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# CHEMICAL MODIFICATION OF NATURAL RUBBER

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## INTRODUCTION

The chemical modification of natural rubber (NR) leads to diversification of its traditional uses. The base polymer of NR can be modified in a number of ways leading to interesting derivatives of NR with new properties. As a challenge to costly imported synthetic substitutes the development of these modified forms of NR seems warranted.

The chemical modifications of the polymer chain in NR can be classified as follows.

a) Isomerisation, without introducing new chemical groups to the molecule

b) Addition or substitution reactions result in an attachment of new chemical groups

c) Grafting reactions of different polymers to the NR molecule

Modifications of type (a) have been extensively investigated in the past and have provided products of commercial interest. Those include cyclised rubber, and depolymerised rubbers. Examples of type (b) modifications are epoxidised natural rubber, chlorinated rubber and rubber hydro chloride. Graft polymers of NR mainly with polymethyl methacrylate fall into the type (c) modifications.

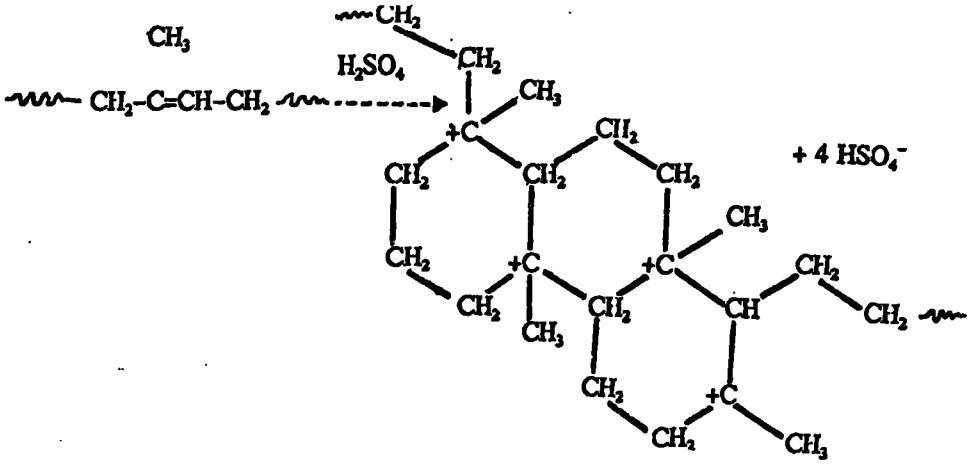
In this work we have directed our attention to the cyclisation of NR from latex as there is a good potential for the cyclised rubber in the surface coating industry.

There are a number of reagents which will bring about the cyclisation of rubber, as evidenced by the fact that the properties of rubber are changed without alteration of the emperical formula and with production of less unsaturated derivative It is a polar reaction occurring by an isomerisation which takes place under the influence of electrophilic agents (Stevens and Miller, 1938) or heat (Staudinger and Geiger, 1927). The first trial on cyclisation was carried out in 1910 and Harries (Harries, 1919) was the first author to publish the work on preparation of cyclised rubber using sulfuric acid as the cyclising agent. Other investigators also studied the

same reaction by using p-toluene sulpfonic acid (Brusion *et al*, 1927) sulfuric acid (Jansen, 1956) and metal halides such as $SnCl_4$, $TiCl_4$ and $FeCl_3$ (Stolka *et al*, 1964).

Cyclised rubber can also be prepared by the reaction with Zinc chloride in Toluene by prolonged heating (Stevens and Miller, 1938). Staudinger and Geiger recognised that the reaction proceeds by isomerisation and intramolecular cyclisation. The double bonds present in the NR backbone involve in formation of cyclic groups causing a reduction in unsaturation. Formation of cyclohexane rings within the polymer chain has been postulated by D'Ianni *et al*, 1946. The mechanism of the reaction was suggested by Van Veersen that random protonation of bonds leads to a formation of bonds giving tricyclic ring structures.

