

Some Properties of Epoxidised Deproteinised Natural Rubber

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Some properties of epoxidised natural rubber (ENR) and epoxidised deproteinised natural rubber (EDPNR) were examined. It was found that DPNR latex reacts with peracetic acid in a similar manner as NR latex. Differences in the properties of modified rubbers are due to differences in the protein level of the raw materials used. Low gel content property of DPNR was also observed in the corresponding modified rubber indicating that the processability of EDPNR was better than that of ENR. Epoxidation of rubber lattices does not cause much change in the non-rubber components of the rubbers.

Natural rubber is a useful 'green' raw material which has been widely used for more than a century. Chemical modification of natural rubber has been an area of interest for many rubber chemists because modified natural rubbers could have many potential commercial applications. Epoxidised natural rubber (ENR) is one such rubber which gives several improved properties in vulcanisates such as better oil resistance, resilience and lower gas permeation than those of natural rubber¹. However, epoxidation of natural rubber leads to an increase in the gel content and hence reduces the processability of modified rubber¹. In this study, the effects of epoxidation on some properties of deproteinised natural rubber (DPNR) such as gel content, density, ash content, acetone extract and glass transition temperature were investigated in comparison

with that of ENR obtained from the same source.

MATERIALS AND METHODS

High ammonia (HA) latex, of dry rubber content 60%, prepared from fresh latex, was used for the preparation of ENR. The same source of latex was processed into DPNR latex of 60% dry rubber content.

The method of producing DPNR has been reported elsewhere². This latex was then used to produce epoxidised DPNR.

Peracetic acid was freshly prepared by adding hydrogen peroxide to acetic anhydride by 40°C. The concentration of this acid was standardised by the method described by Greenspan and Mackeller³.

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Reaction

Samples of NR latex were diluted with the same amount of water and stabilised with non-ionic surfactant, *Vulcastab LW* (from ICI Co., 1% w/v for HA latex and 0.5% w/v for DPNR latex). The pH of the diluted latices was adjusted to 6.0 by the addition of acetic acid. Appropriate amounts of freshly prepared peracetic acid were slowly added to the stirred latices which had been pre-cooled to 10°C. The mixtures were then allowed to react for 3 h at the same temperature. Upon completion of the reaction, the pH was adjusted to 7.1 and the rubber was coagulated by adding the latices to excess methanol with stirring. The rubbers were soaked overnight in water and dried at room temperature under reduced pressure.

Characterisation

For gel content analysis, about 0.5 g of each rubber was allowed to dissolve in 250 ml toluene without agitation in the dark for two weeks. The gel fraction was isolated by centrifugation at 11 000 r.p.m. (17 000 g) and dried at room temperature under reduced pressure to constant weight. The density of each rubber was measured by floatation method using methanol/water as the medium. Acetone extraction was carried out by soxhlet extraction of a 6 g rubber sample with acetone for 16 h in nitrogen atmosphere. Ash content was quantified by ashing 2 g of a rubber sample at 550°C for 8 h. ¹H-NMR measurements were performed by using 1% deuterated chloroform solutions of the rubber with TMS as an internal standard with a JEOL FX-100 NMR spectrometer. The sweep width was 1200 Hz, pulse delay 2.0 seconds and acquisition time 3.0 seconds. The peak areas were used to calculate epoxide content of the rubber by using the following equation:

$$\% \text{ Epoxide} = \frac{A_{2.7 \text{ p.p.m.}}}{A_{5.2 \text{ p.p.m.}} + A_{2.7 \text{ p.p.m.}}} \quad \dots 1$$

where *A* is the area of the peak concerned.

The glass transition temperature (*T_g*) of each rubber was determined by a Seiko Instruments DSC 220 differential scanning calorimeter (DSC). Approximately 10 mg of a rubber sample, encapsulated in an aluminium sample pan, was heated to 80°C and quench-cooled by immersing the sample into liquid nitrogen. The sample was then inserted into the DSC at -140°C and scanned up to 50°C at a rate of 10°C/min. The mid-point value was used as *T_g* of the sample.

RESULTS AND DISCUSSION

Reaction of NR Latex and DPNR Latex with Peracetic Acid

The epoxidation reaction of NR latex with peracetic acid has been reported to be essentially quantitative. For reactions below ambient temperature and in the absence of strong acid catalysis, the side reactions are negligible^{1,4}. This is also found to be the case for DPNR latex in the present study, as shown in *Figure 1*, where no signals due to ring-opened products such as furan and diol (3 p.p.m. – 4 p.p.m.) were detected by ¹H-NMR⁵. The epoxide contents of the modified NR and DPNR were determined by ¹H-NMR and summarised in *Table 1*.

