Structural Characterisation of Wild Rubber: Gel Content

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Samples of natural rubber extracted from wild trees from the Euphorbiaceae and Moraceae families were deproteinised and transesterified to study their gel content. The formation of soluble (soft) gel depends on the period of storage of latex in the tree. Extended storage may cause crosslinks between the polymer chains to make hard gel. The presence of soft gel and the composition of the latex varied with the botanical family.

Natural rubber (NR) coagulated from Hevea fresh latex contains a small amount of insoluble material known as microgel. When a Hevea tree is tapped for the first time, the gel content can be of 70% or more^{1,2}. However, the rubber obtained from trees regularly tapped and evaporated quickly contains less than 5% of microgel³. This gel is different from the microgel formed during the storage of the latex after tapping^{3,4}. The gel formation during the storage of the dry rubber involves a different mechanism than in the latex: the former is accelerated in conditions of low humidity. Therefore the gel content in natural rubber depends on the history of sample; it varies according to the polarity of the solvent used and the time of dissolution. This indicates that the gel phase is not only composed of chemically crosslinked chains but also of polar forces (induced dipole, hydrogen bridges, etc.) which can be decomposed by the addition of polar solvents⁵. The gel phase of NR contains

nitrogenous compounds and mineral substances higher than the sol phase. It was postulated that in the gel phase, proteins through hydrogen bridges would link the chains⁶. This is confirmed by the observation that the gel content in rubber coagulated from latex, conserved with ammonia, decreases after purification⁷.

The FTIR studies of the gel phase of the natural rubber of *Hevea* revealed that the hydrogen bridges involve the amide of proteins and the carboxyl of esters, which were confirmed by the shift of the N-H and C=O stretching bands with the increase in temperature⁸.

The aim of this paper is to verify the behaviour of gel formation in wild rubbers other than *Hevea brasiliensis* Muell. Arg. The latex of three species of the *Hevea* family (*Euphorbiaceae*) and two species of *Ficus* (*Moraceae* family) were examined.

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EXPERIMENTAL

The preparation of the untreated latex (HANR), deproteinised rubber (DPNR), transesterified rubber (TEDPNR), saponified NR samples and fractionation of the resulting rubbers by molecular weight followed a method described in the literature^{3,9}, as in our previous paper¹⁰. First a portion of the rubber latex was precipitated obtaining the untreated latex. Another part of the latex was deproteinised obtaining the DPNR and finally, part of the deproteinised rubber was transesterified.

 \overline{M}_n was obtained by size exclusion chromatography in a GPC-LALLS equipment with Jasco pump PU980 and TOSO detector LS8000, THF as solvent, elution speed of 1 ml/min, calibration curve of polystyrene standard and wo columns of poly (styrenedivinylbenzene) in series with exclusion limits of 2×10^7 and 5×10^4 g/mole³.

Determination of the gel content was made by putting 100 mg of the rubber in 20 ml of toluene in flasks protected from light and after one week, the solution was filtered and the gel weighted and estimation of molecular weight between anchoring points (\overline{M}_c) followed a method described previously in the literature^{3,7}.

¹³C-NMR data were obtained with a JEOL GX400 spectrometer at 100 MHz, 323 K and CDCl₃ solutions with pulse delay of 7s and 11 000 to 13 000 scans.

RESULTS AND DISCUSSION

In *Table 1*, *Ficus* showed the largest values of molecular weight and practically does not present gel. In the samples of *Hevea*, the high gel content could be masking the true value of molecular weight of the polymer. The sol fraction of the HANR samples showed \overline{M}_n

values of 1.3×10^5 g/mole or more, even with a gel content as high as 96% (*H. brasiliensis*), that contrasts with other works¹¹.

In the present case, the gel content in the *Hevea* species is different from the normal level of rubber. As it was observed with mangabeira rubber¹², the substances produced by the trees depend on the soil, on the amount of organic matter in the soil, the climate, the age of the tree, the type of close vegetation (phytosociology) and the frequency of tapping. *Hevea* and *Ficus* used in this work were never tapped before.

The *H. brasiliensis* (Muell. Arg.) var. *randiana* Pax, is in an airy, very illuminated place, with good spacing from the other trees and in humid soil with medium content of organic matter (compared to the other *Hevea* trees). The *Hevea guyanensis* (H.B.K.) Muell. Arg. is isolated in a stonemason with bushes, receiving more sun, wind and the soil is more dry with less organic matter and the *Hevea pauciflora* (Muell. Arg.) var. *coryaceae* Duke is very close to higher species, in the location with less light, high humidity and organic matter levels in the soil.

Apparently, the tapping periodicity in the trees was an important factor in the gel content in the latex, because the three *Hevea* samples present a high gel content in the rubber from HANR, this value being reduced after deproteinisation and transesterification. The gel content drops practically to zero in *H. guyanensis* TEDPNR, but still remains in the rubbers of *H. pauciflora* and *brasiliensis*.

