CHEMICAL MODIFICATION BY PHOSPHORUS ADDITION

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4.1. INTRODUCTION

Modification of liquid natural rubber was attempted through chemical reactions such as epoxidation and phosphorus addition. These modified forms find use in various specialized applications[1]. Epoxidised rubber improves adhesion of rubber compounds to various substrates. Phosphorus modification was attempted with a view to find application in fire retardant formulations because of the advantage of reduced emission of toxic combustion products of phosphorus containing flame retardant materials, over their chlorine containing counterparts. Easy dissolution of low molecular weight rubber can be taken as an advantage in the preparation of various other forms[2]. Natural rubber contains substantial quantity of gel which makes dissolution of rubber in solvent, a time consuming process. In addition, the concentration of rubber has to be limited to less than 3 to 5 per cent to ensure a free flowing solution. In the present case natural rubber was depolymerized in the latex stage by the action of phenyl hydrazine-oxygen redox system[3], and the depolymerized latex was epoxidised by performic acid, formed in-situ by the reaction between formic acid and hydrogen peroxide[4]. The epoxidised liquid natural rubber (ELNR) was dried as a thin film. The ELNR was purified by solvent extraction and phosphorus addition was carried out by the action of dibutyl phosphate in bulk and also in solution. The scheme of the process is given below.
Scheme of work

NR LATEX
  ▶️ depolymerization

LNR LATEX
  ▶️ epoxidation

ELNR LATEX
  ▶️ coagulation and drying

ELNR
  ▶️ purification with methanol

soluble
  ▶️ insoluble

ELNR A

ELNR B
  ▶️ phosphorus modification

bulk
  ▶️ solution

PELNR I
  ▶️ PELNR III
  ▶️ extraction with dichloromethane

PELNR I
  ▶️ PELNR IV
  ▶️ precipitation in methanol

soluble
  ▶️ insoluble

1P1  1P2
3P1  3P2

2P1  2P2
4P1  4P2
LNR used in this study was produced in latex phase, through the combined action of phenylhydrazine and atmospheric oxygen. Phenylhydrazine with oxygen in air gives phenyl radicals which attack the isoprene chain by addition and transfer reactions. Oxygen is grafted on to the macromolecular radical to form peroxy group, which causes scission of the polymer chain leading to smaller molecules.

$\text{addition} \quad \text{transfer}$

In addition to the main reaction of depolymerization, side reactions are also possible in the presence of excess phenyl hydrazine which can react with carbonyl groups leading to phenyl hydrazones.

*Epoxidation reaction*

Epoxidised natural rubber (ENR) is a chemically modified form of natural rubber which has been commercially established now. It has many salient features like strain induced crystallization, improved adhesion, reduced gas permeation, resistance to hydrocarbon oils.
etc. The reaction of natural rubber and other unsaturated polymers with epoxidation reagents are well documented. Epoxidised polymers are derivatives of ethylene oxide.

Epoxidation is carried out by reacting NR with a peroxycacid, generally performic acid or peracetic acid. By employing suitable conditions for the reaction, it is possible to epoxidise natural rubber to varying degrees from soft rubbery polymer to hard thermoplastic material. With the escalation of petroleum prices the interest in chemical modification of natural rubber to provide a number of polymer derivatives has increased. New attractive routes in latex phase involving relatively low cost reagents have also been attempted.
Epoxidation to different mole percent epoxide levels is possible by selecting suitable concentrations of peracid.

Side reactions

Studies carried out by different workers have revealed that epoxidation of natural rubber latex with peroxy acid leads to the formation of secondary ring opened products influenced by the acid concentration and temperature. Two types of ring opened products have been isolated. At low levels of epoxidation the product is normally a diol. For higher levels of modification, as the number of epoxide groups increases, five member cyclic ether becomes the major product. Furanisation is another type of reaction. Oxidation products that contain ring opened structures have reduced solubility due to crosslinking reaction that follows the epoxidation reaction.