The anticipated epoxide content was obtained based on the amount of standardised peracetic acid added to the latex, assuming a 100% conversion. Although a greater accuracy

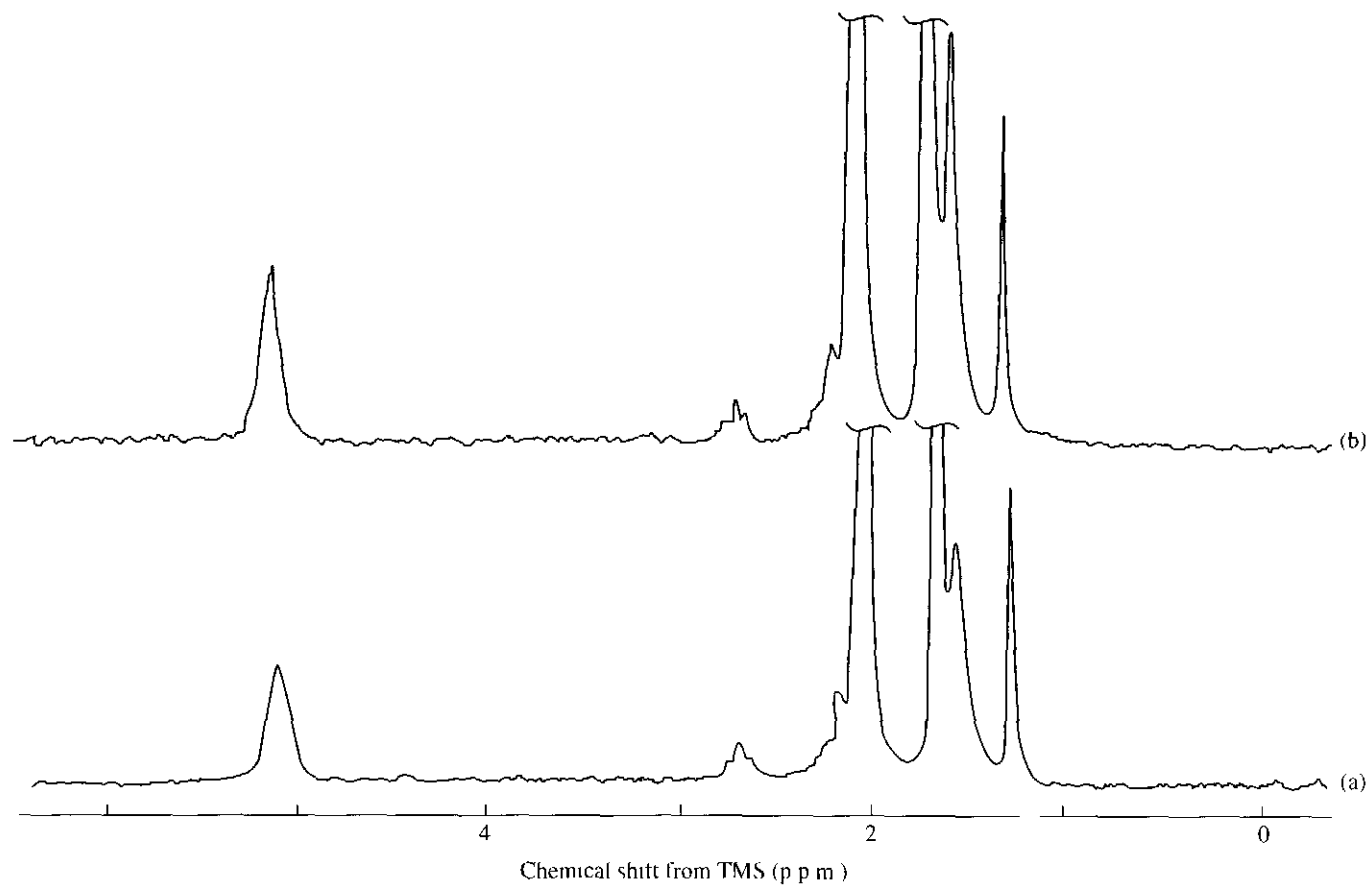


Figure 1 ^1H NMR spectra of (a) 20% epoxidised natural rubber and (b) 20% epoxidised deproteinised natural rubber

