Geometrical Isomerisation of Polyisoprenes. Part 2. Factors Determining the Trans-alkene Content of Natural Rubber

P.S. FARLEY*

A series of specially prepared samples from a single latex source have been used to investigate the trans-alkene content of bale, crumb and latex grades of Malaysian natural rubber. A minimum level of trans-alkene content arises from polyisoprenoid biosynthesis in Hevea brasiliensis and the average degree of chain branching. Additional cis-trans isomerisation can arise from the acid-catalysed decomposition of sodium metabisulphite, a preservative for field latex, and the conditions under which wet coagula are dried.

Natural rubber is primarily composed of isoprene units coupled together in a cis-1,4-addition mode. However, Tanaka has demonstrated that fractionated samples of natural rubber have a trans-alkene content consistent with the incorporation of 2.0-3.9 consecutive trans-units at the ω-terminal of each polymer chain (Figure 1) corresponding to a modification level of 0.10-0.15 mole% (assuming an average molecular weight of 150 000 - 200 000 and unbranched polymer chains). The presence of trans-alkene units in natural rubber has been confirmed by both 1H and 13C-NMR spectroscopy, but at significantly higher concentrations than that anticipated from polyisoprenoid biosynthesis in Hevea brasiliensis and a theoretical content of 0.10-0.15 mole% should be compared to an experimentally determined average trans-alkene content of 0.45 mole% for samples of natural rubber. Variability in trans-alkene content has been found not to correlate with rubber grade and hence possible sources of additional isomerisation have been considered. The conditions under which field latex is processed to produce natural rubber have been examined for chemical species which can isomerise double bonds in alkenes. Geometrical isomerisation in alkenes is well known and chemical methods to promote isomerisation in cis-1,4-polyisoprenes have been reviewed. A survey of the chemical reagents capable of isomerising alkenes and which could interact with natural rubber during processing leads to the conclusion that sulphur dioxide and nitrogen dioxide may be involved. The treatment of natural rubber with

![Figure 1. Polymer chain structure in natural rubber.](image)

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sulphur dioxide is patented and has been used to increase the trans-alkene content of natural rubber in order to produce a modified polymer which exhibits a retarded rate of crystallisation in low temperature applications. Nitrogen dioxide leads to the facile isomerisation of double bonds in both low molecular weight alkenes and cis-1,4-polybutadiene. Both of these gases are combustion products from hydrocarbon fuels and suggest that the conditions under which natural rubber is dried may determine the extent of isomerisation in the final product.

This paper describes the analysis of a series of natural rubber samples originating from a single latex source which differed primarily in the method of drying.

EXPERIMENTAL

'H-NMR Spectroscopy

'H-NMR spectra were acquired at a Larmor frequency of 400 MHz using a Varian VXR-400 NMR spectrometer. Quantitative data was acquired for sol fractions prepared as 1\% w/v solutions in deuteriated chloroform (CDCl$_3$).

Separation of Sol and Gel Fractions

Samples of natural rubber were adequately separated by swelling in CDCl$_3$. Samples were taken from the centre of each bale to prevent the distortion of results arising from surface chemistry.

Molecular Weight Determination

The molecular weight distribution in natural rubber samples was measured using gel permeation chromatography. Whole samples were swollen in dilute solutions of tetrahydrofuran (0.38\% w/v THF) and filtered through lens tissue to remove macrogel. Sol fractions were isolated from the microgel using ultracentrifugation for 60 min at 30 000 r.p.m. and separated by decantation. Sol fractions were analysed in THF (0.02\% w/v) containing 2,6-di-tert-butyl-4-methylphenol (0.005\%, BHT) as an antioxidant and retention time marker. Rubber solutions were analysed at a flow rate of 0.5 ml/min through four PL gel columns (Polymer Laboratories) in series; three 30 cm columns, 10$^4$ Å, 10$^5$ Å and 500 Å porosity and a 60 cm mixed bed column. UV detection at 215 nm was used and molecular weights were calculated from the hydrodynamic constants determined by Subramaniam.

