Hydrogenation of epoxidized natural rubber in the presence of palladium acetate catalyst

Susmita Bhattacharjee*, Anil K. Bhowmick* and Bhola Nath Avasthi†‡
** Rubber Technology Centre, and † Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India*
(Received 29 April 1992; revised 24 February 1993)

Epoxidized natural rubber has been selectively hydrogenated in the presence of a homogeneous palladium acetate catalyst. The hydrogenated product has been characterized by infra-red and nuclear magnetic resonance spectroscopies. No change is noted in the epoxy content of the polymer after the reaction. The catalyst is highly selective in reducing carbon–carbon double bonds in the presence of epoxy groups. Natural rubber has also been hydrogenated for a comparative study. The rate constant of hydrogenation is decreased with increase in epoxy content of the polymer.

(Keywords: epoxidized natural rubber; palladium acetate; hydrogenation)

INTRODUCTION

Chemical modification of diene elastomers has emerged as an active field of research because of the technological importance of the modified products. The olefin functionality present in the unsaturated polymer is a useful target for modification owing to its varied reactivity. Epoxidized natural rubber (ENR) is one of the chemically modified forms of natural rubber[1]. Epoxidation increases the damping and improves the adhesion, wet traction, gas permeability and oil and hydrocarbon-solvent resistance of natural rubber vulcanizates. However, its storage stability is very poor[2]. Degradation occurs through two mechanisms: one is cleavage of carbon–carbon double bonds on oxidation; and the other is ring opening of epoxide groups by traces of acids in the system due to other ingredients[3]. Thermo-oxidative degradation through olefinic unsaturation can be avoided and the stability of ENR may be improved by hydrogenation of residual unsaturation in ENR.

Hydrogenation is one of the important methods for improving and changing the properties of an existing unsaturated elastomer. The conversion of an unsaturated polymer to a saturated one can be brought about by homogeneous and heterogeneous catalytic as well as non-catalytic hydrogenation. A survey of the available literature reveals that homogeneous catalysis is preferred for the hydrogenation of unsaturated polymers containing various functional groups, because of its higher catalytic activity and selectivity. Hydrogenation of functionalized rubbers presents a special problem since the functional groups interfere during the reaction. A few methods have been developed for hydrogenation of carbon–carbon double bonds in polymers containing other reducible functional groups. Tris(triphenylphosphine)chlororhodium(I) has been used as a catalyst for the hydrogenation of acrylonitrile–butadiene copolymer[4–6]. Bouchal and coworkers[7] studied the hydrogenation of hydroxy-terminated telechelic polybutadienes by using the above catalyst. They observed a partial loss of hydroxyl groups in the modified polymers. In an earlier communication[8], the present authors have reported that carboxylated nitrile rubber undergoes sufficient decarboxylation during hydrogenation in the presence of a rhodium catalyst. Several catalyst systems based on nickel[9–12], rhodium[13], ruthenium[14,15] and titanium[16] have been developed for homogeneous and heterogeneous hydrogenation of functionalized diene polymers.

We have developed organometallic complex catalysts based on palladium metal for selective hydrogenation of nitrile[17,18] and carboxylated nitrile rubbers[19]. The degradation behaviour of hydrogenated nitrile rubbers is improved significantly on hydrogenation[20]. It has been reported that palladium acetate[17] imparts excellent selectivity in reducing olefinic unsaturation in the presence of nitrile groups under mild reaction conditions. Though many methods have been explored for hydrogenation of functional diene polymers, no attempt has so far been made to hydrogenate epoxidized natural rubber. In the present work, we have studied the hydrogenation of epoxidized natural rubber in the presence of palladium acetate catalyst. Natural rubber has also been hydrogenated for a comparative study. The epoxy content of the rubber has been varied. The product has been thoroughly characterized by infra-red and nuclear magnetic resonance spectroscopies.

EXPERIMENTAL

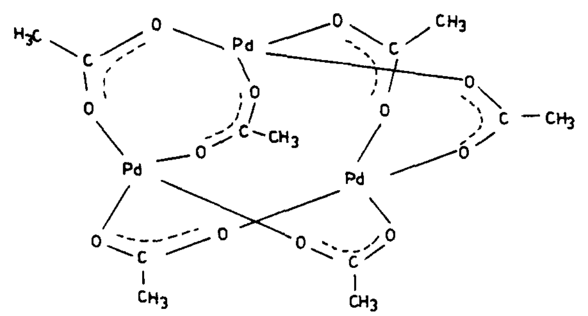
A commercial sample of palladium acetate was obtained from Arora–Matthey Ltd, India. The compound was recrystallized by dissolving it in warm benzene, mixing the solution with half its volume of glacial acetic acid

---

‡ To whom correspondence should be addressed

0032-3861/93/245168-06

and allowing the mixture to evaporate slowly at room temperature. The decomposition temperature of the recrystallized sample was 200°C. The structure of the complex is shown in *Scheme 1*.



