Epoxide Groups in Natural Rubber. I. ¹³C-NMR Study of Oxidative Degraded Rubbers

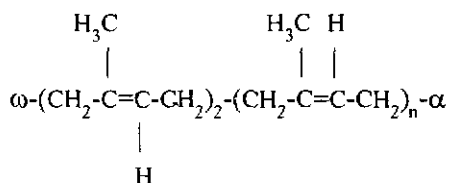A.H. ENG[*#], J. TANGPAKDEE[**], S. KAWAHARA[**] AND Y. TANAKA[**]

Epoxide groups in natural rubber, which are derived from oxidative degradation of the polymer, are found to be mainly in cis configuration The amount of trans epoxide, on the other hand, increases with increasing degradation temperature of the natural rubber The presence of cis epoxide groups in low molecular weight fractions of natural rubber, therefore, may be associated to by-products of oxidative degradation of the polymer.

Natural rubber is known to contain not only *cis*-1,4-polyisoprene, but also various naturally occurring non-rubber materials such as proteins, carbohydrates and lipids. Most of these non-rubber materials can be removed from the rubber hydrocarbon *via* several purification techniques. Although the purified natural rubber hydrocarbon is nearly pure *cis*-1,4-polyisoprene, small amounts of non-*cis* isoprene groups, which are also known as abnormal groups, have been found to be present on the main-chain molecule. These abnormal groups are very low in concentration but they exert a strong influence on the properties of the polymer which distinguish it from the synthetic analogue The abnormal groups, which have been reported to be on the main-chain molecule, include *trans*-1,4-isoprene[1 2], ester[3], aldehyde[4 5], and epoxide[6 7] groups.

On the basis of information on the diad sequences of *cis* and *trans* isoprene units in natural rubber obtained by ¹³C-NMR, *trans* isoprene units were shown to be exclusively in ω-*trans* or *trans*-*trans* arrangements[1]. Further triad sequential analysis of *trans* and *cis* isoprene units in highly purified natural rubber by ¹H-NMR revealed that two *trans* isoprene units are present at the initiating terminal of the rubber molecule[1,2]. The fundamental structure of natural rubber is thus confirmed to be as follows where ω and α are unidentified terminal groups:

$$\omega\text{-}(CH_2\text{-}\underset{\underset{H_3C}{|}}{C}\text{=}C\text{-}CH_2)_2\text{-}(CH_2\text{-}\underset{\underset{H_3C}{|}}{C}\text{=}\underset{\underset{H}{|}}{C}\text{-}CH_2)_n\text{-}\alpha$$

The ester groups, on the other hand, have been confirmed to be due to fatty acids bonded to the polymer chain[3]. Examination of fractionated purified natural rubbers showed fairly even distribution of these groups in the polymer with each linear rubber molecule containing 1–2 ester groups irrespective of its

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molecular weight. The ester groups have been postulated to be located at the branching point of the rubber molecule *via* association with phospholipid complex[3].

Further investigation indicated that both aldehyde and ester groups have a similar distribution in‧fractionated natural rubber of different molecular weights[8]. A drastic reduction in the aldehyde content of the rubber after the removal of the ester groups, *i.e.*, the bonded fatty acids, was observed, indicating that the aldehyde groups were derived from oxidative degradation of the olefinic groups of unsaturated fatty acids bonded to the rubber molecule[8].

The direct evidence for the presence of *cis* epoxide (epoxidised *cis* isoprene) on natural rubber main-chain molecule was based on ^{13}C-NMR studies of low molecular weight rubber that derived from commercial latex[9]. However, similar studies carried out on the rubber from fresh latex showed no significant amount of epoxide groups in the polymer. It was reported[10] that oxidative degradation of natural rubber produces only *trans* epoxide groups as a by-product whereas the non-radical route, presumably enzymatic action, produces naturally occurring *cis* epoxide as detected in the ^{13}C-NMR studies. This paper examines the validity of this claim by using ^{13}C-NMR technique.

MATERIALS AND METHODS

Field latex used was of RRIM 600 clonal origin. Purified natural rubber was prepared by treating 1% w/v sodium dodecyl sulphate stabilised field latex with 0.04% w/v protease enzyme, *Alcalase 2.0T* (Novo Nordisk Bioindustry) at pH 9.5 and 37°C for 24 h

followed by successive centrifugation at 13 000 r.p.m. for 30 min as described elsewhere[11].

