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THE INFLUENCE OF TEMPERATURE AND REACTION TIME IN THE DEGRADATION OF NATURAL RUBBER LATEX

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Abstract

Liquid natural rubber (LNR /LENR) should be considered as a new material instead of a new type of rubber though they have the same configuration as the rubber used. In this work, thermal degradation of natural rubber latex was carried out to obtain LNR/LENR by varying the reaction time at different temperatures. The degraded polymers were characterized structurally using FTIR and NMR spectroscopies and the average molecular weights were determined by membrane-osmometry and viscometry.

Abstrak

Getah asli cecair (LNR/LENR) harus dianggap sebagai suatu bahan baru dan bukan jenis getah baru walaupun mempunyai konfigurasi yang sama seperti getah asli yang digunakan. Dalam kajian ini, degradasi terma terhadap getah asli latek dijalankan untuk memperolehi LNR/LENR dengan masa tindak balas dan suhu yang berbeza. Pengkelasan struktur bagi polimer degradasi diperolehi dengan menggunakan kaedah spektrometer FTIR dan NMR manakala berat purata molekul ditentukan oleh osmometer membran dan viskometer.

Introduction

There are many methods of preparing epoxidised natural rubber (ENR) in latex. The modification of NR and other unsaturated polymers by epoxidation were known to increase solvent resistance and improve wear resistance and other mechanical properties. It is well documented in the literature [1,2] that during the epoxidation of NR, ring-opening occurred.

In general, degradation of NR can be achieved by mechanical, chemical or thermal means [1,3,4]. *Brose et al* [4] demonstrated the degradation of the natural rubber using the phenylhydrazine/O_2 couple under the influence of a redox system. The intensity and the extent of the chain-scissoring reaction depend upon temperature, reaction time and concentration of the degradation agent.

By varying reaction conditions and addition of certain chemicals, different degraded NR products can be obtained [1,3,4,5,7]. Factors which influence scissoring of NR chains and reaction at C=C bonds need to be considered in this degradation reaction [5,7,8,9]. In earlier studies[2], degradation of NR carried out at 65^{o}C using peroxide acid has resulted in ring-opened products. In our study, natural rubber latex degradation was carried out under similar conditions but different temperatures and reaction times in the presence of sodium nitrite.

Experimental

Materials

High ammonia NR latex concentrate [60% dry rubber content] and Vulcastab LW were supplied by Lembaga Getah Malaysia (LGM) Sungai Buluh, Malaysia. Sodium nitrite and hydrogen peroxide (30%) were purchased from R&M Chemical. Formic acid (99%) was purchased from Ajax Chemical.

Preparation of materials

NR latex was stabilised by Vulcastab under continuous stirring. The NR latex was acidified by formic acid to the required pH followed by successive treatment with 30% aqueous H_2O_2 and 10% solution of $NaNO_2$. The reaction was performed at temperatures of 60^{o}C and 70^{o}C. The product obtained was washed with methanol and dried in a vacuum oven.

Analysis of products

Products were analysed by ^{1}H-NMR (Jeol model JNM-LA 400 spectrometer) with $CDCl_3$ as solvent and the FTIR spectra were recorded on Perkin-Elmer 820 IR spectrometer, with a resolution of 4 cm^{-1} by direct casting on a NaCl cell. Intrinsic viscosity [?] of the products was determined using an Ubbelhode viscometer of 0.1g/ dL in toluene solution at 30°C. Number-average molecular weight was obtained from membrane osmometer (Gonatex Osmomat 090) at 45°C.

Results and discussion

The degraded NR product obtained in all cases was a light yellow viscous liquid with sticky elastomeric character. Figures 1b and 1c, showed the presence of the hydroxyl group as indicated by the broad peak in the region between 3400-3500 cm^{-1} and the absorption peak of epoxide ring at 873 cm^{-1}, under both temperatures (60°C and 70°C) at various reaction times; while such peaks were absent in NR, Figure 1a. Similar observations were observed in ENR [10]. This shows that the product has both epoxy and hydroxyl groups present, indicating that the C=C bonds have undergone epoxidation and hydrolysis.