Scheme 1

Benzene, acetic acid, chloroform, acetone and methanol were used as received from a commercial source (E. Merck (India) Ltd) with purities in excess of 99 mol%.

Epoxidized natural rubber with 25 and 50 mol% epoxy content was procured from the Rubber Research Institute of Malaysia. Natural rubber (ISNR-5) was obtained from the Rubber Board, Kottayam, India. Commercially available hydrogen gas (purity 99.9%) supplied by Indian Oxygen Ltd, Calcutta, was used directly.

High-pressure autoclave

A high-pressure rocking autoclave (High Pressure Equipment Co., USA of 300 ml capacity, having an angular play of 15° with 30 oscillations per minute, was used. The autoclave was electrically heated and the temperature was controlled by a temperature controller.

Hydrogenation procedure

The polymer sample (2 g) was dissolved in chloroform/acetone mixture (50/50 ml) and 40 mg catalyst was added to the solution. The mixture was introduced into a glass liner in order to minimize the corrosion inside the autoclave. The liner was placed into the autoclave and hydrogen gas was passed through it up to a pressure of 2.7 MPa. The autoclave was heated slowly to 60°C and the temperature was maintained constant for 1 h with continuous rocking. The autoclave was allowed to cool to room temperature and the polymer was coagulated into methanol. The polymer was washed with methanol and hexane and finally dried in vacuum.

Characterization

Infra-red (i.r.) spectroscopy studies were carried out using a Perkin–Elmer 843 spectrophotometer by casting thin films of the polymer on KBr plates.

Nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian EM-390 spectrophotometer operating at 90 MHz. Deuterated chloroform was used as the solvent in all cases.

RESULTS AND DISCUSSION

Figure 1a shows the i.r. spectrum of ENR (50 mol% epoxy content). The aliphatic C–H stretching vibration appears between 3010 and 2850 cm^{-1}. The –CH_2– deformation vibration absorbs in the region of 1454 cm^{-1}. A sharp peak is observed at 1376 cm^{-1} due to the deformation vibration of the –CH_3 group. A weak peak at 1250 cm^{-1} associated with a strong absorbance band at 877 cm^{-1} appears from the C–O–C ring vibration of epoxide groups. The out-of-plane deformation of *cis* double bonds is observed at around 840 cm^{-1}. *Figure 1b* presents the i.r. spectrum of hydrogenated epoxidized natural rubber (HENR). The reduction of carbon–carbon double bonds in the polymer is understood from the sharp decrease in the absorbance at 840 cm^{-1} (*Figure 2*). For comparison, the i.r. spectra of natural rubber (NR) and hydrogenated natural rubber (HNR) are shown in *Figure 3*. The hydrogenation of *cis* double bonds is well understood from the spectra. Since the epoxide ring is quite strained, there is always the probability of formation of ring-opened product during the reaction process. It is observed, however, that there is no change in the epoxy content of the polymer after hydrogenation. The ratio of peak absorbance at 877 cm^{-1} to that at 1376 cm^{-1} remains almost constant for the product and starting material. The absorption band at 1376 cm^{-1} is considered as the internal standard as no change is expected at the methyl group on hydrogenation. No additional absorption bands are traced on the spectrum that may arise due to possible side reactions such as formation of aliphatic ethers or furans, etc. A slight trace of –OH is observed in the spectrum of ENR (3515 cm^{-1}), which does not change on hydrogenation (*Figure 1b*). A quantitative estimation of extent of hydrogenation is obtained from the relative decrease in peak absorbance at 840 cm^{-1} with respect to that at 1376 cm^{-1}. A plot (*Figure 4*) of the ratio of these i.r. absorbances as a function of time shows that the concentration of double bonds decreases with the progress of the reaction, while the same plot for epoxide group remains almost constant. Hence, palladium acetate reduces carbon–carbon double bonds selectively in the presence of epoxy groups.