Hydrogen peroxide catalysed UV-degradation was carried out on the purified rubber according to the method described by Burfield[10]. Thermal oxidative degradation of the purified rubber was performed by heating the solid rubber sample at 120°C for 2 h. Cobalt catalysed oxidative degraded rubber was prepared by shaking the purified rubber/toluene solution, 2% w/v, with cobalt acetylacetonate, 1% w/w with reference to rubber, at 65°C for 5 h. The degraded rubber was purified by reprecipitation from hexane solution.

^{13}C-NMR measurements were performed on deuterated chloroform solution on the rubbers with TMS as internal standard using a JEOL FX-200 NMR spectrometer under the conditions shown in *Table 1*. All NMR samples were prepared under nitrogen atmosphere to minimise the oxidative degradation of the rubbers.

Epoxidation of diene polymers was carried out with peracetic acid[12].

RESULTS AND DISCUSSION

It is well known that epoxidation of diene polymers by peracetic acid is stereospecific, *i.e.*, *cis* diene polymers produce *cis* epoxide and *trans* diene polymers *trans* epoxide. This stereospecificity can be confirmed by ^{13}C-NMR technique. *Figures 1* and *2* show the ^{13}C-NMR spectra of partially epoxidised *cis*-1,4-polyisoprene and *trans*-1,4-polyisoprene, respectively. The C2 and C3 in the *cis* epoxide group were found to resonate at 60.7 p.p.m. and 64.5 p.p.m., while those in the *trans*
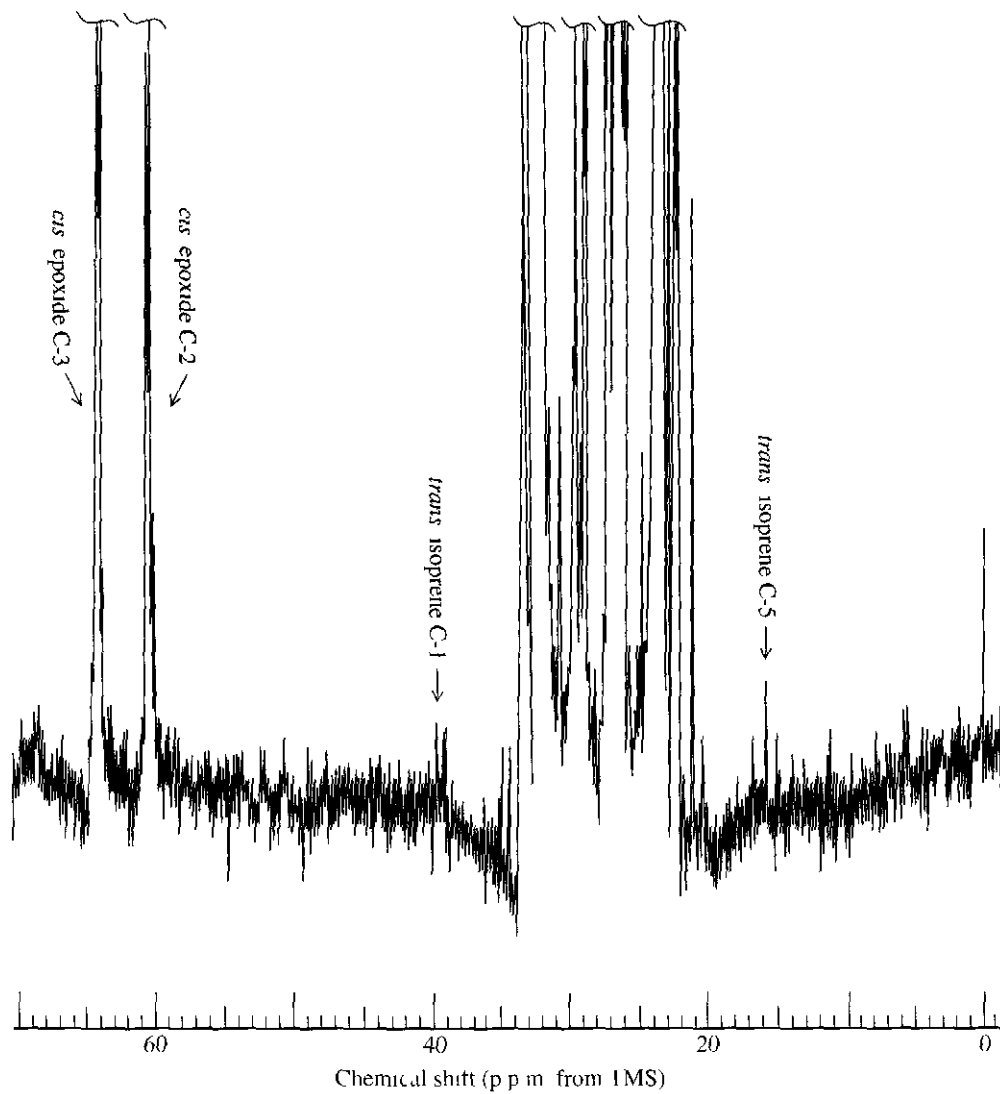
cis epoxide C-3 →