RESULTS AND DISCUSSION

Geometrical Isomerisation and Biosynthesis of Natural Rubber

'H-NMR spectroscopic analysis of samples derived from bale, crumb and latex grades demonstrates that the trans-alkene content of natural rubber can range between 0.17 mole\% and 0.79 mole\% (Table 1). There is no general correlation between trans-alkene content and grade of rubber although there is evidence for a lower threshold level on trans-alkene content of approximately 0.20 mole\%. This threshold level is generally found for natural rubber derived from latex (in comparison with dry rubber prepared from cup lump, tree lace and earth scrap) and is consistent with trans-alkene content values of 0.20-0.21 mole\% found for samples of commercial 'high-ammonia' (HA) latex concentrate which have been precipitated and dried in vacuo in the laboratory (Table 1). The difference between the experimental (0.20 mole\%) and theoretical (0.10-0.15 mole\%) thresholds is believed to arise from chain branching and the occurrence of several $\omega$-terminal structures in each molecule of natural rubber hydrocarbon.

Geometrical Isomerisation and Oxidation of Natural Rubber

Some oxidation of natural must occur during commercial drying procedures and the suggestion that cis-trans isomerisation is a direct result of the chemistry associated...
TABLE 1. TRANS-ALKENE CONTENT IN NATURAL RUBBER GRADES

<table>
<thead>
<tr>
<th>Rubber grade</th>
<th>Trans-alkene content (mole%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMRL</td>
<td>0.50, 0.44, 0.34, 0.51</td>
</tr>
<tr>
<td>SMR 5</td>
<td>0.24, 0.36, 0.42, 0.79</td>
</tr>
<tr>
<td>SMR 10</td>
<td>0.40, 0.36, 0.37, 0.51</td>
</tr>
<tr>
<td>SMRCV</td>
<td>0.25</td>
</tr>
<tr>
<td>DPNR</td>
<td>0.23</td>
</tr>
<tr>
<td>DPNR (CV)</td>
<td>0.44</td>
</tr>
<tr>
<td>ADS</td>
<td>0.17</td>
</tr>
<tr>
<td>RSS</td>
<td>0.43</td>
</tr>
<tr>
<td>HA latex</td>
<td>0.20, 0.21</td>
</tr>
</tbody>
</table>

*Samples from different bales

with oxidation should be considered. Some support for this suggestion can be derived from a recent study by Chasset and co-workers\(^1\) on variability in crystallisation rate at low temperatures for raw natural rubber. In this study, it was found that differences arose from the temperature of drying with high temperatures resulting in a significant decrease in the rate of crystallisation. Although factors such as the fatty acid content and clonal composition of natural rubber have been claimed to influence crystallisation rate\(^2\), the evidence is circumstantial and the results of Chasset and co-workers probably reflect differences in trans-alkene content. Hence, these results could be interpreted as the promotion of cis-trans isomerism via autoxidation at high temperatures. However, it is evident from extensive NMR studies within these laboratories that geometrical isomerisation does not occur as a result of the free-radical autoxidation of natural rubber\(^3\).

**Geometrical Isomerisation and Drying Procedures**

The potential of flue gas to promote geometrical isomerisation in natural rubber during drying is difficult to prove without access to specially prepared samples. Fortunately, the Rubber Research Institute of Malaysia was able to provide suitable bales which had been prepared from a single latex source and differed primarily in their method of drying (Table 2). The trans-alkene content of each sample was measured.