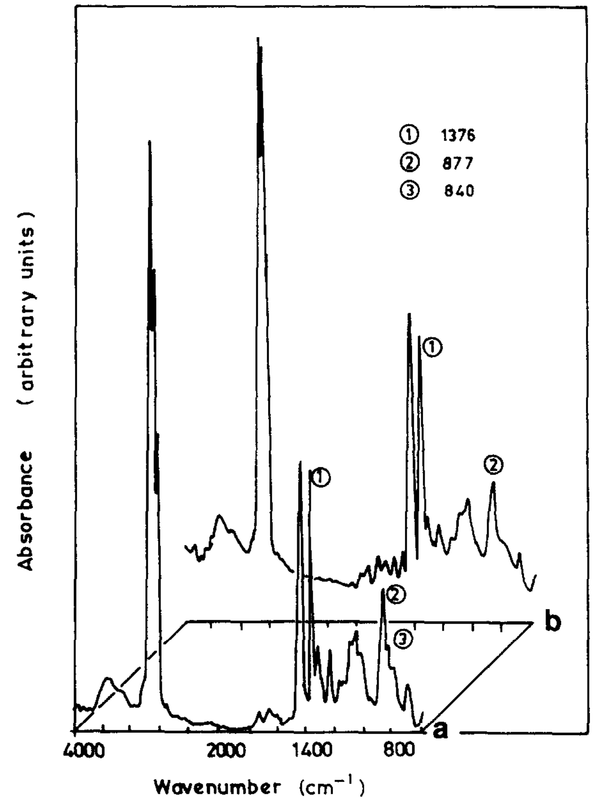


Figure 1 Infra-red spectra of (a) ENR (50 mol% epoxy content) and (b) HENR (50 mol% epoxy and 80% hydrogenation)

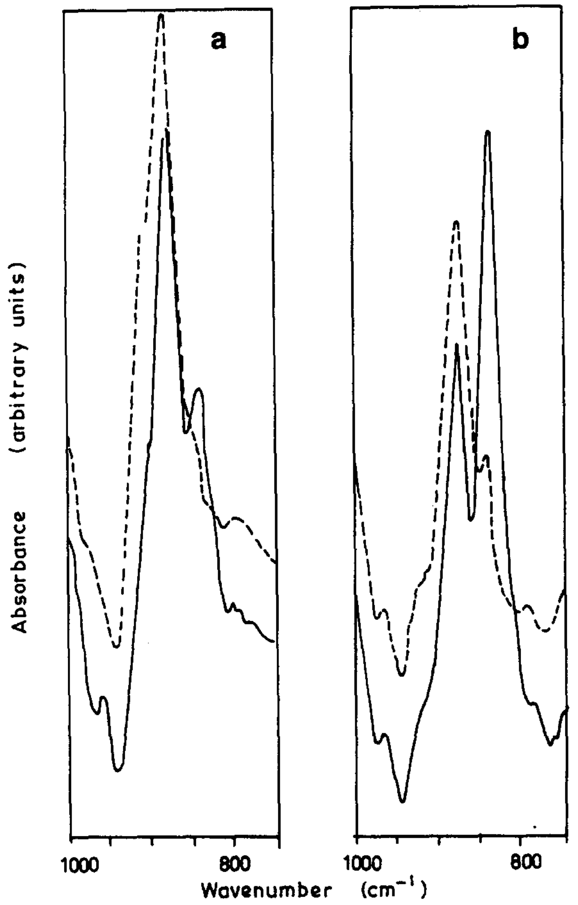


Figure 2 Decrease in absorbance at 840 cm^{-1} due to reduction of double bonds in infra-red spectrum: (a) (——) ENR (50 mol% epoxy content), (– – –) HENR (80% hydrogenation); (b) (——) ENR (25 mol% epoxy content), (– – –) HENR (75% hydrogenation)