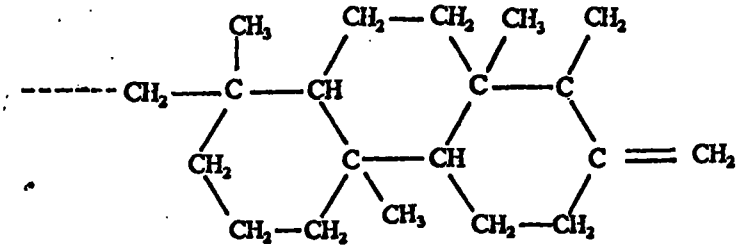
**Cyclisation Mechanism**




(Intermediate Product) Cyclised Rubber

In the first step carbonium ion is formed under the influence of strongly proton donor properties of $H_2SO_4$.

Reaction is completed in the second step giving tricyclohexyl ring structure (I).



The reduction in the number of double bonds is attributed to the formation of cyclic structure (Lee *et al,* 1963). However, they proposed that the left over unsaturation is due to the double bonds forming in this structure. Golub and Heller,1963 have also suggested a tricyclic structure according to their investigations.

Cyclised rubber is a non polar, non crystalline polymer in which the molecular chains have been stiffened by ring formation. The nature of the product varies according to the extent of cyclisation. It can be described as ranging from soft materials through stages of hard, brittle resinous substance to the final stage which may be a white, amorphous powder or tough, fibrous insoluble material or a very brittle shellac–like material. The most important property of the product is the solubility in rubber solvents. In this work we were successful in developing highly soluble cyclised rubber by employing suitable conditions to accelerate cyclisation reaction and to identify the causes which inhibits cyclisation reaction.

## EXPERIMENTAL

### Preparation of Latex

Centrifuged Latex (CL) was prepared by centrifuging the field latex. Stabilised with vulcastab LW(VLW) low nitrogen centrifuged latex was also prepared by field latex treated to remove the protein layer in the rubber particle. Depolymerised latex was prepared by reducing the molecular weight of NR. It was carried out by adding $H_2O_2$ and Sodium Hypochlorite. Resultant latex was centrifuged and molecular weight, nitrogen content and dry rubber content were determined.

Positex was prepared by adding the field latex into a solution of a cationic surfactant.

### Determination of Viscosity Average/Molecular Weight

Molecular weight of the rubber was determined by means of viscosity using the Ubbelhode viscometer. The time taken for different solutions of rubber to flow through the capillary has been measured against the concentration. The time taken by the solvent was also measured. Viscosity averaged molecular weight was determined by the following equation.

$T / (T-T_0) = \mu_{sp}$, specific viscosity

where $T$ = flow time of solution
$T_0$ = flow time of solvent

$\mu_{sp} / C = Y$
$C = X$

By plotting Y vs. X the intercept at Y axis gives concentration.

$\mu = kM^{\alpha}$

$\log M = \log (\mu/k)/\alpha$

For toluene–rubber system $k = 5.02 \times 10^{-4}$

$\alpha = 0.67$

## Cyclisation of Natural Rubber Latex

Commercial grade concentrated sulphuric acid (98% w/v) was added to the latex with stirring and the latex was heated for two hours at 100°C. The mixture becomes purple in colour when the cyclisation reaction is started. Resultant latex was added to a large excess of boiling water. Powder of cyclised rubber was obtained by neutralisation of the latex followed by filtration under vacuum. A fine, white powder of cyclised rubber was obtained by drying the precipitate in air for 1–2 days. The same method has been employed for all types of latices described above.

## Analysis of Cyclised Rubber

*Iodometric analysis*: 0.1g sample of the dry powder was dissolved by shaking in 50 mL of Analar chloroform. To this 25mL of 0.2N Iodine monochloride in carbon tetrachloride was added. The contents were thoroughly mixed by swirling and allowed to stand in the dark for one hour. After that 25mL of 15% potassium iodide solution was added and the contents were agitated. Resultant solutions were titrated with a standard 0.1N sodium thiosulphate solution to a milky white end point.