cis epoxide C-2 →

trans isoprene C-1 →

trans isoprene C-5 →

60   40   20   0

Chemical shift (p p m from TMS)

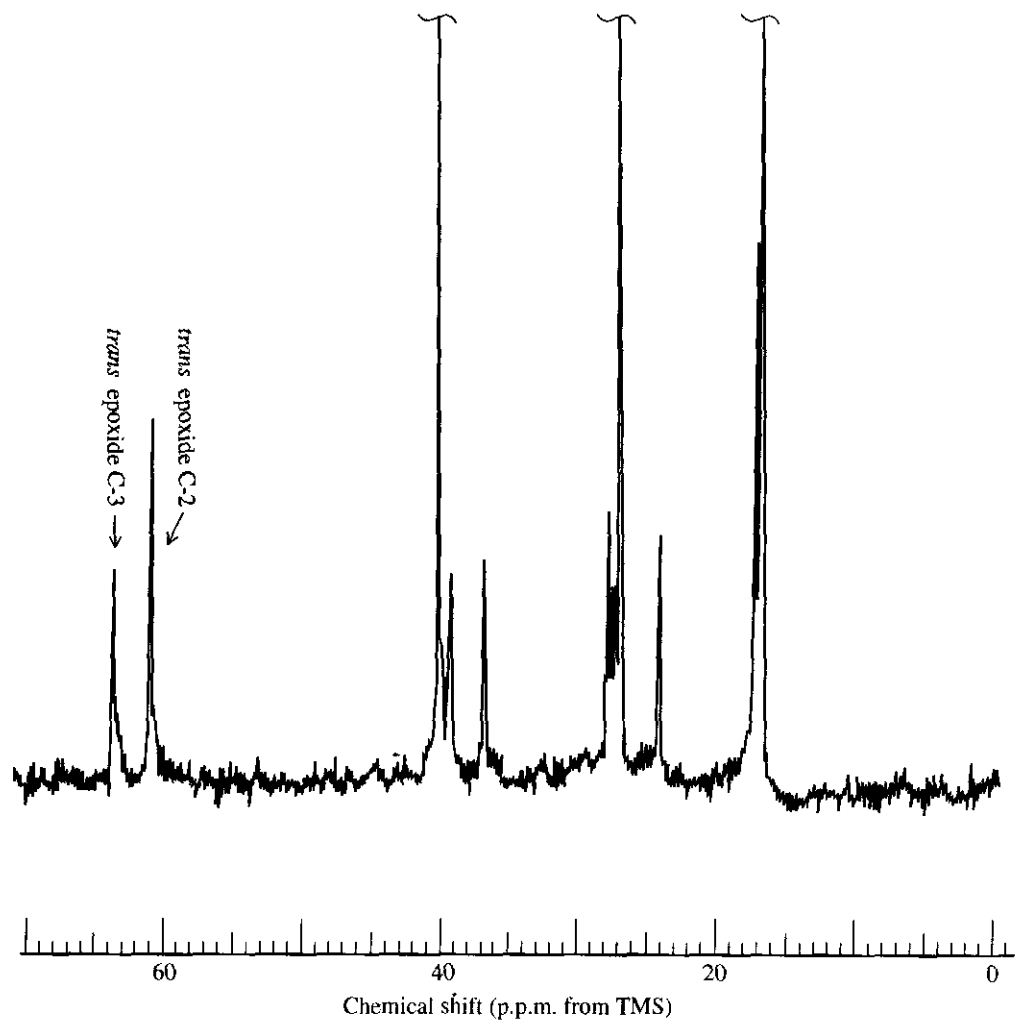Figure 1 13C-NMR spectrum of partially epoxidised cis-1 4 polyisoprene

