STUDIES IN HEVEA RUBBER
Part II
## The Gel-Content of Rubber in Freshly-Tapped Latex

By

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Extraction of vacuum-dried films, prepared from fresh latex, with purified petroleum ether under conditions avoiding agitation or disturbance of the rubber reveals the presence of a considerable proportion of gel rubber, even when the latex is extracted from the tree by a technique avoiding contact with the air or exposure to light. Evidence is presented indicating that the gel component is cross-linked, but that cross-liking is confined to the individual latex particles, i.e. as microgel. Storage of latex increases the gel content, and the gel then appears to be more extensively cross-linked.

It has long been known that by diffusion into a non-polar solvent *Hevea* rubber can be divided into two distinct components. The two components, which from early days have been designated " sol " and " gel ", differ in solubility and composition; for whereas sol rubber dissolves easily without much preliminary swelling and is comparatively free from nitrogenous and mineral constituents, gel rubber retains the bulk of these impurities and swells without dissolving in non-polar solvents. The distinction between " sol " and " gel " is however not well defined. Mechanical agitation, addition of a polar liquid, access of traces of oxygen to the diffusion system, or the presence of small amounts of peroxidic impurity in the solvent, substantially increase the proportion of sol to gel rubber. Kemp and Peters[1] have in fact suggested that sol rubber is an oxidation product of gel rubber.

To what extent gel rubber owes its insolubility to its association with nitrogenous or other non-rubber material, or to oxygen-bridging, has not hitherto been determined with any certainty owing to the practical difficulties of establishing the existence of primary linkages in the presence of nitrogenous and mineral impurities. It is known that even after extensive purification under conditions precluding chemical fission of bonds a small amount of nitrogen (.01 to .03%) remains firmly bound with the rubber[2, 3], and even this amount might be

FIG. I CONSTANT EXTRACTION APPARATUS

N₂ → N_2
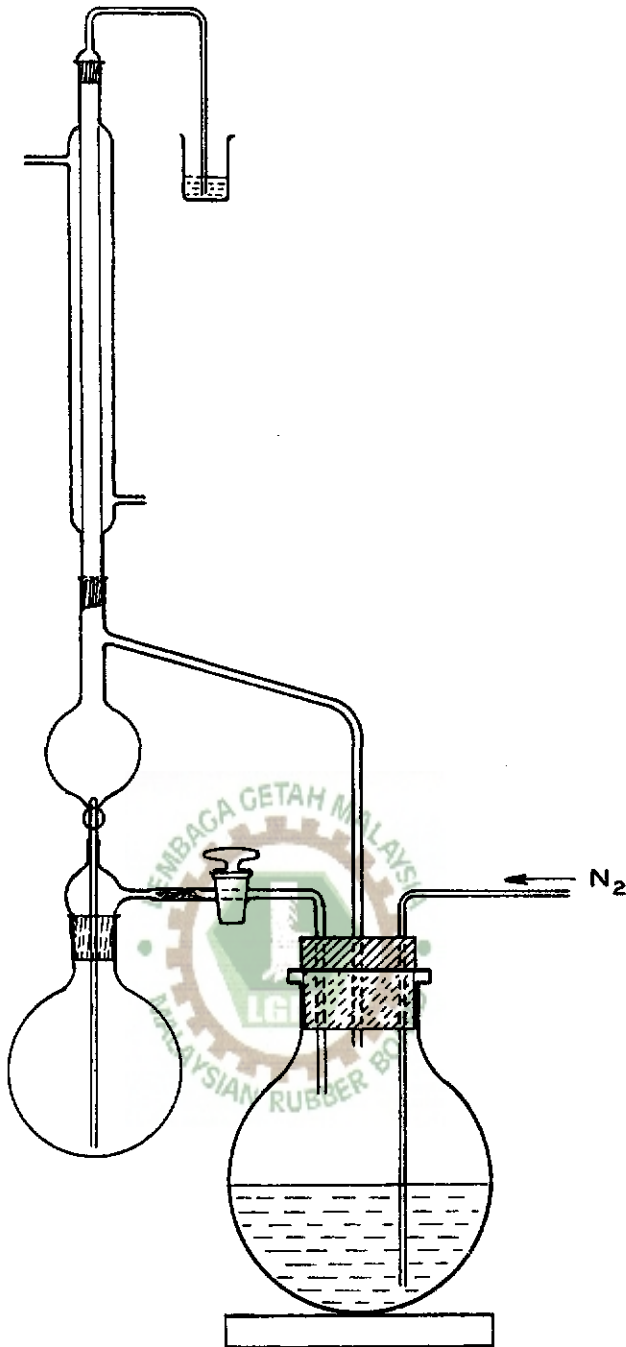
sufficient to account for the insolubility and swelling of gel rubber if it were efficiently combined in cross-linkages. The same line of thought applies to considerations of the oxygen-content of gel rubber.