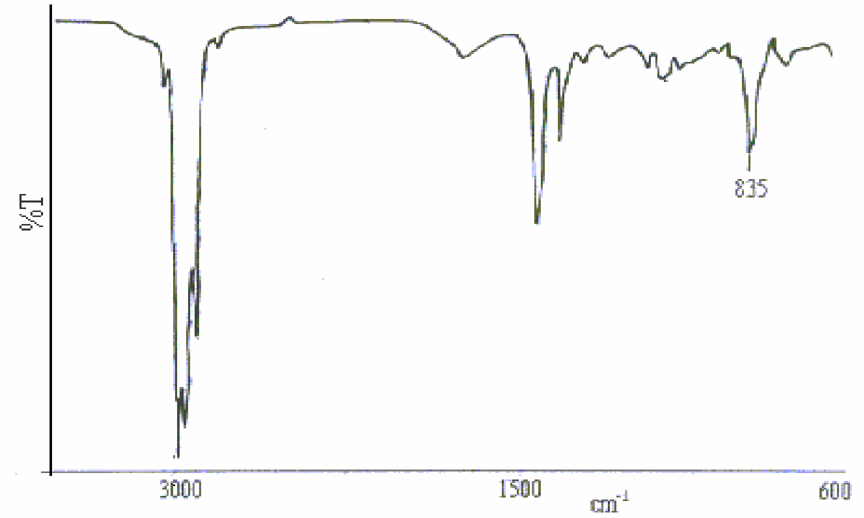

Figure 1a. NR – before degradation

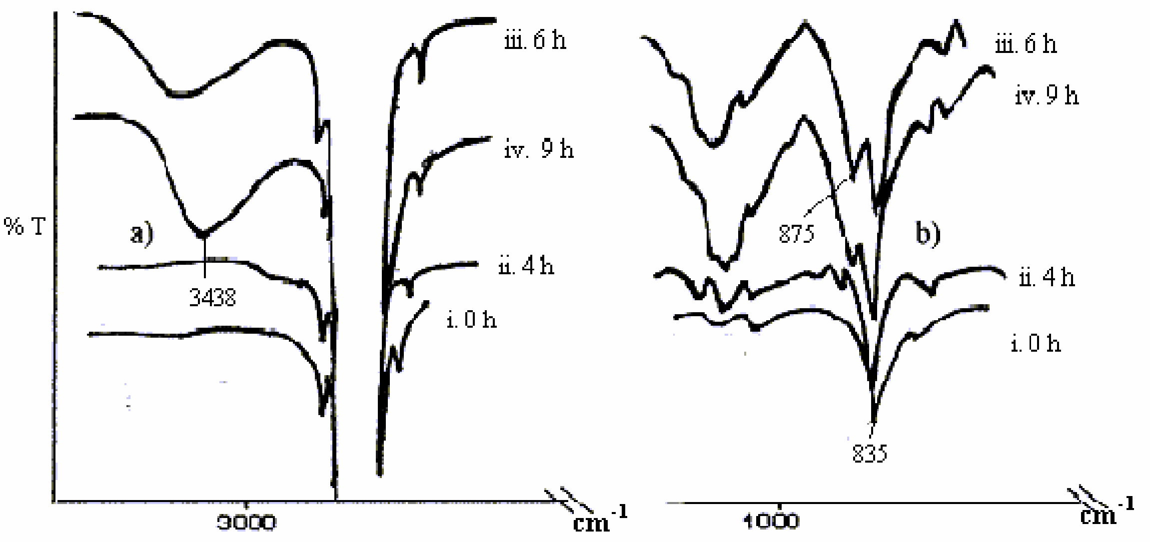

Figure 1b. IR bands showing the hydroxyl groups (a) and the epoxy groups (b) present in the LENR product at 60°C