The level of carbon–carbon double bond unsaturation was measured using the calculation given below.

Iodine value (g $I_2$ per 100g polymer)

$$= \frac{N \times (B-A) \times 126.9 \times 100}{W \times 1000}$$

where N = normality of sodium thiosulphate solution (mol/L)
A = The titre of sodium thiosulphate (mL) in sample
B = The titre of sodium thiosulphate (mL) in blank
W = weight of the polymer used (g)
126.9 = atomic weight of iodin
1000 = conversion factor for milliliters to liters
100 = conversion factor for sample size (100g)

**Infrared analysis**

*Sample preparation*: Cyclised rubber samples were dried under vacuum at 50$^0$C to remove any moisture left. 0.01g of sample was ground with 0.20g of KBr and made into a pellet under vacuum by applying a load of 10 tons.

*Spectrometric measurements*: For each sample, a single beam spectra between 4600 – 400 $cm^{-1}$ was obtained using Shimadzu 9801 FTIR spectrophotometer operating at 4$cm^{-1}$ resolution and 20 co-added scans. The analytical bands chosen to monitor the extent of cyclisation along with their assignments are listed below.

| Peak $cm^{-1}$ | Assignment |
|---|---|
| 1662, 837 | $R_1R_2$ C=CHR |
| 1652, 881 | $R_1R_2$ C=$CH_2$ |

*NMR analysis*: Cyclised rubber samples were dissolved in $CDCl_3$ and diluted with $CCl_4$. A minimum of 20 scans were collected for each spectrum. $^1$H –NMR spectra were run on a Perkin Elmer NMR spectrophotometer (60MHz).

*Determination of glass transition temperature:* Shimadzu Differential Scanning Calorimeter (DSC) equipped with a liquid nitrogen subambient cooling accessory and helium as purge gas was used to determine the glass transition temperature and softening point of CR. Samples of 10mg were used for the analysis. Scanning was done at 20°C/min. Tg value was obtained as the inflexion point.

## RESULTS AND DISCUSSION

Natural rubber (NR) is a polymer of isoprene with 3000–15,000 units per chain and the molecular weight is in the range of $10^6$. NR latex contains about 1–1.5% proteinious substances. Rubber particles are surrounded by layers of lipids and proteins as shown below.

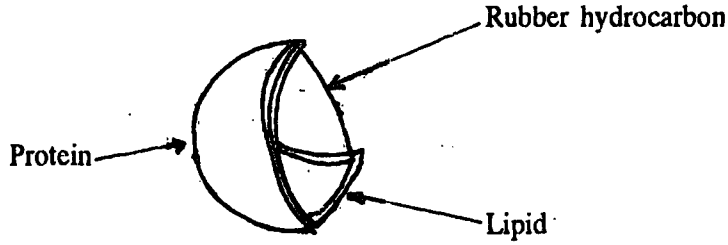



Table 1 gives the molecular weight values obtained for NR treated with two different concentrations of NaOCl and hydrogen peroxide.

Table 1. *Reduction of Molecular weight of NR*

| Type of latex | Molecular weight |
|---|---|
| LNCL | 100,0000 |
| LNDCL(1) | 79,0000 |
| LNDCL(2) | 15,4000 |

Sodium hypochlorite and hydrogen peroxide system produces singlet oxygen, 'O' which reacts with the olefinic double bonds present in NR cleavaging the NR molecule to smaller segments of reduced molecular weight. Due to the high initial molecular weight of NR, cyclised rubber obtained from NR latex is not soluble in organic solvents. Earlier workers have been trying to reduce the molecular weight by masticating rubber for several times. In this study we have managed to obtain 15% reduction in molecular weight (MWt) of NR by controlling the concentration of reagents which are added to latex for the NR chain scission to occur.