TABLE 2. ANALYTICAL DATA FOR EXPERIMENTAL NATURAL RUBBER SAMPLES

<table>
<thead>
<tr>
<th>Rubber grade</th>
<th>Colour</th>
<th>10^5 M_n</th>
<th>10^6 M_z</th>
<th>Gel content (wt%, THF(^8))</th>
<th>Drying regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADS</td>
<td>Yellow</td>
<td>1.5</td>
<td>2.36</td>
<td>12</td>
<td>Air-dried sheet</td>
</tr>
<tr>
<td>RSS</td>
<td>Kipper-brown</td>
<td>1.45</td>
<td>2.40</td>
<td>10</td>
<td>Ribbed smoked sheet</td>
</tr>
<tr>
<td>SMRL</td>
<td>Mustard</td>
<td>1.59</td>
<td>2.20</td>
<td>11</td>
<td>Indirect drying</td>
</tr>
<tr>
<td>SMRL</td>
<td>Mustard-brown</td>
<td>1.51</td>
<td>1.91</td>
<td>9</td>
<td>Direct drying</td>
</tr>
<tr>
<td>SMRL</td>
<td>Mustard</td>
<td>1.52</td>
<td>2.20</td>
<td>10</td>
<td>Indirect (15% d.r.c.)</td>
</tr>
<tr>
<td>SMRL</td>
<td>Orange-brown</td>
<td>1.42</td>
<td>1.85</td>
<td>8</td>
<td>Direct (15% d.r.c.)</td>
</tr>
</tbody>
</table>

\(^a\)Number-average molecular weight as determined by GPC

\(^b\)Z-average molecular weight as determined by GPC

\(^c\)Tetrahydrofuran
using $^1$H-NMR spectroscopy (Table 3) and the results were interpreted relative to the standard processing methods used to prepare different grades of Malaysian natural rubber. Ribbed smoked sheet (RSS) grades are prepared from field latex which may initially be treated with an anticoagulant; sodium sulphite, formalin or ammonia may all be used as preservatives according to local plantation conditions. The field latex is bulked and diluted to 15% dry rubber content (d.r.c.) before transfer to coagulating tanks in which the rubber is precipitated using 2% formic acid. The coagulum is left to stand overnight before sheeting and washing. Wet sheets are hung and allowed to partially dry at ambient temperature. Final drying occurs in a smokehouse in which a mixture of hot air and smoke is used, both as drying medium and as a mould deterrent. Traditional smokehouses are based on wood furnaces while more modern smokehouses use an oil-fired heat exchanger to heat the air during smoking. Drying regimes can be classified as direct or indirect according to whether the products of fuel combustion are allowed into the atmosphere of the drying area. Air-dried sheet (ADS) grades are prepared from field latex which is treated with sodium sulphite or ammonium borate to prevent premature coagulation. The latex is bulked at the factory and then treated with sodium metabisulphite to remove oxygen. After dilution to 12.5% d.r.c., the latex is coagulated and the rubber dried in an analogous manner to RSS grades except that smoking is not used. SMR L (Standard Malaysian Rubber Latex) grades are prepared from field latex which may be preserved with sodium sulphite, formalin or ammonia before transfer to bulking tanks. Sodium metabisulphite solution is added to the bulk latex to a concentration of 0.05% on the latex to inhibit discolouration and the bulk latex is coagulated using 2% formic acid. After coagulation, the coagulum is crushed, crumbed and dried.

It is evident from the analytical results (Table 3) for comparable samples that direct drying (i.e. exposure of the rubber to the combustion gases from fuel oil or wood) has yielded an increase in trans-alkene content of 0.10-0.15 mole% over analogues prepared by indirect drying. These results are consistent with additional cis-trans isomerisation arising in the presence of combustion gases since both nitrogen dioxide and sulphur dioxide are well known constituents of flue gas and indirect drying through a heat exchanger precludes contact between flue gas and the drying rubber. The consistency of results for ADS and SMR L (indirect drying) grades (0.24 mole%) relative to the general variability in trans-alkene content within these grades (0.17-0.51 mole%) illustrates the importance of a knowledge of the processing history of each batch of rubber and explains the lack of correlation between trans-alkene content and grade of rubber.

