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SHORT COMMUNICATION

Characterisation of Natural Rubber from Manicoba (Manihot glaziovii): *Microstructure and Average Molecular Weight*

JUDITH F. RODRIGUES*, ANGELO S. RODRIGUES* AND ANDRÉ L. H. CARDOSO*

The microstructure and average molecular weight of Manihot glaziovii *rubber, are presented. This natural rubber constitutes mainly of* cis-*1,4-polyisoprene units and shows* $\overline{M}_v$ *values ranging between 1.0* $\times$ 10^6 *and 1.5* $\times$ 10^6. $\overline{M}_n$ *and* $\overline{M}_w$ *were found to be 1.1* $\times$ 10^6 *and 2.0* $\times$ 10^6, *respectively, with a polydispersity of 1.3. The structural determination was based on infra-red (ir),* ^1H *and* ^{13}C *NMR. The average molecular weights were obtained from viscosity experiments and GPC.*

There is great interest in developing alternative sources of natural rubber (NR). NR can be obtained from about 2000 different vegetal species; however only about a dozen of these plants have been commercially exploited. *Manihot glaziovii,* popularly known in Brazil as manicoba, is a tree of 8–12 m, well adapted to dry climates and found in north-eastern Brazil. It belongs to the Euphorbiaceae family and could be an alternative source of NR, the chemical composition of which, has been determined[1-6]. In 1985, Bastos *et al.*[7] reported their results on manicoba from agricultural and technological experiments. In 1988, Serier[8] discussed its history, biology, cultivation and economic aspects. No further study has been carried out to confirm the polymer microstructure and the average molecular weight, which is the objective of this report. The possibility of industrial application was examined using mechanical properties of vulcanised rubber[7] in addition to the results of this study.

MATERIALS AND METHODS

Samples of rubber were collected in Maranguape and Pacatuba Counties, State of Ceará, north-east of Brazil. They were purified by dissolution in benzene or chloroform (25 g/litre) and coagulated in methanol in the absence of light.

Films for ir were made by vapourisation of benzene solution over NaCl windows. A Perkin Elmer spectrophotometer, Model 293-B was used. The ^1H NMR spectrum was recorded in $CDCl_3$ solution, using a Brucker spectrometer (80 MHz) and the chemical shifts were related to TMS, used as the internal standard. The ^{13}C NMR spectrum was acquired on a Varian VXR-300 spectrometer (75 MHz).

Ostwald viscometers with t_0 of 95 s and 117 s were used for determination of the flow time. The system was thermostated by immersion in a water bath with a 0.1°C accuracy. For gel permeation chromatography, a Waters Associates Model 200 with styragel columns and toluene as solvent was used.

RESULTS AND DISCUSSION

The ir spectrum of *Manihot glaziovii* rubber is characteristic of polyisoprene. Selection of the 1,4 structure was based on the absence of

*Departmento de Química Orgânica e Inorgânica – Universidade Federal do Ceará; C. Postal, 12.200; 60.021 – Fortaleza – CE – Brazil

intense bands at 888–889 cm^{-1} and 909 cm^{-1}, characteristic of 3,4 and 1,2 structures, respectively[9-12]. In addition, there is a band at 835 cm^{-1} due to the 1,4 linkage in polyisoprene[9,11,13]. The spectrum also exhibits bands at 1130 cm^{-1} and 1378 cm^{-1}, all comparable to the values for *cis*-1,4-polyisoprene found by Binder and Ransaw[10], as well as Tanaka *et al.*[11] The absence of bands at 1152 cm^{-1} and 1385 cm^{-1} confirms the suggestion of the *cis* configuration.