Table 2. *Nitrogen contents present in different latices*

| Type of latex/rubber | % Nitrogen content |
|---|---|
| Crepe rubber | 0.30 |
| LNFL | 0.21 |
| LNDCL | 0.07 |
| CL | 0.15 |
| LNCL | 0.11 |

LNCL – Low Nitrogen Centrifuged Latex
LNDCL – Low Nitrogen Depolymerised Centrifuged Latex
CL – Centrifuged Latex
LNFL – Low Nitrogen Field Latex
POSITEX – Latex stabilised by a cationic surfactant and is positively charged.

Table 3. *Effect of the type of latex on efficiency of cyclisation.*

| Type of latex | Nature of the product | Solubility in Solvents |
|---|---|---|
| CL | NO precipitate | – |
| POSITEX | NO precipitate | – |
| LNCL | White, fine powder | Insoluble |
| LNDCL | White, fine powder | Soluble |

Table 4. *Unsaturation of Cyclised and uncyclised rubber*

| Sample | Iodine value | % left over unsaturation |
|---|---|---|
| Uncyclised rubber | 430 | – |
| Cyclised rubber(I) | 267 | 62.2 |
| Cyclised rubber(II) | 250 | 58.0 |
| Cyclised rubber(III) | 200 | 46.5 |
| Cyclised rubber(IV) | 185 | 43.0 |

Nitrogen content of samples of different latices and a sample of crepe rubber are tabulated in Table 2. Deproteinisation of latex has brought the nitrogen content down to 0.07% in LNDCL and 0.11% in LNCL.

For any kind of chemical reaction of rubber hydrocarbon, the chemical reactants have to penetrate through the protein and lipid layers of rubber particle and hence they act as barriers. Therefore the removal of these layers may enhance the efficiency of the reaction.

Low nitrogen latex systems show high efficiency for the cyclisation reaction. LNDCL has the lowest nitrogen content and as a result it is highly reactive towards cyclisation. Cyclised rubber obtained by LNDCL is highly soluble in most of the rubber solvents but the product obtained from LNCL is insoluble.

We have also studied the effect of type of latex on the efficiency of cyclisation reaction. As can be seen from Table 3 some latices do not show any reactivity towards cyclisation. The removal of the protein layer of the rubber particle has a marked effect on the reactivity of the rubber hydrocarbon.

## Characterisation of CR

During the cyclisation reaction resinification occurs and causes the loss of unsaturation. Therefore the extent of modification of the NR molecule determines the properties of the product. The partially cyclised product is rubbery and brown in colour whereas the fully cyclised rubber product is a very fine, white powder.

The characterisation of the product is a very important part of this work. Degree of cyclisation was monitored by change in unsaturation as determined by Iodine values which are given in Table 4. Cyclised rubber gives higher values for unsaturation than the expected values. This could be due to the side reactions occurring during the addition reaction of Iodine monochloride.

IR spectra of cyclised (a) and uncyclised (b) rubbers are given in Figure 1. Intense bands in the region of 2700–3000 $cm^{-1}$ and also in 1450 $cm^{-1}$ region are attested to the $-CH_3$ and $-CH_2$ groups present in both rubbers. As can be seen in Figure 2(a) the peak at 1662 $cm^{-1}$ present in NR which is attributed to the C=C in the polyisoprene unit is shifted to 1652 $cm^{-1}$ in the CR. This is due to the change in the structure of the C=C double bond in CR. Also the presence of exocyclic double bond in CR is clearly evident by the appearance of a new peak at 880 $cm^{-1}$ and the disappearance of peak at 840 $cm^{-1}$ which is attributed to the C–H deformation in trialkyl substituted double bond in NR as can be seen from Figure 2(b). Therefore this is strong evidence to prove that the rubber is fully cyclised.

This observation has been supported by NMR data too. Figure 3 shows the NMR spectrum of NR and Figure 4 shows NMR spectra of different CR samples. It can be seen that three prominent peaks are always present at 0.99 $\delta$, 1.25 $\delta$ and 1.65 $\delta$. The assignments of the groups to which the respective protons belong, are listed in Table 5.

