

## Thesis Summaries

### Thermal Degradation of 1,4 Polyisoprenes Including Natural Rubber

In a novel application of the technique of pyrolysis of natural rubber (*cis* 1,4-polyisoprene, NR) by high-frequency induction heating not employed previously, NR was compounded with ferromagnetic powders to ensure uniform heating throughout the samples. Although rubber samples of only 0.5 - 4.0 g in size were used in the study, this technique could be used for much larger samples, the limiting factor being the size of the cavity inside the radio-frequency coil, notwithstanding NR conducts heat very poorly.

The pyrolysis of NR was found to yield the monomer, isoprene (2-methylbuta-1,3-diene), and an isoprene dimer, dipentene [1-methyl-4-(1-methylethenyl) cyclohexene] as the two major products. A second isoprene dimer, formed in about a tenth the yield of dipentene, was found to be unequivocally 2,4-dimethyl-4-ethenyl-cyclohexene (2,4-DMEC). Other isoprene dimers such as 1,4-dimethyl-4-ethenylcyclohexene (1,4-DMEC) and diprene (the 2-methyl isomer of dipentene) were not formed.

With the experimental set-up employed in this study, variation in pyrolysis conditions produced maximum yields of isoprene and dipentene in the regions of 30% and 20% (on original weight of rubber pyrolysed) respectively, while yields of 2,4-DMEC did not significantly exceed 2.0%. The bulk of the remaining pyrolysis products consisted of fragmented polyisoprenes of low molecular weight (mainly five to ten isoprene units). Although the major proportion of the fragmented polyisoprenes consisted of the *cis*-1,4-structure, there were some *trans* 1,4-, 3,4- and 1,2-structures, and some cyclisation had occurred.

Variations in pyrolysis conditions, the presence of additives such as metals and metallic oxides (but not acidic alumina), as well as the use of furnace heating, instead of induction heating, were found only to change the pyrolysis products quantitatively but not qualitatively. The presence of additives did not enhance very much the yields of the pyrolysis products. Formation of new products, principally *p*-cymene, was observed during pyrolysis in the presence of acidic alumina and palladium on alumina. This difference was attributed to some disproportionation of dipentene catalysed by the mentioned additives. Both *cis* and *trans* 1,4-polyisoprenes were also found to form similar products both qualitatively and quantitatively. This similarity was used as a basis for the selection of several all *trans* 1,4-oligoisoprenes as model compounds in the pyrolysis study of NR.

The pyrolysis of squalene (a hexaisoprene) and digeranyl (a tetraisoprene) yielded identical products, with the monomer isoprene, as the most abundant product. The other significant products are diisoprenes, namely dipentene, diprene, 1-*p*-menthene [1-methyl-4-(1-methylethyl) cyclohexene], *cis* and *trans* 2,6-dimethylocta-2,6-dienes, 3,3,6-trimethylhepta-1,5-diene (TMHD) and 2,4-DMEC. The formation of diprene is particularly significant as it is postulated to be a consequence of the tail-to-tail isoprene sequence present in both model compounds.

In the pyrolysis of NR the formation of isoprene dimers by Diels-Alder dimerisation of isoprene is considered to be insignificant. This would be particularly the case where the pyrolysis products were removed immediately from the reaction zone. Dimerisation of isoprene in a sealed tube under pyrolytic conditions was found to yield all the six-

and eight-membered ring dimers, while in the pyrolysis of NR only dipentene and 2,4-DMEC were formed.

The minimum temperature at which NR began to undergo main-chain scission under anaerobic conditions was 200°C – 210°C. Dipentene was the only volatile product formed and detected at this early stage of degradation. A very stable radical believed to be highly conjugated in nature also began to form at similar temperatures. It appeared that the conjugated species was associated with the gel which was formed at the same time. Structurally, the degraded NR also contained cyclic structures. Evidence for isomerisation of 1,4-polyisoprene units to 3,4- and 1,2-structures was not conclusive. The similarity or dissimilarity of the cyclic structures to those in acid-cyclised 1,4-polyisoprene was not established but the formation of condensed cyclic structures by a free-radical mechanism was unlikely.

The investigation on vulcanised NR with crosslinks of the same nature as that of the isoprene link supported anaerobic thermal degradation commencing at 200°C – 210°C. Thus, the evidence for the production of dipentene, the formation of stable radicals and the drastic drop in the modulus (MR 100) of vulcanisates all suggested that 200°C was the temperature for NR to be subjected to, as in the vulcanisation process. However, in high-temperature vulcanisation (180°C – 200°C) the time employed is usually very short (several minutes) and thermal main-chain scission would be insignificant. If rubber were to be exposed to temperatures of above 200°C for longer time periods (>1 h) deterioration of physical properties due to main-chain scission was likely to become serious.

Under certain pyrolysis conditions, dipentene formed from the pyrolysis of *cis* 1,4-polyisoprenes was found to undergo a dis-

proportionation reaction. This disproportionation reaction and the thermal cyclisation of *cis* 1,4-polyisoprenes are controlled by compounding ingredients and minor constituents in the polymer, thus enabling one to differentiate between natural and synthetic *cis* 1,4-polyisoprenes.

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### **Microbiological Studies on *Hevea* Latex with Particular Reference to Its Keeping Quality and Coagulation**

Although latex within the rubber tree is sterile, after tapping it becomes heavily contaminated by micro-organisms which proliferate rapidly at the expense of the non-rubbers, destabilising it in a matter of hours. The sources of contamination were traced to tree lace, tapping panel, bark and cuplump serum. The bacterial populations of fresh latex increased to log 8.90 per millilitre in about 8 h with partial coagulation of latex. On the other hand, sterile latex remained fluid without any drop in pH for about two weeks, indicating that the destabilisation of latex is primarily a microbial phenomenon. Sucrose, glucose and fructose and to a certain extent galactose were found to be important substrates for volatile fatty acid (VFA) formation in latex.