Figure 2. ^{13}*C-NMR spectrum of partially epoxidised* trans-*1,4-polyisoprene*

TABLE 1. PARAMETERS FOR ^{13}C-NMR MEASUREMENTS

Sample concentration	10% w/v in CDCl[3]
Temperature	50°C
Observation frequency	50.1 MHz
Sweep width	10 000 Hz
Data point	16 000
Pulse width	10 μs
Pulse delay	4.0 s
Acquisition time	0.8 s
Scans	20 000 – 40 000

epoxide at 60.6 p.p.m. and 63.2 p.p.m., respectively. The carbon atoms of the isoprene or epoxidised isoprene units are designated as follows:

$$C(5)$$
$$|$$
$$C(1)\text{-}C(2)\text{-}C(3)\text{-}C(4)\text{-}$$
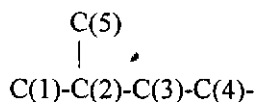
The distinctive difference in the chemical shift of the C3 carbon allows one to differentiate *cis* epoxide from *trans* epoxide by using ^{13}C-NMR.

Burfield[10] reported that hydrogen peroxide catalysed degradation of *cis* polyisoprene to liquid rubber produces only *trans* epoxide. However, no ^{13}C-NMR signals due to *trans* epoxide were found in the spectrum of the degraded rubber sample. In view of this, the experiment on hydrogen peroxide catalysed degradation of natural rubber in the presence of UV radiation was repeated in the present study.

Figure 3 indicates the ^{13}C-NMR spectrum of the hydrogen peroxide catalysed UV-degraded natural rubber. The characteristic

^{13}C-NMR signals due to C2 and C3 in *cis* epoxide were found at 60.7 p.p.m. and 64.5 p.p.m., respectively. A much smaller signal due to C3 in *trans* epoxide was observed at 63.2 p.p.m. The intensity ratio of the signals due to C3 in *cis* to *trans* epoxides was estimated to be 40:3. These results clearly indicate that degradation of natural rubber under the conditions employed produces much higher *cis* epoxide than *trans* epoxide as by-products. The failure to observe the ^{13}C-NMR signals of epoxide groups in Burfield's[10] analysis was probably due to insufficient number of spectral accumulations. A similar result was obtained when the rubber was degraded at higher temperature, 65°C *in the presence of cobalt* catalyst as shown in *Figure 4*. In this case, however, the signals intensity ratio of *cis* to *trans* epoxide was found to be 4:1. This ratio further shifted to 2:1 when the degradation was carried at 120°C in the absence of added catalyst and solvent as indicated in *Figure 5*. These results are summarised in *Table 2*.