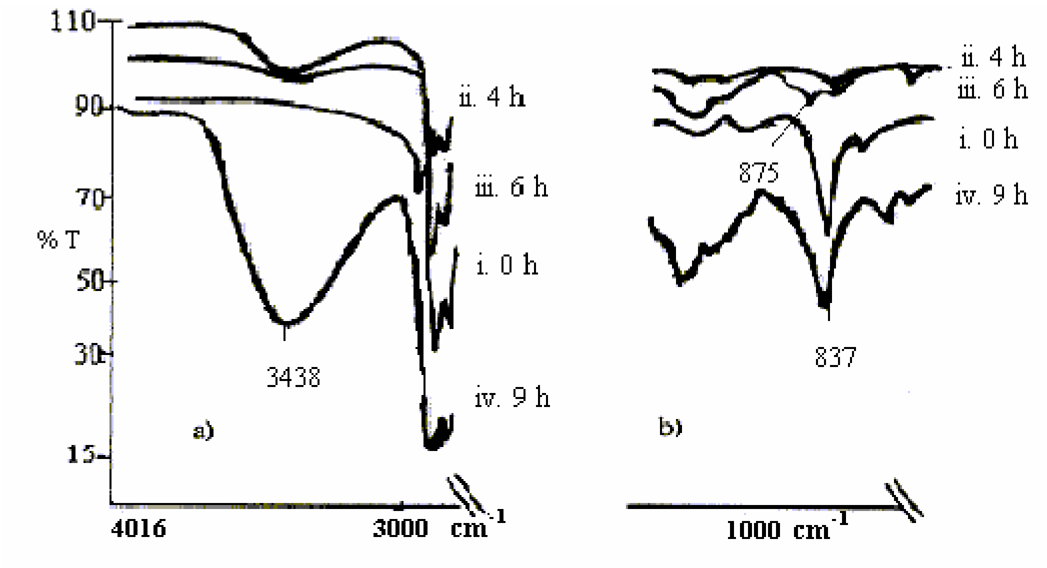

Figure 1c. IR bands showing the hydroxyl groups (a) and epoxy groups (b) present in the LENR product at 70ºC

The absorption peak at 3400 cm^{-1} region at high temperature (70^{o}C) is broader than that at low temperature (60^{o}C). This indicates that epoxide group has further hydrolyze to form the ring-opened product.

The presence of hydroxyl and epoxide groups in the degraded products is further confirmed from the ^{1}H-NMR spectrum. As shown in Figure 2a, methyl, methine and methylene protons of isoprene unit in ^{1}H-NMR spectrum gave rise to signals at 1.6, 2.1 and 5.1 ppm, respectively. After epoxidation and hydrolysis of NR (Figure 2b), two other signals appeared at 2.7 and 1.2 ppm, which correspond to methylene and methyl protons of the resulting epoxy group and another signal corresponding to hydroxyl group appeared at 3.7 ppm .

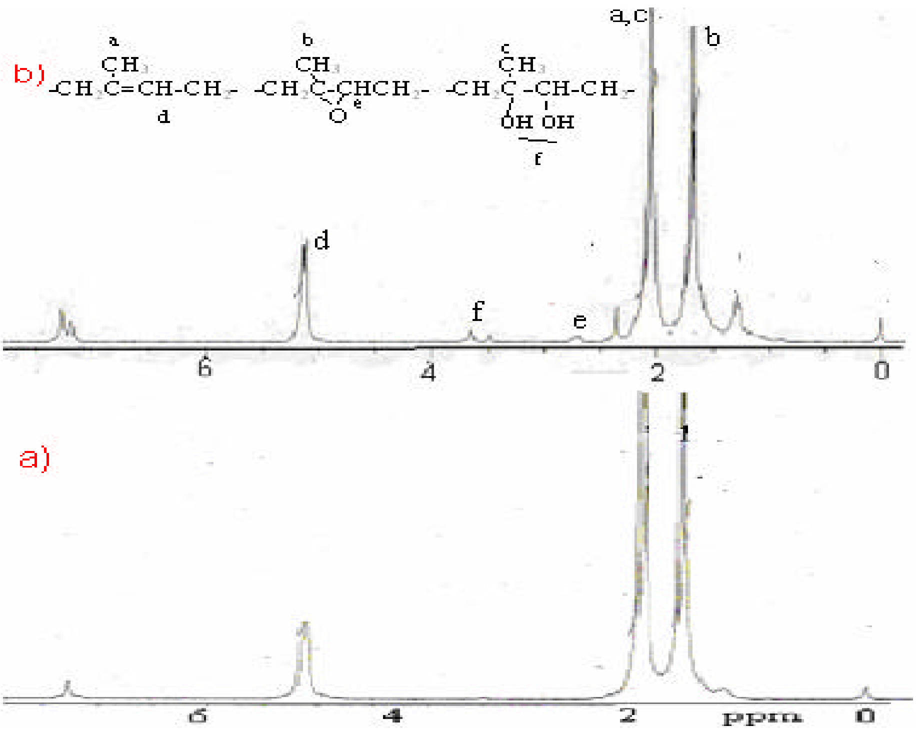

Figure 2. ^{1}H-NMR spectrum of NR before degradation (a) and after 9 hours degradation (b)

The molecular weight of this liquid epoxidised natural rubber (LENR) was determined by viscometry and membrane osmometer (Tables 1 and 2). The higher temperature and higher reaction time give rise to products of lower intrinsic viscosity. From Figures 3 and 4, the longer the reaction time, the lower will be the molecular weight of the products formed. Prolonged reaction times allow more degradation chain into shorter chain segments. As for temperature effect, similar trends in intrinsic viscosity and molecular weight were obtained for both temperatures (60°C and 70°C). This indicates that degradation of NR increases with temperature under the employed conditions.