TABLE 1 EPOXIDE CONTENT OF MODIFIED NR AND DPNR

Sample		Epoxide (anticipated) ^a (% mol)	Epoxide (¹ H-NMR) (% mol)
1	ENR	13	11.0
2	EDPNR	13	11.5
3	ENR	25	21.8
4	EDPNR	25	21.6
5	ENR	50	48.8
6	EDPNR	50	51.1

^aCalculated from the amount of peracetic acid added

of measuring the epoxide content could be obtained by hydrogen bromide (HBr) titration, the presence of gel in the sample, as shown in the later part of this paper, makes this difficult to be achieved. Data in *Table 1* indicate that NR and DPNR latices each gave a similar epoxide content, when the same amount of peracetic acid was added to the latex. This implies that the presence of proteins in natural rubber does not interfere with the formation of epoxide in latices.

These results, however, do not show the rate of epoxidation of each latex. Thus, the formation of epoxide, at different time intervals, was investigated. *Figure 2* shows that both NR and DPNR reacted at similar rates with peracetic acid, and that no induction period was observed. This probably implies that the size of peracetic acid molecule is small enough to diffuse through the protein layer surrounding the rubber particles as soon as it is added to the latex.

Gel and Nitrogen Content of ENR and EDPNR

The gel content of natural rubber has been reported to increase after epoxidation with

peracetic acid⁶. This was also observed in the present study as shown in *Figure 3*. In the case of EDPNR, the increase in the gel content is less significant than in the case of ENR. This indicates that proteins play an important role in the gel formation in epoxidised natural rubber. This trend has also been observed in the case of natural rubber containing different amounts of protein². For the level of epoxidation investigated, a small decrease in the protein content of the modified natural rubber with the level of modification was observed as indicated in *Table 2*. As substantial amounts of protein were still present in the modified NR as compared to DPNR, the increase in the gel content of ENR, therefore, is due to the interaction between epoxide groups and rubber proteins.

Gel in ENR has been reported to reduce the processability of the modified rubber. In this study, EDPNR was found to contain lower amounts of gel than ENR, implying that the processability of EDPNR is better than that of ENR.

Ash Content

The ash is the mineral component of natural rubber, which is held by polar non-rubber