Table 5. *Assignments of peaks in NMR*

| Group | δ |
|---|---|
| $-CH_2-C-$ | 1.65 |
| $-CH_3-C-$ | 0.99 |
| $-CH-C=$ | 1.95 |
| $-CH_2-C=$ | 1.95 |
| $-C=CH_2$ | 4.60 |
| $CH_3-C=$ | 1.25 |

Spectra (d) of Figure 4 is of the highly cyclised rubber sample and (a) is of the less cyclised. The prominent peak at 5.12 δ of uncyclised rubber in Figure 3 is disappearing with the increase of degree of cyclisation. In spectra (d) the most prominent feature is the intense peak at 1.6 δ which indicates that the protons corresponding to $CH_2-C-$ group is very high. This supports the conclusion that this cyclised rubber sample is highly cyclised.

The softening point and Tg of two different CR samples are given below.

| | Tm/°C | Tg/°C | d/cm$^{-3}$g | particle size, micrometer |
|---|---|---|---|---|
| CR(a) | 206 | 87 | 0.95 | 0.34 |
| CR(b) | 220 | 90 | – | |
| Uncyclised NR | – | –70 | | |

High Glass transition temperature of CR represents a higher modification level of the NR chain after cyclisation. Stevens *et al*, 1938 also have observed that the soluble grade of CR possesses a softening point of 220°C. Density of cyclised rubber was found to be 0.95 gcm$^{-3}$ which is lower than the density of most inorganic white fillers.

## CONCLUSION

This study in general shows that soluble cyclised rubber can be prepared by using specially treated natural rubber latex of reduced molecular weight. The degree of cyclisation can easily be monitored by IR spectroscopy or NMR spectroscopy whichever is available. The physical properties of cycilsed rubber reveals that the rubber is fully cyclised.