<table>
<thead>
<tr>
<th>Rubber grade</th>
<th>Trans-alkene content (mole%)</th>
<th>$^5\text{M}_n$</th>
<th>Trans-alkene units per chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADS</td>
<td>0.24</td>
<td>1.50</td>
<td>4</td>
</tr>
<tr>
<td>RSS</td>
<td>0.30</td>
<td>1.45</td>
<td>4</td>
</tr>
<tr>
<td>SMR L (Direct)</td>
<td>0.38</td>
<td>1.51</td>
<td>6</td>
</tr>
<tr>
<td>SMR L (Indirect)</td>
<td>0.24</td>
<td>1.59</td>
<td>4</td>
</tr>
<tr>
<td>SMR L (Direct, 15% d.r.c.)</td>
<td>0.35</td>
<td>1.42</td>
<td>5</td>
</tr>
<tr>
<td>SMR L (Indirect, 15% d.r.c.)</td>
<td>0.24</td>
<td>1.52</td>
<td>4</td>
</tr>
</tbody>
</table>
Further analysis of the results (Tables 1 and 3) for dried HA latices (0.20-0.21 mole\%) relative to the experimental ADS and SMR L (indirect drying) grades (0.24 mole\%) shows a small increase in trans-alkene content (0.03-0.04 mole\%) for latex grades which have been treated with sodium metabisulphite during processing. Sodium metabisulphite decomposes in acidic conditions to yield sulphur dioxide and hence the coagulation of latex grade rubber in the presence of formic acid would be anticipated to increase trans-alkene content as found experimentally.

The trans-alkene content of the RSS sample (0.30 mole\%) is significantly higher than that found in the indirectly dried samples (0.24 mole\%) and the ADS sample (0.24 mole\%), but lower than that found in directly dried rubbers (0.35-0.38 mole\%). It is believed that this comparison reflects the relative lack of both sulphur dioxide and nitrogen dioxide formation from the burning of wood in comparison to fuel oils (in which the intrinsic nitrogen and sulphur content are both highly variable, but tend to be higher than in wood).

Overall, the observed variability in trans-alkene content within a rubber grade (Table 2) results from the heating of smokehouses and drying tunnels by either wood or fuel oils, directly or indirectly.

There are several methods to remove sulphur and nitrogen oxides from flue gas\(^\text{21,22}\), however, since these gases promote cis-trans isomerisation in natural rubber and have a resulting beneficial effect on the physical properties of natural rubber (i.e. the retardation of crystallisation at low temperatures\(^\text{17}\)), there is no compelling reason why flue gas should be purged of these gases. However, the resultant increase in the trans-alkene content of natural rubber is not controllable and it would be preferable if a controllable isomerisation reaction could be substituted in its place.

**Nitrogen Dioxide and Enhanced Oxidative Scission**

Enhanced cis-trans isomerisation during direct drying processes is believed to result from the action of sulphur dioxide and nitrogen dioxide. Nitrogen dioxide is known to abstract allylic hydrogen atoms from model alkenes\(^\text{25}\) and polymers\(^\text{24,25,26}\) in a facile manner and may therefore promote oxidative scission in cis-1,4-polyisoprenes. Under the conditions of direct drying, nitrogen dioxide is formed in the presence of oxygen and there is evidence for enhanced oxidative scission in unsaturated polymers\(^\text{25,26}\) arising from a synergistic combination of the two gases. Comparable information for sulphur dioxide is not extensive, but this gas does promote chain scission for polymers in the presence of oxygen\(^\text{24}\).

**CONCLUSIONS**

\(^{1}\)H-NMR spectroscopic analysis of natural rubber samples derived from a single latex source and processed using a range of different conditions has shown that the trans-alkene content of natural rubber arises from a variety of sources. The extent of cis-trans isomerisation results from the cumulative effects of isomerisation during the biosynthesis of cis-1,4-polyisoprene, the degree of chain branching, the decomposition of sodium metabisulphite (for latex grades) and the conditions under which the wet coagulum is dried.

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