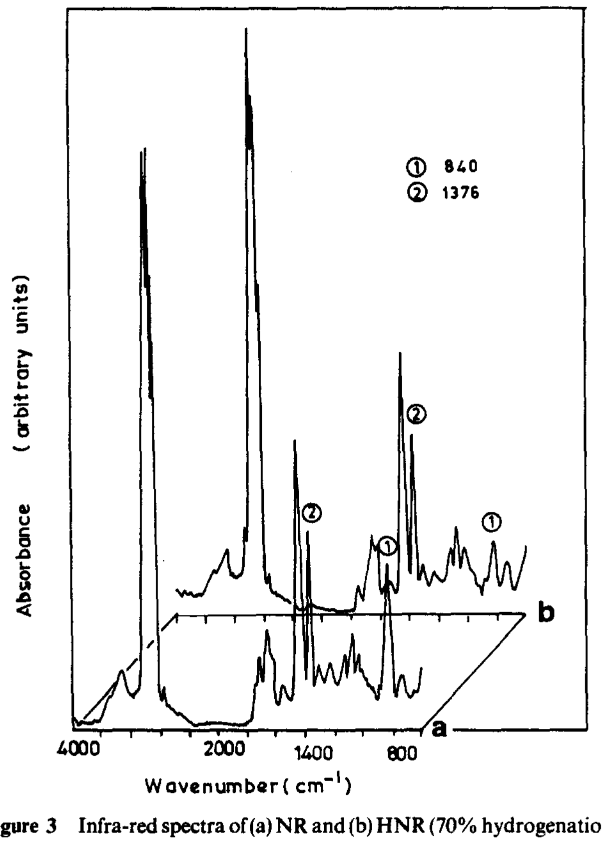


Figure 3 Infra-red spectra of (a) NR and (b) HNR (70% hydrogenation)

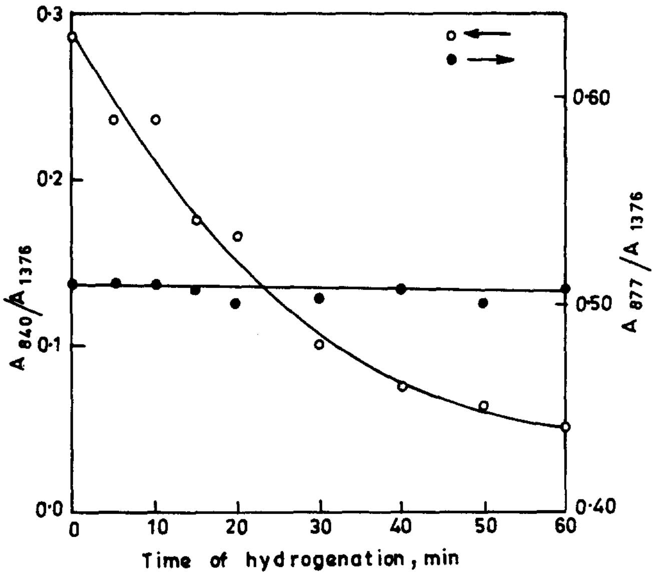


Figure 4 Change in A_{840}/A_{1376} (○) and A_{877}/A_{1376} (●) with reaction time in ENR (50 mol% epoxy content)

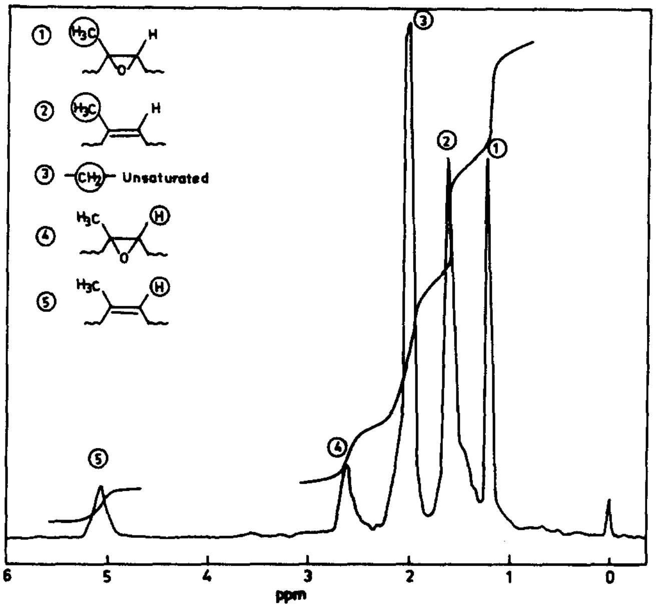


Figure 5 ^{1}H n.m.r. spectrum of ENR (50 mol% epoxy content)