^1H NMR spectrum shows absorption at 1.68 p.p.m. (*cis* $CH_3-C=$), 2.02 p.p.m. and 2.06 p.p.m. ($-CH_2-C=$) and 5.13 p.p.m. ($=C-H$), typical values for *cis*-polyisoprene[14] in $CDCl_3$. The proportion between the areas under the peaks at 1.68 p.p.m., 2.02–2.06 p.p.m. and 5.13 p.p.m. is 3:4:1 which is comparable to the relation of methyl, methylene and olefinic protons of the structure $[-CH_2C(CH_3)=CHCH_2-]_n$. No signals at 1.36 p.p.m. and 4.75 p.p.m. eliminate the possibility of the 3,4 isomer. The characteristic signal of *trans*-1,4 isomer at 1.61 p.p.m. was also not detected[15]. The ^{13}C chemical shift at 135.2, 125.0 32.2, 26.4 and 23.4 p.p.m. attributed to carbon α, β, γ, δ and ϵ of the monomeric unit, are also in agreement with a *cis*-1,4 structure[16]. Thus, *Manihot glaziovii* rubber is constituted predominantly of *cis*-1,4-polyisoprene.

To obtain more representative $\overline{M}_v$ values, five determinations under different conditions were made: NR origin, purification process, viscometer type and solvent-temperature system *(Table 1)*. Intrinsic viscosity values were obtained from plots of η_{sp}/c *versus* c. These data, plotted in linear graphs, yielded correlation coefficients between 0.983 and 0.998, calculated using the least squares method. For the calculation of $\overline{M}_v$ the Mark-Houwink-Sakurada equations: $[\eta] = 1.90 \times 10^{-4}\overline{M}_v^{0.745}$ for toluene solution[17] at 30.0°C and $[\eta] = 1.77 \times 10^{-4}\ \overline{M}_v^{0.735}$ for THF solution[18] at 20.0°C were used. From the data, we can conclude that the $\overline{M}_v$ values of *Manihot glaziovii* rubber range between 1.0×10^6 and 1.5×10^6, with a mean value of 1.2×10^6.

Using GPC and polystyrene as a reference, we have calculated $\overline{M}_n$ and $\overline{M}_w$ of Pacatuba NR. The values found were 1.1×10^6 and 2.0×10^6, respectively, with a polydispersity of 1.3. This $\overline{M}_w$ value falls within the typical range for non-masticated *Hevea brasiliensis* NR (1.6×10^6 to 2.3×10^6). However, the $\overline{M}_n$ value is higher, the typical values are between 2.0×10^5 and 5.0×10^5. Therefore, the molecular weight polydispersity is much lower than *Hevea* rubber $\overline{M}_w/\overline{M}_n$, which ranges from 2.8 to 10, according to Tanaka[15].

TABLE 1. VARIABLES IN THE DETERMINATION OF $[\eta]$ AND M_v OF *MANIHOT GLAZIOVII* RUBBER

Origin	Purification process		Viscometer type	$[\eta]$ (d litre/g)	$\overline{M}_v$
	Solvent	Repetition number			
Maranguape	C_6H_6	1	I	5.45[a]	960 000
Maranguape	C_6H_6	1	II	5.60[a]	1 000 000
Pacatuba	C_6H_6	1	II	7.20[a]	1 370 000
Pacatuba	C_6H_6	3	II	5.50[a]	1 090 000
Pacatuba	$CHCl_3$	2	I	6.20[b]	1 530 000

I – capillary diameter and length, 0.5 mm and 16 cm respectively
II – capillary diameter and length, 0.6 mm and 15 cm respectively
[a]Toluene solution at 30.0°C
[b]THF solution at 20.0°C

The possibility of industrial application of manicoba rubber was reported by Bastos *et al.*[7] Mechanical properties of pure-gum vulcanised rubber were compared with those of *Hevea* vulcanised rubber in the same formulation: Shore A hardness was 44 and 35; elongation at break, 784% and 860%; tensile strength, 16.8 MPa and 17.7 MPa; and, modulus at 300%, 3.58 MPa and 2.21 MPa, respectively.