The gel content of fresh Hevea rubber

Owing to the sensitivity of sol-gel separation to traces of oxygen and to peroxidic or polar impurities in the solvent, estimates of the proportion of the gel component of rubber have varied enormously and in only a few reports ([1, 4]) is there any reliable evidence of significant variation in gel content from one sample of rubber to another. Kemp and Peters([1]), using rubber films prepared, under nitrogen, from freshly-imported ammoniated latex found only a small proportion of sol rubber ($<10\%$) which increased considerably on passage of the rubber through a mill or treatment of the latex with hydrogen peroxide. On the other hand Verbrugh([5]) recently reported that latex tapped in the dark, dried rapidly under nitrogen and extracted with petroleum in a constant extraction apparatus operating in a nitrogen atmosphere was completely soluble and contained no gel phase; exposure of the latex to light during and after tapping prolonged the time required for dissolution but the rubber still dissolved completely. Verbrugh gave no information on the source of his latex, nor on precautions taken to purify the solvent; experience in Malaya has shown that even reagent grade petroleum rapidly becomes peroxidised (as revealed by the Kharasch ferrous thiocyanate reagent([6])) on tropical storage.

Examination of a number of latices under conditions rigidly precluding access of oxygen during extraction, and using only petroleum (b.40-60) which had been first distilled under nitrogen, then passed through a column of alumina and redistilled under nitrogen, and shown to be free from peroxides, revealed the presence of a definite gel component in the rubber phase.

In these extraction experiments a slightly modified form (Fig. 1) of the conventional constant extractor was used. The principal and most essential modification was the introduction of the stopcock in the overflow line between extraction flask and boiler. This stopcock was opened just sufficiently to allow overflow to keep pace with the rate of solvent feed from the reflux condenser (about 30 drops per minute). A slow rate of solvent feed was essential to prevent disturbance of the contents of the extraction

flask, resulting in small specks of gel being floated out of the flask. It was also found advantageous to insert a loose plug of cotton-wool in the overflow line just in front of the stopcock. Unless these precautions were taken a considerable amount of gel was carried over into the boiler, and in one instance with the extractor running fast all of the gel was carried over giving apparently 100% sol rubber. The method of charging the extractor is worthy of mention. The extraction flask (250 ml.) was detached and 2.5 ml. of freshly tapped latex were placed in it after displacing the air with nitrogen. The flask was immediately connected to a high vacuum system, protected by an efficient liquid air trap while distributing the latex in a thin film over the inside of the flask by imparting a rotary motion to it. Drying was complete in a few minutes. Purified nitrogen* was admitted to the flask and the apparatus was assembled. The entire apparatus was then evacuated and filled with nitrogen. Petroleum was placed in the upper reservoir, and nitrogen bubbled through it to displace any dissolved air absorbed while pouring it into the apparatus; this petroleum was then allowed to fill the extraction flask, displaced nitrogen escaping through the overflow line. 500 ml. of petroleum were placed in the boiler flask and the whole set-up was allowed to stand for 24 hours before constant extraction was started by gently warming the boiler. Extraction was run for 96 hours in the dark.

After dissembly, the gel was isolated by siphoning off as much liquid as possible from the extraction flask and consolidating the residue in acetone. The sol was concentrated to small bulk and isolated by precipitation with acetone, so eliminating acetone-soluble components.

Results of extraction of latex films from some of the trees studied in Part I are shown in the table, and to ascertain whether the drying of latex contributes to gel-formation an extraction of a sample of liquid latex is included for comparison. Gel contents are considered to be reproducible to within 5%.

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* Pure nitrogen (oxygen <.001) was specially imported from England through the courtesy of Messrs. Industrial Gases (Malaya) Ltd., to whom the author's thanks are due. It was further purified by passage through alkaline pyrogallol and was shown not to discolour hot freshly-reduced copper.

