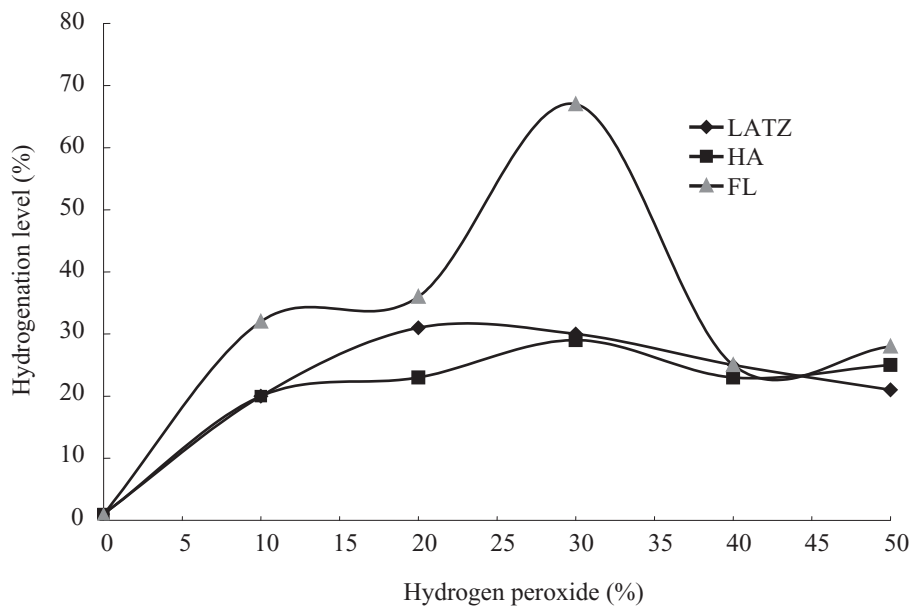


Figure 4. Effect of hydrogen peroxide concentration on hydrogenation level of different types of latices.

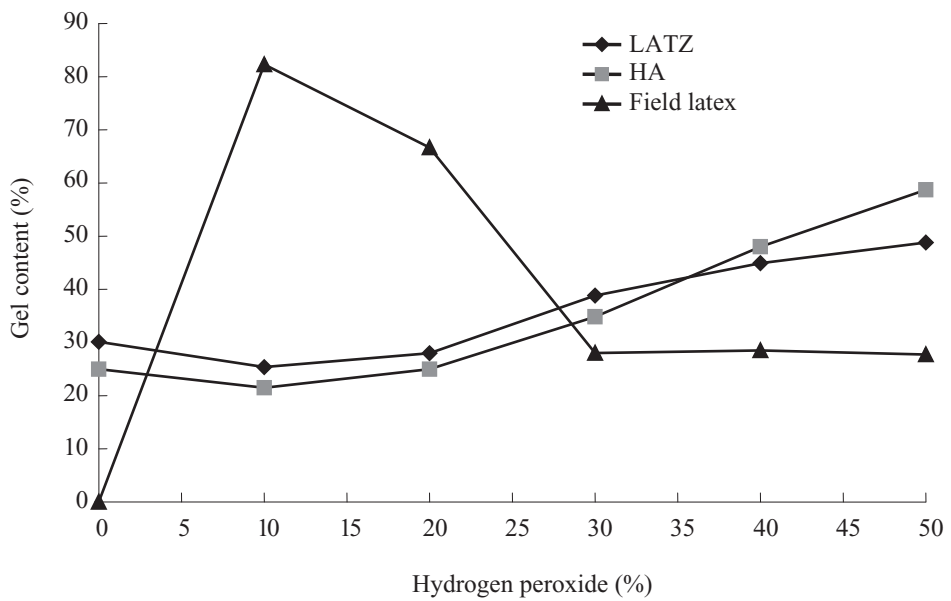


Figure 5. Gel content of HNR using different types of latices with peroxide concentration.

Figure 6 shows the hydrogenation level of natural rubber from different types of preserved latices. The major differences between LATZ, HA and field latex are their non-rubber contents and preservation systems. The high hydrogenation level achieved by using field latex may possibly be attributed to the presence of relatively high levels of absorbed proteins and metal ions¹². These could facilitate the transfer of reagents into the latex particle and may enhance the hydrogenation reaction. The protein content of the latices used in this study in descending order; Field latex > LATZ > HA > DPNRL 1 > DPNRL 2 are indicated by their nitrogen content in Table 1.

TABLE 1. NITROGEN CONTENT OF NR LATICES

Types of latices	Nitrogen content (%)
Field latex	0.54
LATZ	0.30
HA	0.28
DPNRL 1	0.10
DPNRL 2	0.08

Figure 6 shows that the level of hydrogenation changes according to the types of latices used and the hydrogenation level in ascending order; HA (29%) < LATZ (31%) < DPNRL 2 (30%) < DPNRL 1 (45%) < Field latex (67%). Apart from the role of absorbed proteins as explained earlier, the relative chemical stability of the latices probably also influences hydrogenation efficiency. The fresh field latex is probably chemically more stable than the rest of the latices because of higher level of absorbed proteins and phospholipids¹. The DPNRL 1 is more stable than DPNRL 2, HA and LATZ latices because it contains relatively high amount of sodium dodecyl sulphate.

CONCLUSION

Hydrogen peroxide concentration affects the efficiency of hydrogenation significantly and the optimum concentration depending upon the type of latices is in the range 20–30%. Field latex is very suitable for the hydrogenation reaction using hydrazine hydrate and hydrogen peroxide. The reasons for the differences in the hydrogenation efficiency of HA, LATZ,

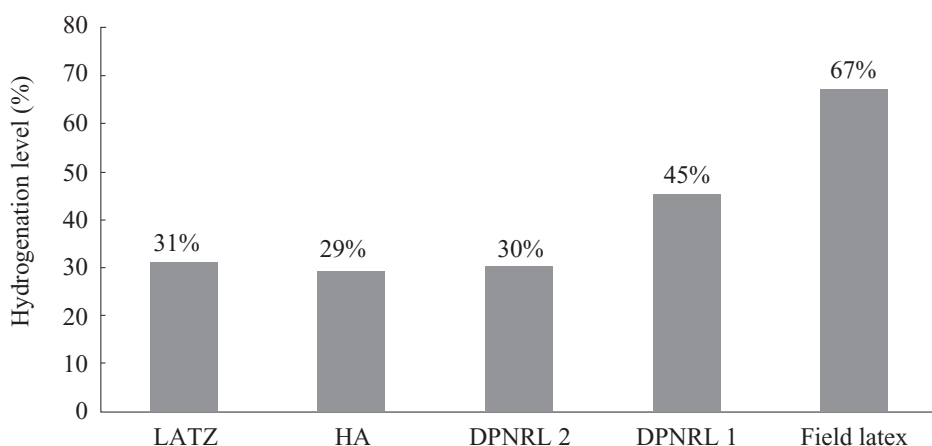


Figure 6. Hydrogenation level of natural rubber using different type of latices.

DPNRL 1, DPNRL 2 and field latices are not clear, but the role of non-rubbers and the chemical stability of the latices may be important.

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