Nuclear magnetic resonance spectroscopy provides insight into the microstructure of the non-hydrogenated and hydrogenated elastomers. The ^{1}H n.m.r. spectrum of ENR is presented in *Figure 5*. The signals due to protons on the saturated carbon, in $-CH_3$ and $>CH_2$ microstructure appear between 1.2 and 2.1 ppm. The proton attached to the epoxide ring gives a signal at 2.6 ppm. The peak due to the olefinic proton appears at 5.1 ppm. For comparison, the ^{1}H n.m.r. spectrum of NR is shown in *Figure 6a*. The *cis* methyl appears at 1.6 ppm, the methylene at 2.0 ppm and vinylene protons at 5.2 ppm. HNR (*Figure 6b*) shows a decrease in vinylic proton and a shift of methylene and methyl protons towards higher field, 1.4 and 0.9 ppm respectively. *Figure 7* is a typical ^{1}H n.m.r. spectrum of hydrogenated ENR. A significant decrease in olefinic protons is observed in the spectrum. The methyl protons associated with the double bonds give a signal at 0.9 ppm after

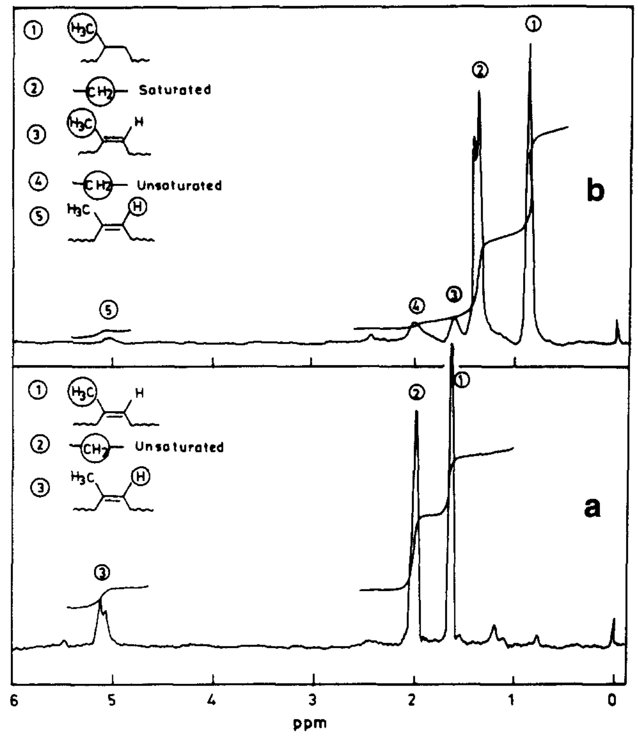


Figure 6 ^1H n.m.r. spectra of (a) natural rubber and (b) hydrogenated natural rubber (85% hydrogenation)

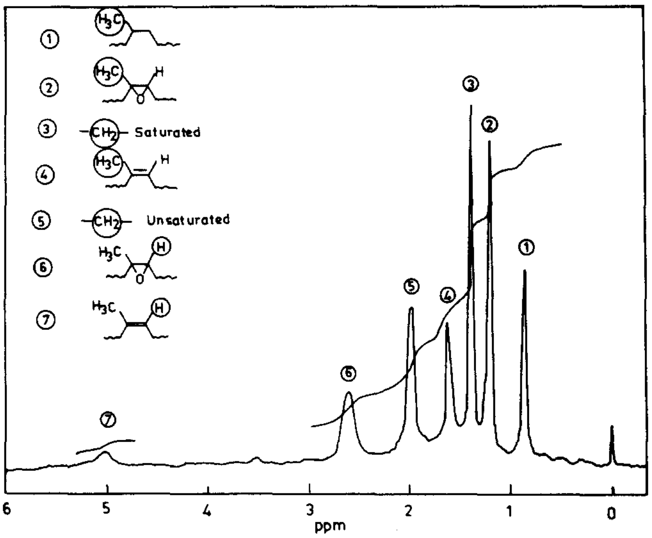


Figure 7 ^1H n.m.r. spectrum of HENR (50 mol% epoxy content, 70% hydrogenation)

hydrogenation. This confirms the hydrogenation of residual carbon–carbon double bonds of the isoprene unit of the polymer chain. It is further evident from the proton n.m.r. spectra that no side reaction has taken place during the catalytic reduction. No additional signals are observed in the spectrum of the hydrogenated sample. Moreover, *Figure 7* does not show a change in the proton signal associated with the epoxy group. Therefore, it is well understood from the spectroscopic studies that olefinic unsaturation in ENR can be reduced selectively in the presence of epoxy groups by using palladium acetate catalyst. It may be noted that similar selectivity has been offered by the catalyst during hydrogenation of nitrile rubber[17].