Chemically epoxidation of rubbers is a stereo specific process and the ENR is cis 1,4 polyisoprene with epoxide groups randomly distributed along the polymer backbone. The rate of the reaction is governed by the substituents on the double bond. The ease and positioning of the ring opening epoxides is also controlled by neighbouring groups influenced by electronic and steric factors. Temperature and pH are two important parameters governing the nature of the reaction of rubber with peracids. At low pH and high temperatures, major products are derived from secondary ring opening reactions. So, for the epoxidation of NR, suitable conditions are chosen. The nature of ring opened products depends on the degree of epoxidation. At low modification levels majority of the epoxide groups are isolated due to random reaction, and the major products expected are hydroxy acetals, diols, intermolecular ethers, etc. while at higher levels of crosslinking, cyclic ethers etc., are produced. The extent of epoxidation chosen was 25%. Mild reaction conditions were so employed to minimise secondary reaction products.
4.2. Preparation of ELNR

The reaction mixture containing the depolymerized rubber in latex form was diluted to bring down its DRC. This reduction in DRC helps to reduce the extent of side reactions that can happen during the course of the reaction. Formic acid was poured into the reactor and the contents were stirred well. Adequate quantity of hydrogen peroxide to achieve the desired level of epoxidation was added into the reactor. Stirring was continued and the temperature was maintained at 60°C. Epoxidation of NR with peracetic acid is a second order reaction. Hydrogen peroxide reacts with formic acid to form performic acid that reacts with the hydrocarbon. The first reaction is endothermic while the second is exothermic.

Formic acid generated during the course of the reaction is recycled. The reaction was allowed to continue for 24 h. The reaction mixture was transferred to a beaker and neutralized with sodium hydroxide. The latex was destabilized and the polymer was separated, washed with water and dried at 110°C.

\[ H_2O_2 + HCOOH \rightleftharpoons HCOOOH + H_2O \]

\[
\begin{array}{c}
\text{H}_2\text{C} \\
\text{HCOOH} + \end{array} \quad \begin{array}{c}
\text{C} \quad \text{CH} \\
\end{array} \quad \begin{array}{c}
\text{H}_2\text{C} \\
\text{C} \quad \text{CH} \quad \text{O} \quad \text{CH} \quad + \quad \text{HCOOH}
\end{array}
\]

Epoxidation of NR with formic acid-hydrogen peroxide system.

4.3. Purification

The epoxidised liquid polymer was first purified by extraction with dichloromethane and then by precipitation with methanol. Small amounts of side reaction products formed during the epoxidation reaction were also characterized. Crosslinked products exhibited
reduced solubility and hence little extractability. Precipitation of the polymer with methanol was expected to free it from relatively more polar fractions containing hydroxyl groups with increased solubility in methanol.

The epoxidised polymer mass was taken into a filter paper cone, inserted in a soxhlet extraction apparatus and extracted with distilling dichloromethane, for 24 h. The polymer was extracted almost completely leaving behind traces (0.7 % by weight) of solid residue on the paper cone. The extract containing the polymer in dichloromethane was partially evaporated and slowly poured into methyl alcohol, agitated vigorously using a magnetic stirrer. The polymer separated and the liquid was allowed to stand undisturbed for distinct separation of the layers. The methyl alcohol phase was decanted and the polymer dissolved in dichloromethane was reprecipitated in methanol. It was then dried on a rotavapor and finally in vacuum desiccator at 40°C (ELNR B). The methanol phase was evaporated and was designated as ELNR A. These two fractions were characterized by different analytical techniques.

4.4. Phosphorus modification

Possibilities of improving fire resistance properties of polymers by incorporating halogen, phosphorus and/or metal have been subjected to extensive studies [5,6]. Phosphorus containing polymers are increasingly becoming popular over their halogen counterparts as they give out less toxic combustion products. Thermostability and flame retardancy of polyamide phosphate esters were reported by Kannan et al. [7]. Polymers based on phosphorus containing compounds are expensive and have, therefore, not attained much commercial significance.

Modification of conventional polymers with small amount of phosphorus monomers or oligomers to impart flame retardancy on its own or to improve other products has become
commercially significant. Phosphorus in the presence of catalysts such as iodine, sulphur, sodium, etc. is converted as red phosphorus at 270 to 400°C, a stable non-toxic form. This makes it a useful additive. To prevent decomposition to the toxic and highly inflammable white form, red phosphorus stabilized with additives is added to thermoset resins[8]. Sulphur is used as a vulcanizing agent in natural rubber formulations and in the present study it is expected to play the dual role of vulcanizing agent as well as phosphorus stabilizer.

Phosphorus is believed to act as a flame retardant by a variety of mechanisms. Probably the most important is its ability to increase markedly the conversion of organic matter to char during burning, and thus to decrease the formation of flammable carbon containing gases. The char also helps to protect the substrate from burning interfering with access to oxygen and heat according to Sanders[9].

Fixing of phosphorus on natural rubber backbone, is effected by the reaction between epoxidised liquid natural rubber and dibutyl phosphate. The anticipated reaction between ELNR and dibutyl phosphate is as follows.