Gel content of fresh-latex films

Source of Latex	% Gel	Conditions of tapping
Tree No. 11 ..	44	Tapped into dark bottle.
	50	Ditto, liquid latex in extractor.
„ 15 ..	71	Tapping cut obscured with dark paper, collection in dark bottle under nitrogen.
„ 1 ..	21	Tapped into dark bottle under nitrogen.
„ 14 ..	27	
„ 2 ..	59	
„ 17 ..	67	
„ 3 ..	42	Latex extracted from tree in darkened sterile latex extractor under nitrogen[8].
Estate 1 ..	63	Normal bulked estate latex.
„ 2 ..	52	Normal bulked estate latex.

In every sample examined the rubber contained a considerable proportion of gel, even under those conditions most rigorously excluding access of light, air, and bacterial infection. The gel remained in the flask in the form of small flocculent particles suspended in the solvent, accompanied by some greatly swollen gelatinous matter in the case of the rubber of highest gel content. Most of the gel passed into " solution " when the flask was gently agitated, giving a cloudy " solution " in contrast to the clear solution of the sol phase. This behaviour is similar to that of the microgel component of GR-S synthetic rubber (Baker[7]) and by analogy with the latter it is believed that the gel in Hevea latex also consists of microgel i.e. hydrocarbon material cross-linked within the latex particles, in contrast to the very insoluble macrogel component of smoked sheet which does not disperse with gentle agitation and is accordingly believed to be more extensively cross-linked.

It is doubtful whether the intrinsic viscosity of gel rubber exceeds that of sol rubber and it may in fact be smaller in so far as it is possible to estimate the former from a guess at the non-rubber content of the gel, thus tree 15 gave intrinsic viscosities 6.96 and 5.92 for the sol

and gel components respectively while an acetone-extracted dried rubber film from the original latex had intrinsic viscosity 6.7.

When the tree 15 latex was purified by addition of ammonium laurate and multi-creaming to a low nitrogen content (0.04% N in rubber) 41% gel was found. Tree 14 latex similarly treated gave 20% gel. The reduction in gel content compared with the unpurified latices cannot with certainty be attributed to removal of impurities, owing to unavoidable exposure to air for brief periods although the creaming was conducted in a nitrogen atmosphere using only boiled-out and nitrogen-saturated solutions. The significant fact is that the gel content was not reduced to a greater extent than that observed. The purified gels could not be redissolved, consequently intrinsic viscosities are not available. The intrinsic viscosities of the sol phases were 8.42 (tree 15) and 7.4 (tree 3) while the corresponding purified rubbers before sol-gel separation had intrinsic viscosities 7.12 and 7.21 respectively, indicating that the gel had lower intrinsic viscosity than the sol. This is in accordance with the idea that dispersed microgel may contribute less to the intrinsic viscosity than would a linear polymer of comparable chain length. Baker[7] considers that microgel molecules provide models intermediate between loose coiled chains yielding " Standinger-Kuhn viscosities " and the hard spheres of " Einstein viscosities ", and has suggested that the ready dispersion of GR-S-microgel by addition of small amounts of polar liquids to the solvent is indicative of hydrogen-bonds rather than more stable primary linkages. The same may well be true of Hevea microgel.

Purified ammoniated (0.5%) latex from tree 15 increased in gel content from 41% to 68% after 20 days storage, and bulk latex from 63% to 80% after 9 months storage. (The Mooney viscosity of the smoked sheet from the latter stored latex was 108, recovery 51, compared with 89, recovery 35 for smoked sheet from the original latex). Unlike the gel in rubber from fresh latex, the gel components separated from the stored latex rubbers were not flocculent and could not be dissolved by gentle shaking, and it was also observed that long-stored ammoniated latices could not be brought completely into solution in benzene by the technique described in Part I. In their study of the solubility of films prepared in an inert atmosphere from latex, Kemp and Peters[9] reported a considerable reduction in the hexane-soluble fraction

when fresh latex was ammoniated and stored for relatively short periods. Hence storage of latex undoubtedly leads to more extensively cross-linked regions, but cross-linking must of necessity still be confined to the latex particles. The increased cross-linking may be connected with the fusion and growth of latex particles observed in the motion picture studies of Lucas[10].

The foregoing investigation provides unambiguous proof of the existence of a gel phase in the rubber particles in latex freshly tapped from the tree. This phase has several characteristics of microgel.

This paper forms part of the programme of fundamental research undertaken by the Boards of the British Rubber Producers' Research Association and the Rubber Research Institute of Malaya. The author particularly desires to record his appreciation of the co-operation of Mr. M. W. Philpott, Head of the Chemical Division of the Rubber Research Institute.

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