Although the three experiments on the degradation of natural rubber were carried under different conditions, it appears that higher degradation temperature favours the formation
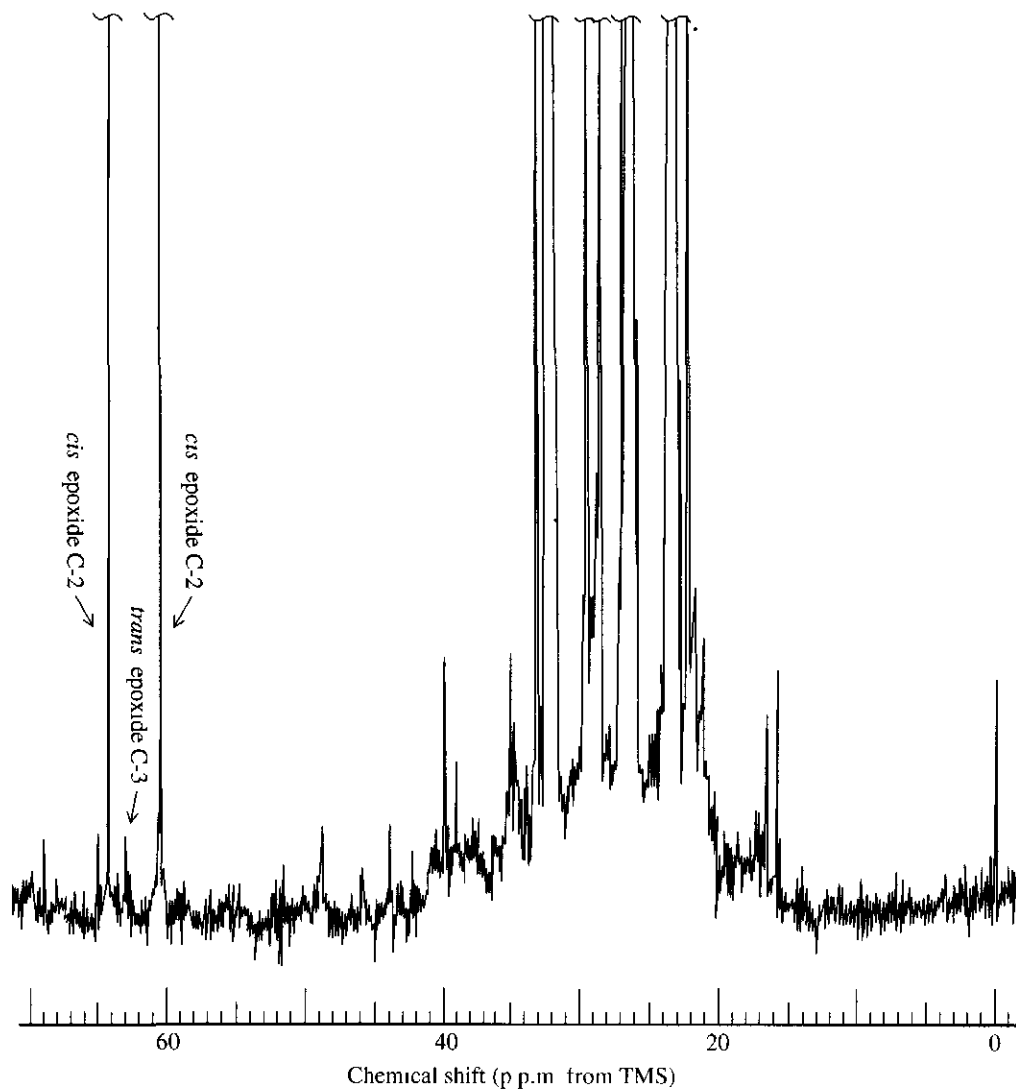
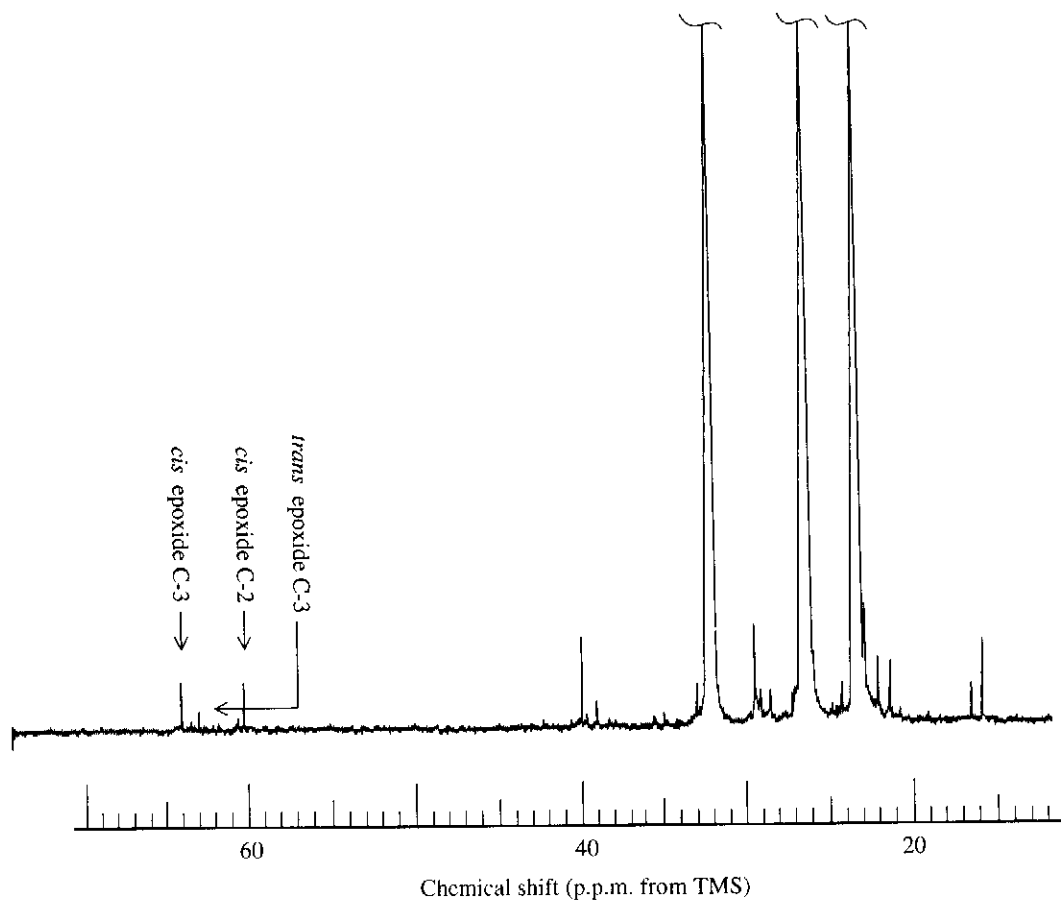*Figure 3.* ^{13}C-NMR spectrum of H_2O_2 catalysed UV degraded rubber. Temperature: 25°C