## ACKNOWLEDGEMENT

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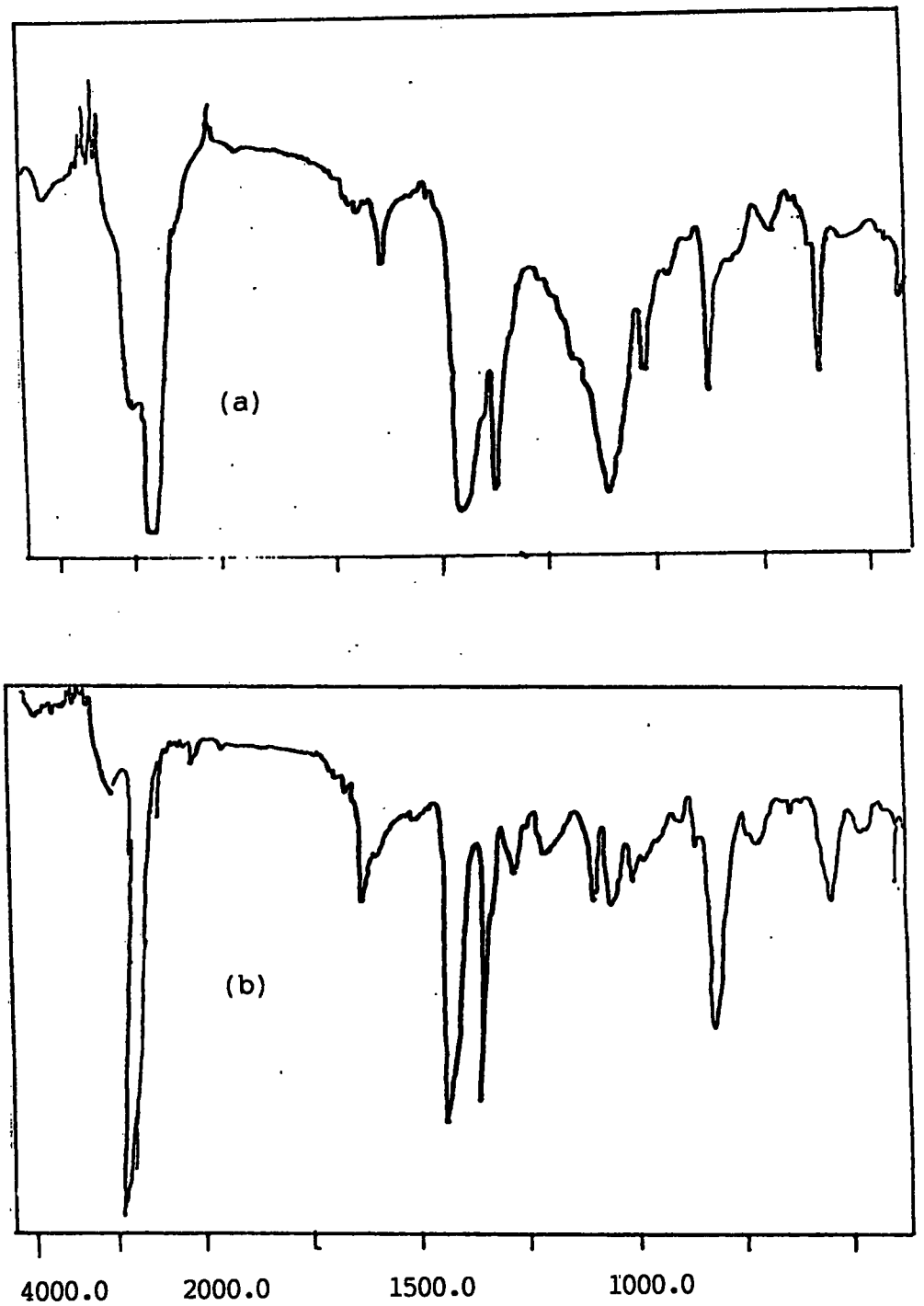