The degree of hydrogenation has been calculated by i.r. and n.m.r. spectroscopies and the results have been correlated by drawing a calibration curve (*Figure 8*). The method developed by Brück[21,22] and Marshell *et al.*[23], and reported by us in earlier communications[6,17], for estimation of extent of hydrogenation in nitrile rubber, has been followed. As the amount of residual double bonds in ENR is known, the degree of hydrogenation is calculated from the ^1H n.m.r. spectra by taking the ratio of integral of olefinic protons to that of aliphatic protons. Similarly, the ratio of absorbance at 840 cm^{-1} with respect to that at 1376 cm^{-1} is calculated from i.r. spectra. The i.r. absorbance ratio is plotted against the degree of hydrogenation obtained from n.m.r. spectra. With the help of this calibration curve, the degree of hydrogenation has been evaluated directly from i.r. spectra.

The hydrogenation reaction has been carried out on ENR containing 25 and 50 mol% epoxy content under identical conditions. The degree of hydrogenation obtained is 80% and 75% for ENR with 25 and 50 mol% epoxy groups. Almost 85% hydrogenation for natural rubber is achieved. Hence, the degree of hydrogenation is reduced with epoxidation.

The change in i.r. absorbance ratio A_{840}/A_{1376} with progress of the reaction is noted for the NR and ENR samples. From *Figure 9*, the decrease in double-bond concentration with time is obtained. When the logarithm of residual double-bond concentration is plotted against time, the resulting linear curve indicates that the reaction is first order with respect to olefinic substrate. The rate constant k is calculated from the slope of the linear plot. *Figure 10* shows that the rate constant of reduction decreases with epoxy content. A similar trend was observed during hydrogenation of nitrile rubbers with increasing nitrile and carboxyl content[5,19]. This behaviour can be explained with the help of the mechanism proposed below.

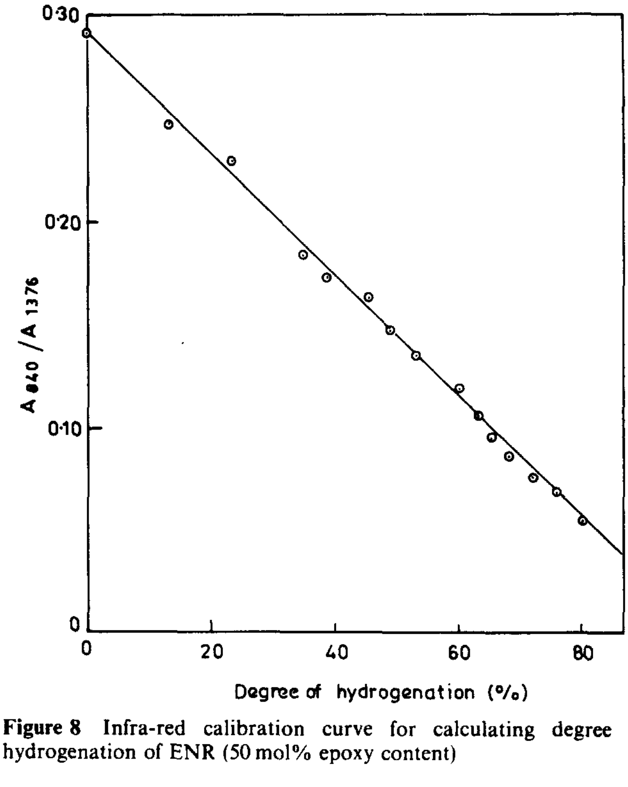


Figure 8 Infra-red calibration curve for calculating degree of hydrogenation of ENR (50 mol% epoxy content)