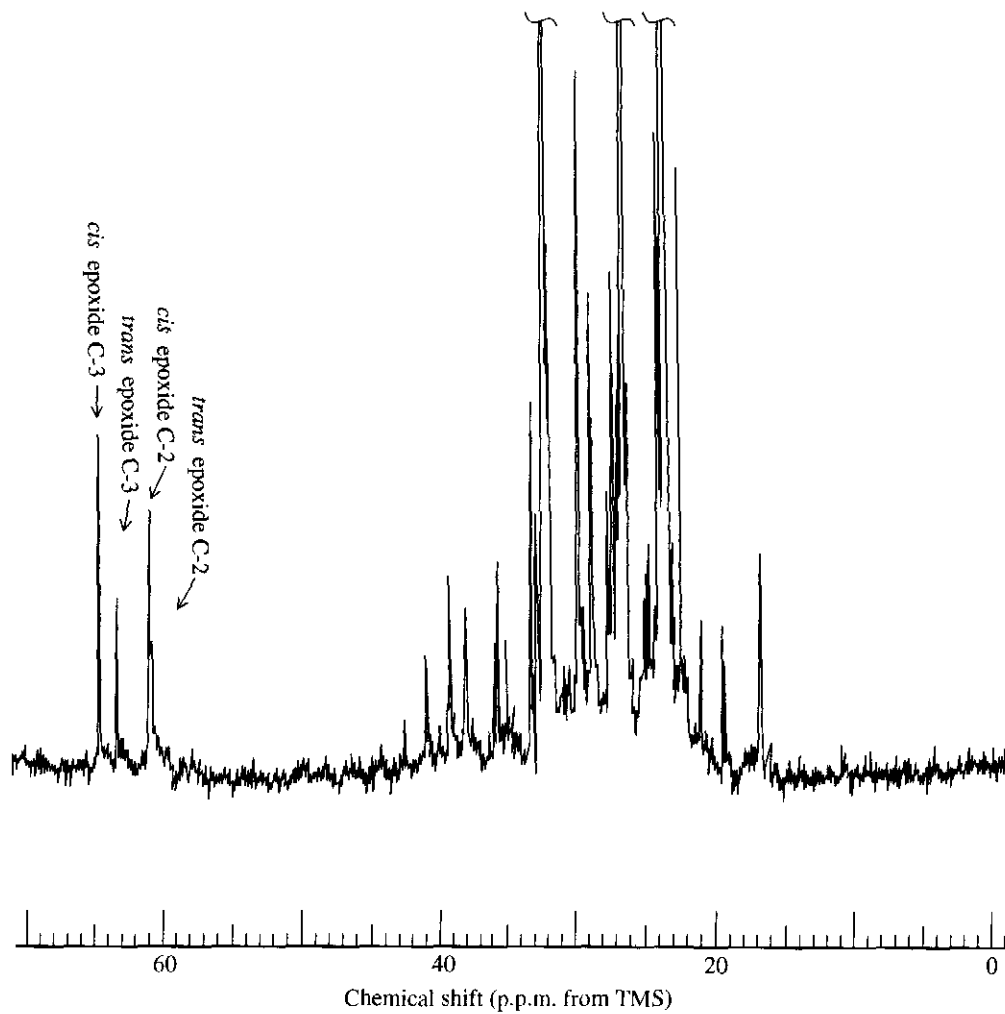*Figure 4. ¹³C-NMR spectrum of cobalt catalysed thermal-degraded rubber. Temperature: 65°C.*
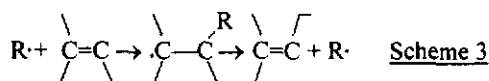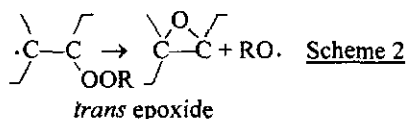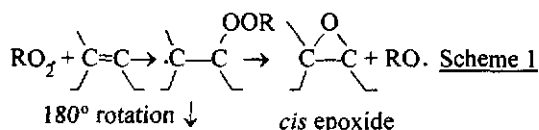
Figure 5. ^{13}C-NMR spectrum of thermal degraded rubber. Temperature: 120°C