Investigations carried out to preserve latex for short and long periods showed that field latex can be kept fluid indefinitely by ammoniating it to pH 9.0 and maintaining the pH by continuous addition of ammonia until a stage is reached when no further additions are required. Alternatively, this can be achieved by urea on its own or in combination with ammonia. Latex thus

stabilised still contains large numbers of bacteria but they are inactive.

Further investigations showed that pre-treatment of the field latex with a small amount of a secondary preservative at the earliest possibility, prior to centrifugation, followed by topping up the concentrate with a further small amount of the same preservative ensures a better concentrate than the one in which the secondary preservative has been added only to the concentrate. A composite system consisting of low levels of ammonia, TMTD and ZnO preserved the field latex for days without any rise in volatile fatty acid. The system was so efficient that it enabled the processing of latex from smallholdings into good quality concentrate or dry rubber.

The addition of carbohydrate substrates such as molasses and pineapple waste juice (assisted biological coagulation) expedited the natural coagulation of latex by natural microbial populations. The addition of latex serum also speeded up the coagulation, reducing the gelling time to almost half. Factors bringing about this effect were associated with cations such as calcium and magnesium salts and the microbial populations.

Although assisted biological coagulation offered some distinct advantages over the natural coagulation system, the former still required about 20 h for coagulation of field latex and considerably longer for latex containing anticoagulants. However, incorporation of an anionic surfactant such as dioctyl sodium sulphosuccinate (in addition to the 0.4% molasses needed for assisted biological coagulation) reduced coagulation time to about 8 hours. The resulting rubbers had excellent heat build-up characteristics. They were also generally fast-curing.

Deammoniated skim latex (pH 8.5–9.0) could be biologically coagulated by the addition of 0.1% dioctyl sodium sulpho-

succinate and 1.0% calcium chloride. The coagulation time required for spontaneous coagulation was reduced to two days from five days. The resulting rubber was much less smelly and had improved technological properties compared to those made from auto and acid coagulation.

A partially deproteinised rubber with 25% reduction in nitrogen was obtained by coagulating latex with dioctyl sodium sulphosuccinate. Deproteinisation was also carried out by proteolytic enzymes such as Papain and Superase. Papain coagulation reduced the nitrogen content to about 0.3% (35% reduction) for field latex rubber, to about 0.2% (57% reduction) if there was prior dilution of latex to 10% dry rubber content, and, to 0.1% (79% reduction) if treated additionally with octylphenol-ethylene oxide condensate (Nonidet-P40). Papain coagulation, however, increased the ash content of the resulting rubber while the use of Nonidet-P40 in excess of 0.5% delayed the coagulation. Papain treated rubber gave low heat build-up and good dynamic properties. Deproteinisation was also achieved by the use of Superase but it was less effective than Papain. Skim latex completely coagulated in two days, when deammoniated to pH 8.5 and treated with 1.0% Papain. The dry rubber contained about 64% less nitrogen, resulting in improved technological properties.

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#### **Laboratory Study on Leaf Gas-exchange Characteristics of *Hevea brasiliensis* Muell. Arg. and their Relationship to Field Performance Data**

The basis of argument in this study is that dry matter accumulation is almost exclu-

sively derived from the product of photosynthetic carbon input. Though it is realised that productions, especially, those not directly related to dry matter accumulation, need not be directly related to photosynthesis, production cannot exceed the rate of carbon input. From a literature review on the variations in the photosynthetic rate of several species and their relationship to yield, it was evident that by increasing the rate of photosynthetic carbon input, yield performance could be ameliorated.

To standardise leaf age physiologically in this experiment, a concept known as the 'Leaf Blade Class' (BLC) was developed. This concept takes advantage of the developmental habit of *Hevea* leaves *i.e.* the increase of the angle between the leaf blade and the leaf stalk. The ability of this concept to describe *Hevea* leaf development morphologically, anatomically and physiologically was shown. Photosynthetic rates of seven *Hevea brasiliensis* clones, namely: RRIM 600, RRIM 612, RRIM 527, PB 5/51, Tjir 1, Gl 1 and F 351, were studied and significant variation in the rates was observed. This variation was associated more with the stomatal and carboxylation resistance rather than the mesophyll resistance though the latter showed a higher value. The magnitudes of the resistance to CO<sub>2</sub> diffusion compared to other plant species were discussed. The study of *Hevea*'s physiological variables – namely photosynthetic rate, dark and light respiration rates and carbon dioxide compensation concentration showed that *Hevea* is a C<sub>3</sub> plant, but having the lower carbon dioxide compensation concentration.

Based on the descriptive field growth dynamics, the clones used in this experiment were divided into two groups. *Group I* consists of clones having high latex production and low growth rate and *Group II* consists of clones having low latex production but high growth rate. Relating the photosynthetic rates of these clones at saturated irradiance to their yield showed a significant positive correlation and the partitioning efficiency of the clones could be discerned. In a separate correlation study relating partitioning efficiency expressed by the ratio of maximum photosynthesis to yield, ( $P_{max}$ : yield) it was shown that these two entities were highly correlated suggesting that economic yield of *Hevea* was highly dependent on the partitioning efficiency.

A relationship between laboratory and field data was made to assess the ability of the gas-exchange study to be incorporated in the schemes of *Hevea* latex production amelioration. Based on the data collected in this study, a simplified version of this procedure which is fast, easy and cheap, namely: the study of stomatal frequency and dimension, carbon dioxide compensation concentration and water regulation efficiency was suggested. Some explanations to empirical experimental results were also attempted using the data in this study which helped to explain the crown budding experimental results.

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