The reduction in the gel content after deproteinisation and transesterification is associated with the presence of 'soft gel', coming from intermolecular interactions among the nonisoprenoid groups present in the macromolecule of rubber, as proteins and fatty acids. The remaining gel after the treatments is called 'hard gel' and it comes from chemical bonds among the chains, producing the crosslinks This can be observed in the values of \overline{M}_c of *H* brasiliensis (Muell Arg) var randiana Pax (Table 1), where practically there is no significant variation in this value, obtained with the remaining gel fraction after each treatment

It seems that the prolonged storage of latex inside the latex vessels is an important factor in the occurrence so much of 'soft gel' as of 'hard gel' and in the accumulation of non-polymeric substances in the latex¹³ Contrary to the latex of periodically tapped *Hevea* trees, whose clot is white (when humid) or transparent (when dry), the presently studied clots of *Hevea* revealed an orange colour that disappeared upon acetone extraction The transesterification reaction was made at ambient temperature and the samples, in spite of having cut in small pieces, did not dissolve totally That could result in an incomplete reaction due to the difficulty of the reagent to penetrate inside the gel. To eliminate this doubt, the saponification reaction of the samples of *Hevea pauciflora* var *coryaceae* and *brasiliensis* var *randiana* DPNR was carried out At the end of the reaction there was no more gel in the sample of *H pauciflora*, while in the sample of *H brasiliensis* the gel content remained unaffected

In the present case, the age of the H brasiliensis (planted in 1917) prevailed over the other ones (planted more than 30 years after) and its content of 'hard gel' is high indicating the presence of crosslinks in the gel Therefore

Specimen	Treatment	$\overline{\mathbf{M}}_{a} \times 10^{5}$ (g/mole)	$\overline{\mathrm{M}}_{w} imes 10^{-5}$ (g/mole)	$\overline{\mathbf{M}}_{\mathbf{w}} / \overline{\mathbf{M}}_{\mathbf{n}}$	Gel content (W%)	$\overline{\mathrm{M}}_{\mathrm{c}} imes$ 10 3
Hevea guyanensis	HA	1 50	8 00	54	45	2 7
	DP	1 15	1 80	15	27	-
(H B K) Muell Arg	TE	0 70	1 70	2 5	<1	_
Hevea pauciflora	HA	1 30	10 00	81	51 6	_
(Muell Arg) var	DP	1 20	4 70	40	54 1	92
coryaceae Duke	TE	0 57	2 20	39	49 9	17 7
Hevea brasılıensıs	HA	1 30	5 20	41	95 6	16
(Muell Arg) var	DP	1 00	3 00	31	96 1	22
randıana Pax	TE	0 50	3 90	77	78 2	22
Ficus 1	HA	5 00	10 00	2 5	<1	_
	DP	1 20	3 00	24	<1	_
Ficus 2	HA	2 20	7 70	3 5	<1	_
	DP	0 25	1 90	74	<1	-

TABLE 1 MOLECULAR WEIGHT, POLYDISPERSITY AND GEL CONTENT IN THE RUBBERS OF *HEVEA* AND *FICUS* GENA

^aHA = Rubber precipitated from high ammonia latex, DP = Deproteinised rubber, and

TE = Transesterified and deproteinsed rubber



Figure 1. Possible structure for the natural rubber macromolecule isolated and in gel phase14.

the content remains unaffected even after saponification and the \overline{M}_c values before and after transesterification are shown in *Table 1*.

Contrary to *Hevea* trees, practically there is no insoluble gel in the latex of the *Ficus* trees (*Table 1*), although they are never tapped. As the polyisoprene concentration in the latex of *Ficus* is around 5% w/v, this dilution and age (20 years) can explain in part the nongel incidence in these species. This result contradicts previous works¹⁴.

In the rubber of three *Hevea* trees the deproteinisation resulted in a reduction of the

number average molecular weight by 23%, 8% and 23%, respectively (*Table 1*). In the samples of *Ficus* this reduction was between 70% and 80% and transesterification of three *Hevea* rubbers reduced the molecular weight to 39%, 52% and 50%, respectively.

This reduction in the molecular weight can be associated with the destruction of a supramolecular structure formed by intermolecular interactions between the peptide groups in the initiating position, *i.e.* ω -terminal group, of the polyisoprene and the chain-end ester groups, *i.e.* α -terminal group of the polymer¹⁰, producing complex macromolecular structures giving the illusion of a molecular weight, for the polymer, larger than the real one¹⁵ (*Figure 1*) It is supposed that the proteins and fatty acids, detected by FTIR¹⁰, are bounded to the polyisoprene molecule and the chemical treatments (deproteinisation and transesterification¹⁰) decompose these branch points³ reducing the molecular weight of the natural rubber

¹³C-NMR show signals of *trans* terminal groups in polyisoprene molecule at 16 03 p p m (*trans* C-5) and 39 85 p p m (*trans* C-1) which agree with literature^{16 17} (*Figure 2*)

A possible outline for what happens after each process can be illustrated¹⁵ in *Figure 3*

CONCLUSIONS

The gel content in species of the same family varies in type and quantity depending on the period of storage and environment of the trees. The storage of rubber in the latex vessels for a short period results in the occurrence of soft gel, but extended period of storage may cause chemical crosslinking between the polymer chains ('hard gel') as in the case of *H brasiliensis* var *randiana*. It is possible to deduce that the occurrence and composition of the gel differ with the botanical family

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Figure 2. ¹³C-NMR of the polyisoprene extracted from Hevea species.



Figure 3. Possible structures for the natural rubber macromolecule after the chemical treatments of deproteinisation and transesterification¹⁶.

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