TABLE 2 ^{13}C-NMR SIGNALS INTENSITY RATIOS OF *CIS* TO *TRANS* EPOXIDES AND *TRANS* EPOXIDE TO *TRANS* ISOPRENE UNITS IN DEGRADED NATURAL RUBBERS

Sample	Temperature (°C)	*Trans. cis* epoxides	*Trans* epoxide: *Trans* isoprene
H_2O_2, UV-degraded rubber	25	3:40	25:60
Cobalt, thermal-degraded rubber	65	10:40	9:60
Thermal-degraded rubber	120	20:40	220:60

of *trans* epoxide. The formation of epoxide groups during degradation of *cis* polyisoprene has been widely postulated to involve the following reaction *(Scheme 1)*.

$$RO_2 + \quad \overset{\backslash}{\underset{/}{C}} = \overset{\backslash}{\underset{\backslash}{C}} \rightarrow \cdot \overset{\backslash}{\underset{/}{C}} - \overset{OOR}{\underset{\backslash}{C}} \rightarrow \quad \overset{\backslash}{\underset{/}{C}} \overset{O}{-} \overset{\backslash}{\underset{\backslash}{C}} + RO. \quad \underline{\text{Scheme 1}}$$

180° rotation $\downarrow$ *cis* epoxide

$$\cdot \overset{\backslash}{\underset{/}{C}} - \overset{\lceil}{\underset{OOR}{C}} \rightarrow \overset{\backslash}{\underset{/}{C}} \overset{O}{-} \overset{\lceil}{C} + RO. \quad \underline{\text{Scheme 2}}$$

trans epoxide

$$R \cdot + \overset{\backslash}{\underset{/}{C}} = \overset{\backslash}{\underset{\backslash}{C}} \rightarrow \cdot \overset{\backslash}{\underset{/}{C}} - \overset{R}{\underset{\backslash}{C}} \rightarrow \overset{\backslash}{C} = \overset{\lceil}{\underset{/}{C}} + R \cdot \quad \underline{\text{Scheme 3}}$$

The formation of *trans* epoxide probably involves a 180° rotation of the peroxy radical species along the polymer chain before releasing an alkoxy radical to form the epoxide group as shown in *Scheme 2*. At low reaction temperature, this rotation is slower than the formation of *cis* epoxide. As the reaction temperature increases, the mobility of the polymer chain becomes higher and therefore more *trans* epoxide groups are formed.

Oxidative degradation of natural rubber has been shown to produce *trans* isoprene units *via* isomerisation[1] as represented in *Scheme 3*.