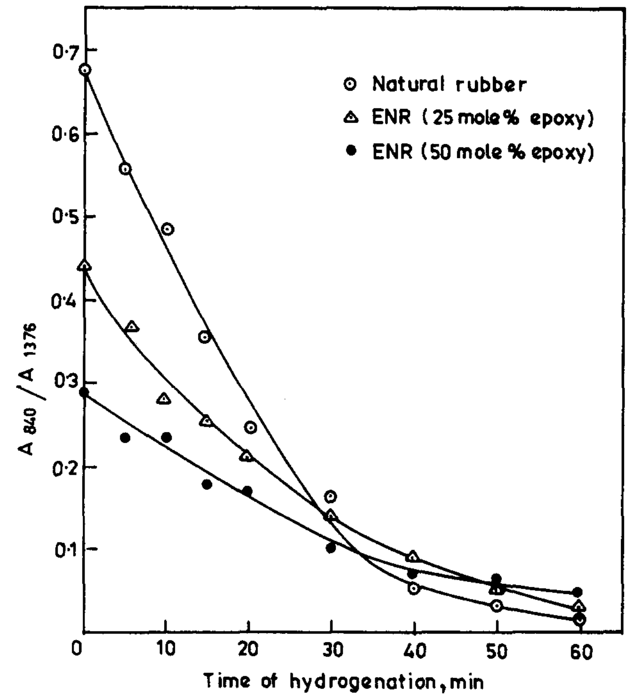


Figure 9 Change in absorbance ratio A_{840}/A_{1376} with the progress of hydrogenation

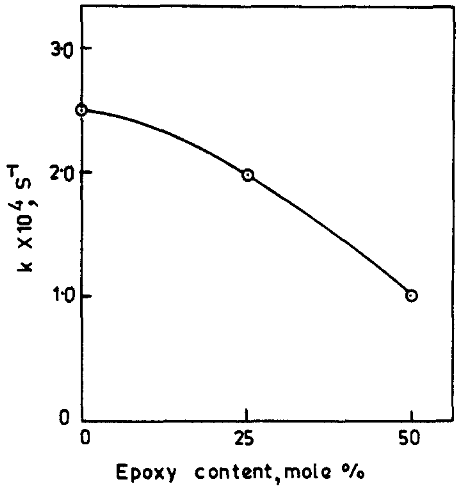
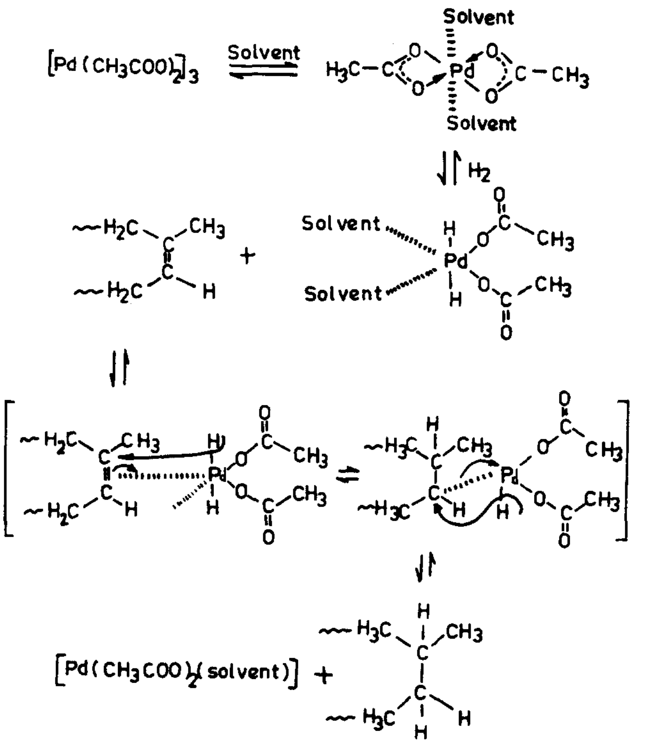


Figure 10 Plot of rate constant *k* against epoxy content of natural rubber

The mechanism of hydrogenation using palladium acetate catalyst may be proposed in line with earlier work[18,24]. It is known that the palladium(II) acetate has an unusual structure comprising three metal atoms in a triangle held together by six bridging acetate groups[25]. When the complex is dissolved in a solvent containing a donor atom, it is dissociated to form monomeric species and solvent occupies the vacant coordination sites of the metal atom. The active catalyst species reacts with hydrogen to form a metal hydride complex. There is possibly simultaneous coordination of olefinic bonds to the metal centre and hydride transfer to the double-bond site to give the saturated product (*Scheme 2*). In presence of epoxy groups, it is assumed that there will be competition between double bonds and oxygen atoms of the epoxy group for coordination to the metal centre.



Scheme 2

Hence, the catalytic activity of the complex will be restricted when there is formation of epoxy coordinated complex. Therefore, the rate of hydrogenation slows down with increasing epoxy content.