The epoxide ring is opened and a five membered ring is formed with the elimination of one molecule of butanol. Crosslinking is another possible side reaction. The phosphorus atom is fixed on to the polymer in either case. The quantity of dibutyl phosphate required for complete reaction with 1 g of ELNR was calculated as follows.
If $n$ is the % epoxidation and $N$ the number of units in 1g of ELNR

weight of 100 units = $100 \times 68 + n \times 16$

$$N = \frac{100}{6800-16n}$$

for 25% epoxidation $N = 0.013888$

quantity of epoxide units in 1g = $N \times n/100 = 3.47 \times 10^{-5}$ mols

or

0.729g of dibutyl phosphate.

The reaction between dibutyl phosphate and ELNR was carried out by two methods, in bulk and in solution. For the reaction in bulk, the required amount of ELNR and stoichiometric quantity of dibutyl phosphate were taken in a corning glass reactor with a cover suitable for attaching a water condenser and a mechanical stirrer. The mixture were stirred well and the temperature of the bath raised to 100°C. Stirring and refluxing were continued for 24 h. The mixture was then transferred to a filter paper cone and extracted with dichloromethane in a soxhlet extraction apparatus for 8 h. The extract was evaporated, dried and designated as 1P1 and the insoluble solid mass left on the filter paper as 1P2.

For conducting the reaction in solution medium, ELNR was dissolved in toluene in a round bottomed flask and stoichiometric quantity of dibutyl phosphate was added. The mixture was stirred well using a magnetic stirrer and heated in the oil bath to 100°C for 24 h under reflux. The resulting homogeneous solution was slowly poured into well agitated methanol so that the polymer got precipitated. It was collected, dried on a rotavapor slowly, and finally under vacuum. The methanol fraction was dried and designated as 2P1 and the separated polymer as 2P2. Two other reactions 3P and 4P were also carried out applying the same conditions and the polymers after modification were purified and designated as 3P2 and 4P2 respectively. All the above samples were subjected to chemical analysis.
4.5. Results and discussion

**LNR:**

Figure 4.1 shows the $^1$H NMR spectrum of LNR. The resonances at 1.69, 2.05 and 5.10 ppm correspond to cis -CH3-C= , CH2-C= and -C=CH- respectively. Figure 4.2 shows the $^{13}$C NMR spectrum of LNR. Five different peaks at 24, 26, 33, 126 and 136 ppm were obtained corresponding to five different states of carbon atoms of the C$_5$H$_8$ cis units. The carbon atoms are identified as 1, 2, 3, 4 and 5 in the figure.

The infra-red spectrum of depolymerized rubber is given in Figure 4.3. Absorption bands at 830 cm$^{-1}$ is due to C=C cis, at 1830 cm$^{-1}$ due to CH$_3$, at 1450 cm$^{-1}$ due to CH$_2$ bending and at 1660 cm$^{-1}$ due to C=C stretching. The weak peak at 1700 cm$^{-1}$ indicated the formation of small amounts of carbonyl groups during the depolymerization process. A broad but small peak was observed in the range of 3400 to 3500 cm$^{-1}$ due to probable presence of -OH and -NH groups in depolymerized rubber. The number average and weight average molecular weights were measured by GPC technique and the results are

$$\bar{M}_n = 7982$$

$$\bar{M}_w = 21060$$

$$\frac{\bar{M}_w}{\bar{M}_n} = 2.64$$

The viscometric average molecular weight $\bar{M}_v$ was determined using an Ubbelhode glass viscometer (0.58 mm diameter capillary) at 25 °C. LNR dissolved in toluene was used for the viscosity measurements. The values of $K$ and coefficient of the Mark-Houwinck equation used are 5.02x10$^{-5}$ (dl/g) and 0.667 respectively. The $\bar{M}_v$ of LNR sample was 10,000.
ELNR:

A quantitative analysis of epoxide groups was made utilizing the $^1$H NMR spectrum by comparison of the integral values corresponding to the proton on the carbon-carbon double bonds with epoxide oxygen. Figure 4.4. gives the $^1$H NMR spectrum of ELNR. The level of epoxidation was calculated from the integrals of the peaks corresponding to olefinic bond at 2.25 and epoxy bond at 2.7, in this case $6/(18+6) = 0.25$ or 25%. In addition to the olefinic protons at 5.1 ppm and epoxy group linked proton at 2.7 ppm, the spectrum revealed protons corresponding to methyl groups at 1.7 (unsaturated units) and epoxide units at 1.3.

A small peak corresponding to the furanisation of epoxide linkages was observed at 3.7 ppm. Hence the spectrum was enlarged in the range 2.5 to 5.4 ppm (Figure 4.5.) and it was found that this reaction has proceeded only to a very small extent.