Table 1. Intrinsic viscosity results of LENR obtained at different reaction times

Reaction time (hours)	[?] (ml /g) 60°C	[?] (ml /g) 70°C
2	3.124	1.884
4	2.181	0.826
6	0.787	0.338
7	0.656	0.309
9	0.408	0.163

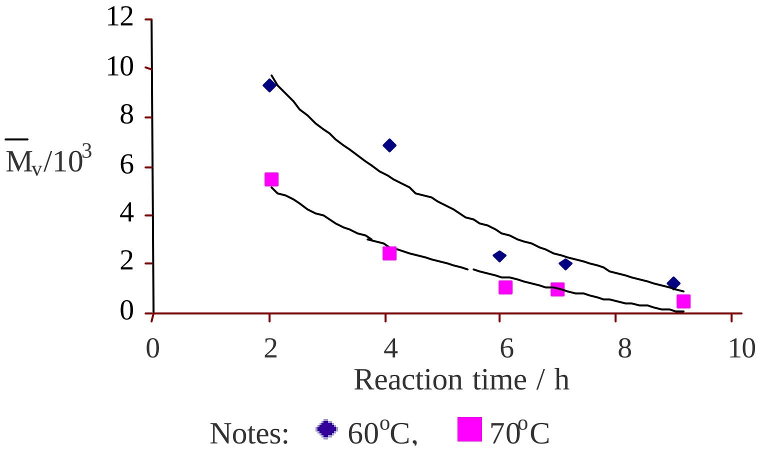

Figure 3. Viscosity average molecular weight $(\overline{M}_v)$ versus reaction times

Table 2. Number average molecular weight (M_n) of LENR obtained at different reaction times.

Reaction time (hour)	$\overline{M}_n$ (10^4)	
	60°C	70°C
2	10.436	9.420
4	9.875	5.260
6	6.654	3.025
7	5.693	2.030
9	3.217	1.717

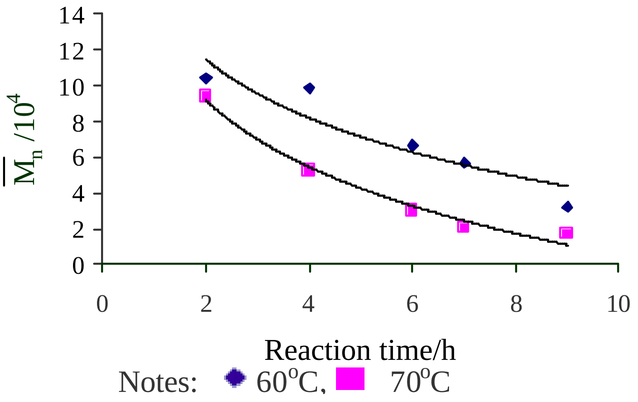

Figure 4. Number average molecular weight (M_n) versus reaction times

Temperature dependent for systems of the same H_2O_2/isoprene ratio and $NaNO_2$ content showed that in-situ epoxidation was highly favorable at high temperature (70°C), where as at low temperature (60°C), epoxidation proceeded at a low rate (Figures 1b and 1c). This is probably due to the low rate of formation of performic acid at low temperature, leading to decrease in the rate of epoxidation, thus less epoxidised products are formed.

In the presence of performic acid and a degradation agent ($NaNO_2$) prepared in-situ, two parallel reactions occur, i.e. epoxidation and chain scissoring process. When the degradation agent was introduced simultaneously with hydrogen peroxide (H_2O_2), chain-scissoring reaction can proceed together with epoxidation. The reaction product has low molecular weight as shown from the intrinsic viscosity measurements. In addition, the product has -OH group, indicating hydrolysis has also taken place. The extent of epoxidation and hydrolysis depend on both reaction time and reaction temperature (as seen from above results). Long reaction time and high temperature results in product of low molecular weight.

Conclusion

Under the presence of performic acid and sodium nitrite prepared in-situ, natural rubber latex degrades to lower molecular weight product having both epoxyl and hydroxyl group. The rate of degradation depends on both temperature and reaction time.

Acknowledgements

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