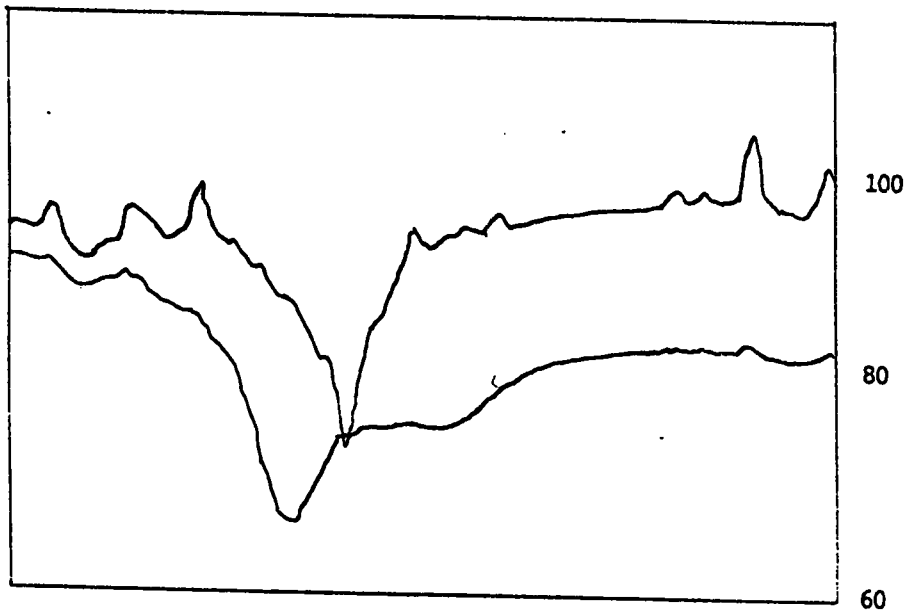
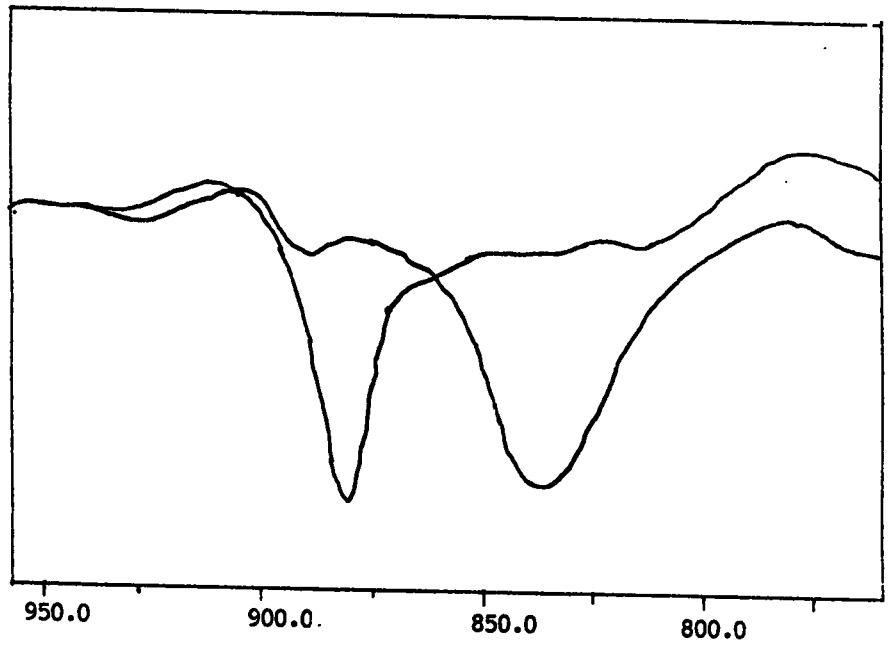