Hevea NR and *Manihot* NR have the same structure, slightly different molecular weights[5,19] and close hydrocarbon contents 87.9–94.5 and 84.1%, respectively). Production of *Hevea* NR was 468 kg/ha/year and of *Manihot* NR 414 kg/ha/year. These data and those of mechanical properties indicate the possibility of manicoba rubber as an economically viable raw material, especially in dry climatic regions. Agricultural, technological, chemical and economical aspects have to be studied to obtain a more definitive conclusion.

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REFERENCES

1. ANON (1912) Ceará Rubber. *Bull. Imp. Inst.*, **10**, 551.
2. ANON (1913) Ceará Rubber from Northern Nigeria. *Bull. Imp. Inst.*, **11**, 380
3. ANON (1914) Ceará Rubber from Papua. *Bull. Imp.* Inst., **12**, 373.
4. JACOBS, F. (1942) African Rubbers. *Rev gén. Caoutchouc*, **19**, 276.
5. BENNETT, H. (1944) Composition of Rubber from Different Botanical Sources. *India Rubb. J.*, **107**, 93.
6. BENNETT, H. (1945) *Rubb. Chem. Technol.*, **18**, 701.
7. BASTOS, J.A.M., MAIA, G.A. AND FIGUEIREDO, R.W. (1985) Manicoba – Produtora de Borracha do Nordeste Brasileiro, Brasilia. Editerra Editorial Ltda.
8 SERIER, J.B. (1988) Le Manicoba: Histoire, Biologie, Culture, Intérêt Economique. *Caoutch. et plast.*, **677**, 117.
9. RICHARDSON, W.S. AND SACHER, A (1953) Infrared Examination of Various Polyisoprenes. *J. Polym. Sci.*, **10**, 353.
10. BINDER, J.L. AND RANSAW, H.C. (1957) Analysis of Polyisoprenes by Infrared Spectroscopy. *Analyt. Chem.*, **29**, 503.
11. TANAKA, Y., TAKEUCHI, Y., KOBAYASHI, M. AND TADOKORO, H. (1971) Characterization of Diene Polymers. I. Infrared and NMR Studies: Nonadditive Behavior of Characteristic Infrared Bands. *J. Polym. Sci.*, A2, **9**, 43.
12. KOESSLER, I. AND VODEHNAL, J. (1963) Infrared Spectra and Analysis of Synthetic Polyisoprenes. *J. Polym. Sci. Pt B*, **1(8)**, 415.
13. BANIGAN, T.F., VERBISCAR, A.J. AND ODA, T.A. (1982) An Infrared Spectrophotometric Analysis for Natural Rubber in Guayule Shrubs. *Rubb. Chem. Technol.*, **55**, 407.
14. GOLUB, M.A., ROSENBERG, M.L. AND GEMMER, R.V. (1973) *NMR and Infrared Study of Photosensitized Oxidation of Polyisoprene Application of Polymer Spectroscopy (Brame Jr, E.G., ed.).* New York: Academic Press.
15. TANAKA, Y. (1989) Structure and Biosynthesis Mechanism of Natural Polyisoprene. *Prog. Polym. Sci.*, **14**, 339.
16. DUCH, M.W. AND GRANT, D.M. (1970) Carbon 13 Chemical Shift Studies of the 1,4-polybutadienes and the 1,4-polyisoprenes. *Macromolecules*, **3**, 165.
17. CHIRICO, A. DE (1964) cis-Tactic Polyisoprene: Intrinsic Viscosity Molecular Weight Relation in a Pseudo-Ideal Solvent. *Chim. Ind.*, **46**, 53.
18. ANSORENA, F.J., REVUELTA, L.M., GUZMAN, G.M. AND IRUIN, J.J. (1982) On the Unperturbed Dimensions of Polyisoprene Chains. *Eur. Polym. J.*, **18**, 19.
19. SEIFRIZ, WM. (1945) The Coagulation of Latex. *Science*, **102**, 378.