Figure 4.6. shows the $^{13}$C NMR spectrum of ELNR. Peak assignments corresponding to different carbon atoms in the isoprene structure are also given in the figure.

Infra-red spectra of the compound (Figure 4.7) shows absorption peaks at 870 and 1240 cm$^{-1}$ corresponding to the double bonds and epoxide groups respectively. The peak at 1600 cm$^{-1}$ corresponding to carbonyl group appears weak. Another weak but enlarged peak at 3500 cm$^{-1}$ is indicative of the presence of traces of -OH and -NH groups.

On purification of epoxidised liquid natural rubber two fractions were obtained. Percentage by weight of the two fractions, extent of epoxidation and results of gel permeation chromatographic analysis are given in Table 4.1.
Table 4.1. Properties of ELNR

<table>
<thead>
<tr>
<th>Sample</th>
<th>% by weight</th>
<th>% epoxidation</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>$\bar{M}_w/\bar{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELNR</td>
<td>100</td>
<td>25</td>
<td>6562</td>
<td>20300</td>
<td>4.47</td>
</tr>
<tr>
<td>ELNR A</td>
<td>33.7</td>
<td>29</td>
<td>3554</td>
<td>13500</td>
<td>3.80</td>
</tr>
<tr>
<td>ELNR B</td>
<td>65.6</td>
<td>23</td>
<td>7623</td>
<td>27860</td>
<td>3.65</td>
</tr>
</tbody>
</table>

The low molecular weight fraction indicated a higher level of epoxidation. Latex stage epoxidations are two phase systems and, therefore, heterogeneous. The homogeneity in size of the molecules present in latex also can influence the end products. The size of rubber particles in latex varies from 0.02 to 2 micrometer and, therefore the size difference exhibited by different particles are 100 fold. A higher rate of epoxidation than the diffusion rate of peroxy carboxylic acid into the rubber particle can lead to a heterogeneous product. At higher epoxidation in particular the interior of the particles may be at a lower level of epoxidation while the surface may be 100% epoxidised. The level of heterogeneity varies according to the size of the particle.

Figure 4.7. also compares the infra-red absorption spectra of ELNR before and after purification. The spectra of methanol soluble fraction showed more pronounced peaks at 1700 cm$^{-1}$ pertaining to carbonyl groups and at 3500 cm$^{-1}$ due to -OH groups and -NH groups. The reduction in the respective peaks observed in ELNR B is indicative of the relatively higher purity of the precipitated portion. Figures 4.8 and 4.9 are the $^1$H NMR spectra of ELNR A and ELNR B respectively. Peak at 3.6 was smaller in the case of ELNR B indicating comparatively smaller amounts of furanised product present after purification.
Phosphorus modified polymer:

Results of chemical analysis of the modified polymers showed that the phosphorus content of the samples were consistently different for the preparations in bulk and in solution. The former retained a higher percentage of phosphorus. Higher value of phosphorus content observed for the product prepared in bulk than in solution may be due to retention of small quantities of unreacted dibutyl phosphate in the highly crosslinked mass even after extraction with dichloromethane. Chemical analysis of the polymers was carried out and the results are given in Table 4.2.

Table 4.2. Results of elemental analysis

<table>
<thead>
<tr>
<th>Phosphorus modified polymer</th>
<th>C%</th>
<th>H%</th>
<th>O%</th>
<th>P%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1P2</td>
<td>64.54</td>
<td>9.42</td>
<td>16.30</td>
<td>6.7</td>
</tr>
<tr>
<td>2P2</td>
<td>69.53</td>
<td>9.40</td>
<td>13.75</td>
<td>5.21</td>
</tr>
<tr>
<td>3P2</td>
<td>67.45</td>
<td>9.58</td>
<td>16.21</td>
<td>6.66</td>
</tr>
<tr>
<td>4P2</td>
<td>68.74</td>
<td>9.60</td>
<td>14.88</td>
<td>5.58</td>
</tr>
</tbody>
</table>

The products 1P2 and 3P2 were prepared by the same method, reaction in bulk and their phosphorus content obtained on chemical analysis were close to each other supporting the repeatability of the reaction. So is the case of 2P2 and 4P2 prepared in solution.

Figure 4.10 shows the $^1$H NMR spectrum of the soluble portion extracted with dichloromethane from the reaction products in bulk (1P1). Assignments of atoms corresponding to different peaks are also given. A weak peak appearing at 1.2 is due to the presence of methyl corresponding to the opened epoxide ring. Two small peaks at 2.1 and 5.1
were also observed corresponding to hydrogen atoms attached to epoxide ring and C=C. This is due to the presence of small quantities of unreacted ELNR.