CONCLUSIONS

Epoxidized natural rubber can be selectively hydrogenated by using palladium acetate as homogeneous catalyst. The catalyst is highly selective in reducing olefinic unsaturation in the presence of epoxy groups. The degree of hydrogenation can be calculated from the i.r. and n.m.r. spectroscopic techniques. Natural rubber can also be hydrogenated in the presence of the same catalyst. An increase in the epoxy content of the rubber results in a decrease in the rate constant for hydrogenation and a decrease in the maximum attainable hydrogenation level.

ACKNOWLEDGEMENT

Susmita Bhattacharjee is grateful to the CSIR, New Delhi, India, for providing a Senior Research Fellowship.

REFERENCES

1 Gelling, I. R. *Rubber Chem. Technol.* 1985, **58**, 86

2 Chaki, T. K., Bhattacharya, A. K. and Bhowmick, A. K. *Kautsch. Gummi. Kunstst.* 1990, **43**, 408

3 Baker, C. S. L. 'Handbook of Elastomers — New Developments and Technology' (Eds A. K. Bhowmick and H. L. Stephens), Marcel Dekker, New York, 1988, Ch. 2, p. 31

4 Weinstein, A. H. *Rubber Chem. Techmol.* 1984, **57**, 203

5 Mohammadi, N. A. and Rempel, G. L. *Macromolecules* 1987, **20**, 2362

6 Bhattacharjee, S., Bhowmick, A. K. and Avasthi, B. N. *Ind. Eng. Chem. Res.* 1991, **30**, 1086

7 Bouchal, K., Ilavsky, M. and Zurkova, E. *Angew. Makromol. Chem.* 1989, **165**, 165

8 Bhattacharjee, S., Bhowmick, A. K. and Avasthi, B. N. *Makromol. Chem.* 1992, **193**, 659

9 Mishumi, A. (Idemitsu Petrochemical Co. Ltd, Japan), Japan Kokai Tokkyo Koho, JP 62 151 405, 1987

10 Mishumi, A. (Idemitsu Petrochemical Co. Ltd, Japan), Japan Kokai Tokkyo Koho, JP 62 151 404, 1987

11 Isii, M., Takamatsu, H., Ishiura, K. and Minatono, S. (Kuraray Co. Ltd, Japan), Eur. Pat. Appl., EP 319 967, 1989

12 Willis, C. L. (Shell International Research Maatschappy B.V.), Eur. Pat. Appl., EP 301 665, 1989

13 Kato, K., Kishimoto, K. and Kameda, T. (Asahi Chemical Industry Co. Ltd, Japan), Japan Kokai Tokkyo Koho, JP 01 289 206, 1989

14 Takamatsu, H., Kazumari, K., Ishii, M. and Nastake, K. (Kuraray Co. Ltd, Japan), Japan Kokai Tokkyo Koho, JP 01 287 113, 1989

15 Wada, H. and Hara, Y. (Mitsubishi Kasei Corp., Japan), Japan Kokai Tokkyo Koho, JP 01 45 404, 1989

16 Hattori, Y. and Kitagawa, Y. (Asahi Chemical Industry Co. Ltd, Japan), Eur. Pat. Appl., EP 302 505, 1989

17 Bhattacharjee, S., Bhowmick, A. K. and Avasthi, B. N. *J. Polym. Sci., Polym. Chem.* 1992, **30**, 471

18 Bhattacharjee, S., Bhowmick, A. K. and Avasthi, B. N. *J. Appl. Polym. Sci.* 1990, **41**, 1357

19 Bhattacharjee, S., Bhowmick, A. K. and Avasthi, B. N. *J. Polym. Sci., Polym. Chem.* 1992, **30**, 1961

20 Bhattacharjee, S., Bhowmick, A. K. and Avasthi, B. N. *Polym. Degrad. Stab.* 1991, **31**, 71

21 Brück, D. *Kautsch. Gummi. Kunstst.* 1989, **42**, 107

22 Brück, D. *Kautsch. Gummi. Kinstst.* 1989, **42**, 194

23 Marshell, A. J., Jobe, I. R., Dee, T. and Taylor, C. *Rubber Chem. Technol.* 1990, **63**, 244

24 House, H. O. in 'Modern Synthetic Reactions', Benjamin/Cummings, California, 1972, Ch. 1, p. 23

25 Barnard, C. F. J. and Russell, M. J. H. in 'Comprehensive Coordination Chemistry' (Ed. G. Wilkinson), Pergamon, New York, 1987, Vol. 5, p. 1099