Fig. 1 IR Spectras of (a) Uncyclised rubber
(b) Cyclised rubber




(a) Peaks at 1662 $cm^{-1}$ and 1652 $cm^{-1}$ of NR and cyclised rubber respectively




(b) Peaks at 880 $cm^{-1}$ of cyclised rubber and at 840 $cm^{-1}$ of uncylised rubber

Fig. 2 Analytical bands of IR spectras of uncyclised and fully cyclised rubbers

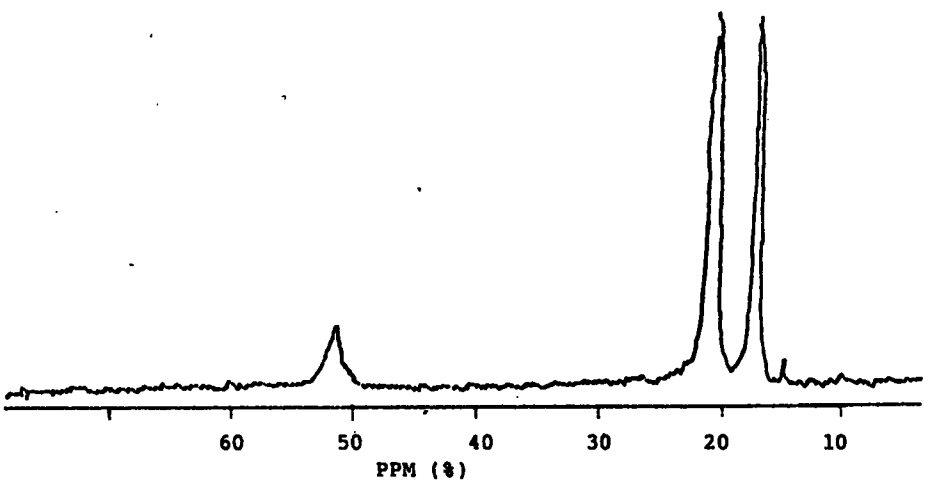



Fig. 3 NMR Spectrum of Natural rubber

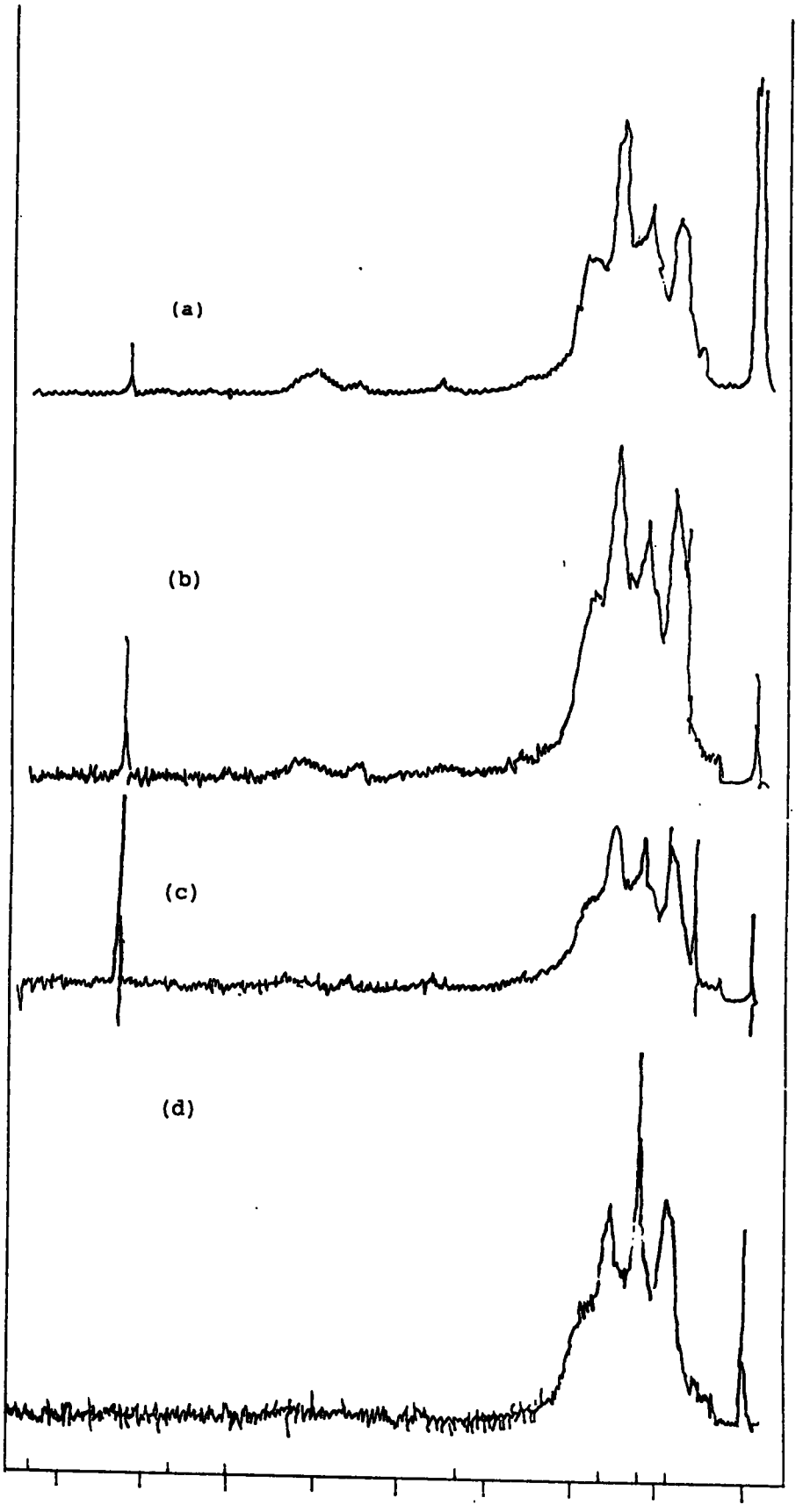



Fig. 4 NMR Spectras of different cyclised rubber samples