$^1$H NMR spectrum of the methanol soluble fraction from the solution reaction products (2P1) is given in Figure 4.11. Weak peaks at 5.1 and 2.1 due to LNR units were more pronounced than in the case of bulk reaction products. This may be attributed to the more efficient purification of the solution reaction product by precipitation than by soxhlet extraction in the case of the bulk reaction product. The reaction in solution medium being slower might also have a contribution to the residual quantity of the reactants.

Figure 4.12. shows the $^1$H NMR spectrum of the methanol insoluble portion of the solution reaction products (2P2). Peaks corresponding to -CH$_2$, -CH$_3$ and C=CH hydrogen atoms are prominent in the figure indicative of the presence of unsaturated cis 1,4 polyisoprene units. Small peaks were observed corresponding to the butyl group, -CH$_3$ at 1.0 ppm, -CH$_2$ at 1.4 ppm and -OCH$_2$ at 3.8 ppm. Addition of dibutyl phosphate is characterized by a signal which appears between 4.1 and 4.2 ppm which corresponds to -CH in the $\beta$ position of the phosphorus atom.

Figures 4.13. and 4.14. are the $^{13}$C NMR spectra of portions extracted with dichloromethane (1P1) and methanol soluble fraction (2P1) respectively. Peaks are explained under LNR in Figure 4.2. Figure 4.15. is the $^{13}$C NMR spectrum of the purified polymer from the reaction in solution (2P2). Peaks correspond to the carbon atoms in the polyisoprene units.

Figure 4.16. gives the $^{31}$P NMR spectrum of dibutyl phosphate. $^{31}$P NMR spectrum of 1P1 and 2P1 are given in Figures 4.17. and 4.18. respectively. These figures indicated the presence of dibutyl phosphate in the extract (peak at 1.81 ppm). The peak at 16 ppm was
small and revealed the presence of only very small quantities of the phosphorus polymer in the extract. Figure 4.19. is the $^{31}$P NMR spectrum of the modified polymer (2P2). Three different peaks close to each other were observed at 15 ppm corresponding to three different states of phosphorus in the modified compound.

DSC plots of the modified polymers in bulk (3P2) and in solution (4P2) are given in Figure 4.20. Tg values recorded were -34.41°C for 3P2 and -18.31°C for 4P2. The shift in Tg may be due to different extents of crosslinking. The curves indicate that the method in which the reaction is carried out influenced the end product.

Figure 4.21. , 4.22. and 4.23. are the TGA thermograms for the samples in nitrogen, air and oxygen respectively. For both the samples weight changes were noticed in three different stages. Reduction in weight around 200°C may be due to the liberation of volatile material owing to the elimination reaction or labile bond scission, that at 400°C may be attributed to the decomposition of hydrocarbons and that at 600°C upwards, due to the burning of char. The slope of the third change was more pronounced in the presence of oxygen due to faster oxidation of the charred mass.
References:


Fig. 4.1. $^1$H NMR spectrum of LNR
Fig. 4.2. $^{13}$C NMR spectrum of LNR
Fig. 4.3. IR spectrum of LNR
Fig. 4.4. $^1$H NMR spectrum of ELNR
Fig. 4.5. $^1$H NMR spectrum of ELNR enlarged.
Fig. 4.6. $^{13}$C NMR spectrum of ELNR
Fig. 4.7. IR spectra of ELNR and separated fractions.
Fig. 4.8. $^1$H NMR spectrum of ELNR A
Fig. 4.10. $^1$H NMR spectrum of dichloromethane extract (1P1)
Fig. 4.11. $^1$H NMR spectrum of methanol solubles (2P1)
Fig. 4.12. $^1$H NMR spectrum of phosphorus modified polymer (2P2)
Fig. 4.13. $^{13}$C NMR spectrum of dichloromethane extract (IP1)
Fig. 4.14. $^{13}$C NMR spectrum of methanol solubles (2P1)
Fig. 4.15. $^{13}$C NMR spectrum of phosphorus modified polymer.
Fig. 4.16. $^{31}$P NMR spectrum of dibutylphosphate
Fig. 4.17. $^{31}$P NMR spectrum of dichloromethane extract (1P1)
Fig. 4.18. $^{31}$P NMR spectrum of methanol solubles
Fig. 4.19. $^{31}$P NMR spectrum of phosphorus modified polymer (2P2)
Fig. 4.20. DSC plots of modified polymer 1P2 and 2P2
Fig. 4.21. TGA curves of the modified polymers in nitrogen
Fig. 4.22. TGA curves of the modified polymers in air
Fig. 4.23. TGA curves of the modified polymers in oxygen