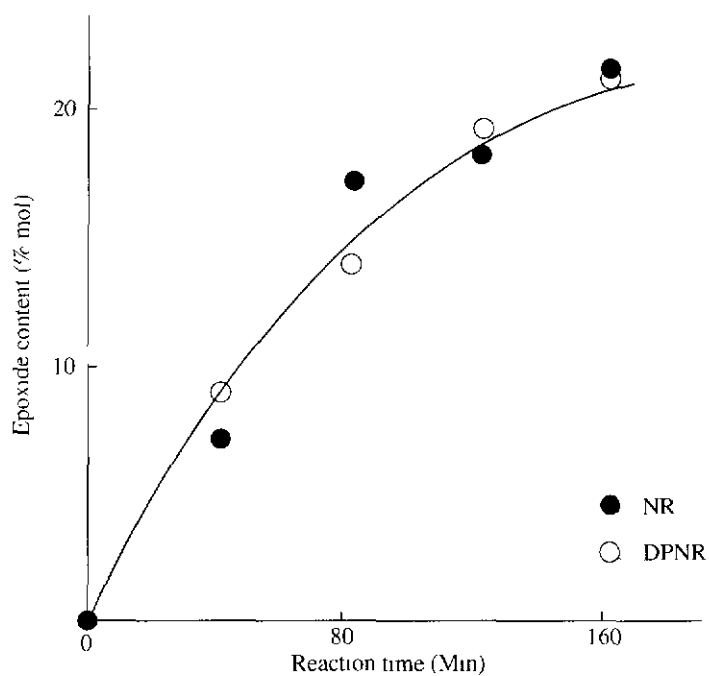


Figure 2. Formation of epoxide at different time intervals

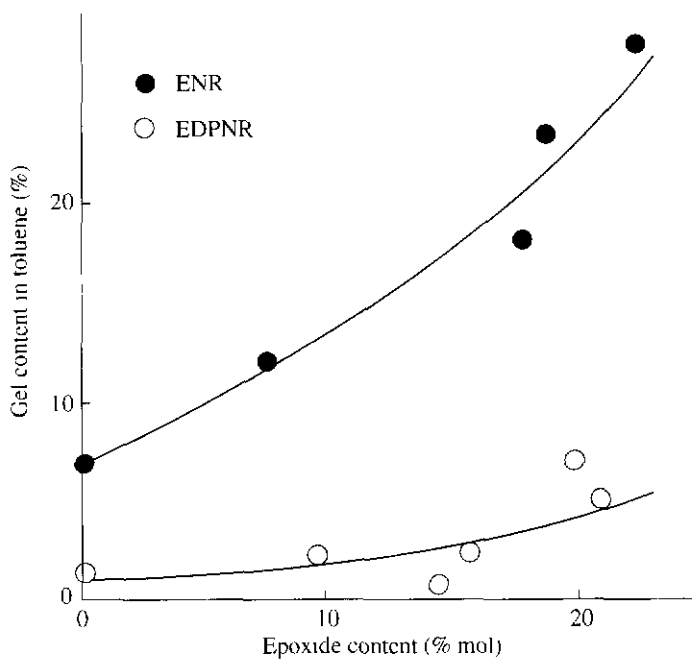


Figure 3. Gel content of modified natural rubbers

TABLE 2 NITROGEN CONTENT OF NR AND DPNR BEFORE AND AFTER EPOXIDATION

Epoxide content (% mol)	Nitrogen content (% wt)	
	NR	DPNR
0	0.18	0.01
22	0.17	0.01
50	0.14	0.01

components in natural rubber such as proteins and lipids. Therefore, in the absence of rubber proteins, DPNR is expected to contain a reduced ash content and this was found to be the case in the present study, as indicated in Table 3.

TABLE 3 ASH CONTENT OF NR AND DPNR BEFORE AND AFTER EPOXIDATION

Epoxide content (% mol)	Ash content (% wt)	
	NR	DPNR
0	0.23	0.12
22	0.19	0.12
35	0.21	0.13
50	0.18	0.11

Upon epoxidation, the ash content of both rubbers showed insignificant changes, probably because most of the polar non-rubber components, such as proteins which hold the mineral components of natural rubber⁷, were still present in the modified rubber.

Acetone Extract

Extraction of natural rubber with acetone removes resins such as phenolic compounds, colouring materials, free fatty acids and their esters. There is no significant difference

between the amount of acetone extract from NR and DPNR as shown in Table 4

TABLE 4 ACETONE EXTRACT OF NR AND DPNR BEFORE AND AFTER EPOXIDATION

Epoxide content (% mol)	Acetone content (% wt)	
	NR	DPNR
0	2.2	2.2
22	2.1	2.3
50	2.4	2.5

Epoxidation of NR and DPNR did not change the amount of acetone extract in the modified rubbers; this implies that peracetic acid does not change the solubility of non-rubber components in acetone.

Glass Transition Temperature

Continual epoxidation of polydienes invariably leads to an increase in the T_g value because the presence of bulky epoxide^g group in the polymer main-chain lowers rotational freedom of the modified segment. In the present study, the T_g 's of the quenched amorphous polymers are indeed found to increase in step with the level of modification, as shown in Figure 4. Both ENR and EDPNR showed an increase of 0.82 K per mol% in their T_g 's which is quite similar to the reported value of 0.85 K per mol%⁸. These results indicate that rubber proteins have no significant effect on the segmental mobility of both *cis* polyisoprene and partially epoxidised *cis* polyisoprene. This has also been confirmed in a study on the thermal properties of DPNR⁹.

Density

Purification of natural rubber is expected to affect the density of the polymer. Figure 5

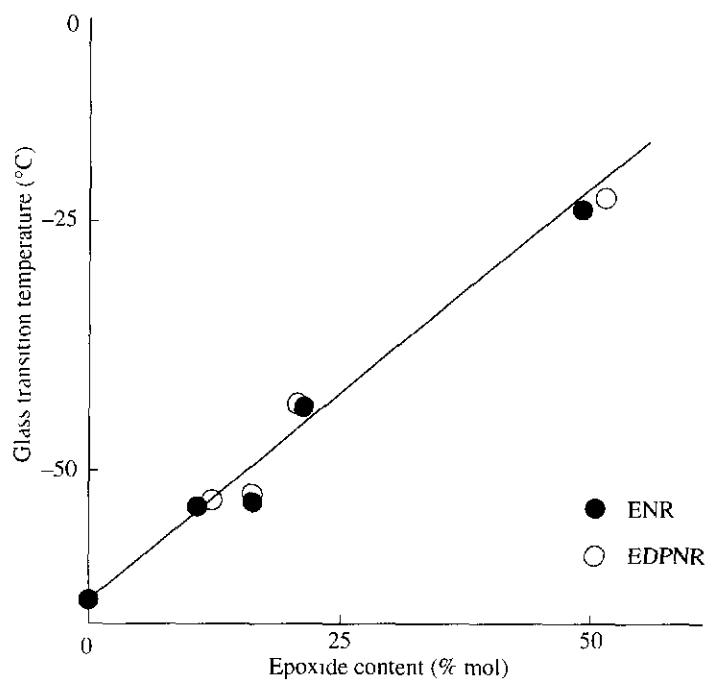


Figure 4. Glass transition temperature of modified natural rubbers.