All the three degraded rubber samples examined in the present study showed the ^{13}C-NMR signal of C1 of *trans* isoprene in *cis-trans* arrangement at 40.0 p.p.m. This signal is different from that of biosynthesis origin, which appears at 39.8 p.p.m. It is perhaps tempting to suggest that the *trans* epoxide is derived from the *trans* isoprene *via* the similar route shown in *Scheme 1*. However, the low level of *trans* isoprene found, as shown in *Table 2*, weakens this argument.

Since oxidative degradation of natural rubber produces more *cis* than *trans* epoxides, this has cast some doubt on the suggestion that *cis* epoxide detected in the ^{13}C-NMR study of low molecular weight rubber from preserved latex is of non-radical origin[10]. The failure to observe any epoxide in the rubber sample from fresh latex further strengthens the view that natural rubber contains no significant amount of naturally occurring epoxide. However, most of the ^{13}C-NMR studies on natural rubber have so far been concentrated on low molecular weight fractions; it is therefore tempting to suggest that the naturally occurring epoxide groups are concentrated in the higher molecular weight or gel fractions[7]. Further ^{13}C-NMR studies on various natural rubbers have been carried out and these will be the subject of the next paper.

CONCLUSION

Oxidative degradation of natural rubber produces epoxides as by-products, of which the *cis* configuration is found to be the major product while that of *trans* configuration the minor product. A slight increase in the *trans* epoxide is observed as the degradation temperature increases. The *cis* epoxide group, which was previously detected in the low molecular weight fractions of natural rubber, thus cannot be concluded as a product derived from non-radical route.

REFERENCE

1. ENG, A.H., KAWAHARA, S. AND TANAKA, Y. (1994) *Trans* isoprene Units in Natural Rubber. *Rubb. Chem Technol* , 67, 159–168.

2. TANAKA, Y., ENG, A.H., OHYA, N., NISHIYAMA, N., TANGPAKDEE, J., KAWAHARA, S. AND WITITSUWANNAKUL, R (1996) Initiation of Rubber Biosynthesis in *Hevea brasiliensis*: Characterisation of Initiation of Initiating Species by Structural Analysis. *Phytochemistry*, 41, 1501–1505.

3. ENG, A.H., EJIRI, S., KAWAHARA, S. AND TANAKA, Y. (1994) Structural Characterisation of Natural Rubber: Role of Ester Groups. *J Appl Polym Sci Appl Polym Symp* , 53, 5–14.

4. SUBRAMANIAM, A. (1976) Molecular Weight and Other Properties of Natural Rubber. A Study of Clonal Variations. *Proc. Int Rubb Conf Kuala Lumpur 1975*, 4, 3–27.

5. SUBRAMANIAM, A. (1977) Estimation of Aldehyde Groups in Natural Rubber with 2,4-dinitrophenylhydrazine. *J Rubb Res Inst Malaysia*, 25, 61–68.

6. BURFIELD, D.R. (1976) Epoxy Groups Responsible for Crosslinking in Natural Rubber. *Nature*, 249, 29–30.

7. BURFIELD, D.R (1986) Storage Hardening of Natural Rubber: An Examination on Current Mechanistic Proposals. *J nat Rubb Res* , 1, 202–208.

8. ENG, A.H., TANGPAKDEE, J., KAWAHARA, S AND TANAKA, Y. (1997) Distribution and Origin of Abnormal Groups in Natural Rubber. *J nat Rubb Res.*, 12(1), 11–20.

9. TANAKA, Y (1984) Structural Characterisation of Naturally Occurring *Cis* Polyisoprenes. *ACS Symposium Series No 247 'NMR and Macromolecules' (Randall, J C ed) p233–244 Washington. American Society.*

10. BURFIELD, D.R (1988) The Formation of *Trans* Epoxide during the Photochemical Oxidation of *Cis* Polyisoprene to Liquid Rubbers. *Makromol Chem Rapid Commun* , 189, 523–527.

11. ENG, A.H., TANAKA. Y. AND GAN, S.N. (1992) FT-IR Studies on Amino Groups in Purified *Hevea* Rubber. *J nat Rubb Res* , 7, 152–155.

12. BURFIELD, D.R. AND ENG, A.H. (1989) Glass Transition and Crystallisation Phenomena in Epoxidised *Trans* Polyisoprene: A DSC Study. *Polymer*, 30, 2019–2022.