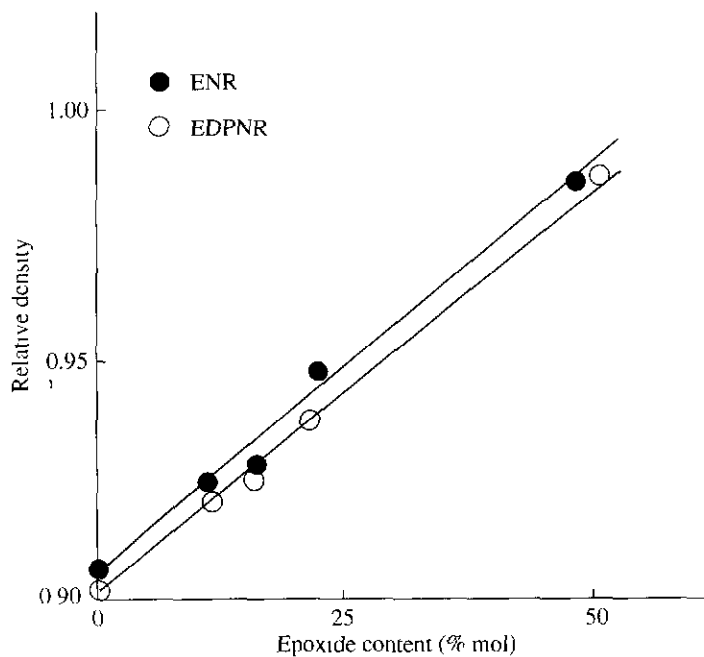


Figure 5 Density of modified natural rubber

indicates that the density of NR is slightly higher than that of DPNR. This is not unexpected because DPNR contains less rubber proteins and ash, both of which have higher density than the rubber hydrocarbon. It has been reported that the density of epoxidised NR increases with the epoxide content⁴. In the present study, as the level of epoxidation of NR and DPNR increases, the density of both rubbers increases in a parallel manner. Epoxidation does not change the non-rubber composition of the modified rubber very much. Therefore, the difference between the densities of ENR and EDPNR of the same epoxide content is very similar to that between NR and DPNR.

CONCLUSION

Although there are several differences between properties of ENR and those of EDPNR, such as ash and gel contents, epoxidation does not change the non-rubber content of the modified rubbers very much. The differences are therefore derived from the raw materials used to produce the modified rubbers. Deproteinisation of NR before epoxidation lowers the gel content and therefore improves the processability of the modified rubber.

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REFERENCES

1. GELLING, I R (1991) Epoxidised Natural Rubber *J nat Rubb Res*, **6**, 184.
2. ICHIKAWA, N, ENG, A H AND TANAKA, Y (1993) Properties of Deproteinised Natural Rubber Latex. *Proc. Int Rubb Technol Conf Kuala Lumpur, Malaysia 1993*, 101.
3. GREENSPAN, F P AND MACKELLER, D G (1948) Analysis of Aliphatic Acids *Anal Chem*, **20**, 1061.
4. BURFIELD, D R, LIM, K L AND LAW, K S (1984) Epoxidation of Natural Rubber Latexes. Methods of Preparation and Properties of Modified Rubbers. *J Appl Polym Sci*, **29**, 1661.
5. DAVIES, C K L AND LOADMAN, M J R (1984) A Chemical Demonstration of the Randomness of Epoxidation of Natural Rubber *Brit Polym J.*, **16**, 134.
6. GELLING, I R (1987) Epoxidised Natural Rubber *NR Technol.*, **18**, 21.
7. GRECHANOVSKII, V A AND DMITRIEVA, I P (1985) Preliminary Characterisation of Protein Component from Commercial Varieties of *Hevea* Rubber. *Kauch Rezina*, **3**, 15.
8. DAVIES, C K L, WOLFE, S V, GELLING, I R AND THOMAS, A G (1983) Strain Crystallisation in Random Copolymer Produced by Epoxidation of *cis*-1,4 Polyisoprene *Polym*, **24**, 107.
9. KAWAHARA, S AND TANAKA, Y (1997) Some Thermal Properties of Deproteinised Natural Rubber *Polym.*, submitted.