

Molecular Weights of Natural Rubbers from Selected Temperate Zone Plants*

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Synopsis

Molecular weights and molecular weight distributions are compared by gel permeation chromatography for rubbers from 33 north temperate zone plants, guayule, and Hevea. Rubbers isolated from all the northern plants had much lower weight-average molecular weight (\bar{M}_w) values (9.72×10^4 – 4.95×10^5) than milled Hevea (1.31×10^6) or guayule (1.28×10^6) rubber. *Pycnanthemum incanum*, *Lamiaeum galeobdolon*, *Monarda fistulosa*, and *Vernonia fasciculata* produced potentially useful natural rubbers having \bar{M}_w values above 4×10^5 and polydispersity factors of 3.1–4.5.

INTRODUCTION

Natural rubber has been identified in many plants native to the United States.^{1–4} Rubber has been produced in commercial quantities from at least one, guayule (*Parthenium argentatum* A. Gray), in which there is much current interest.^{5–7} Some of these rubbers may provide valuable replacements for imported natural rubber and even for synthetic rubber as fossilized hydrocarbon feedstocks become depleted. However, little has been reported about yields and properties of most of these materials.

Molecular weights and molecular weight distributions (MWDs) are particularly important because of their relationship to processability of the rubber. The black incorporation time, a widely accepted index of processability, has been shown by Mills et al.⁸ to be closely related to \bar{M}_w . The \bar{M}_w for the soluble portion of usual commercial (Hevea) natural rubber exceeds 1×10^6 , but these rubbers are made more workable before compounding through partial depolymerization by mastication. Processability of some goldenrod rubbers is improved by slight preulcanization, presumably because the molecular weight of the raw rubber is too low.^{9,10} Most SBR synthetic rubbers have \bar{M}_w values in the range of 3×10^5 – 1×10^6 and polydispersity factors of 1.4–3.2.¹¹ Tokita and Pliskin suggest that higher mixing speeds are facilitated by broader MWDs in SBR.¹²

Buchanan et al. examined the yields of oils, polyphenols, hydrocarbons, and fibrous residues from more than 206 species of plants from the Central United States.^{3,4} Exhaustive extraction of the pulverized plant materials with acetone removed the oil and polyphenol fractions. The hydrocarbon fraction, composed primarily of isoprene polymers, waxes, and terpenoids, was recovered from the residue by extraction with cyclohexane. Hydrocarbon fractions from 33 species

* Presented at the 1977 International Symposium on Liquid Chromatography Analysis of Polymers and Related Materials, Chicago, Illinois, November 7–10, 1977.

gave infrared spectra indicative of substantial rubber contents. In the present work, these have been examined by gel permeation chromatography (GPC) to learn which have the most desirable \bar{M}_w and MWD properties.

EXPERIMENTAL

Plant Materials

Rubbers from the plant species listed in Table I were chromatographed. Excepting Hevea (SMR 5L) and guayule (provided by George P. Hanson of the Los Angeles, California, Arboretum), the plants were collected in Illinois, Indiana, and Wisconsin. The Hevea rubber was passed through rubber rolls five times at room temperature to make it more soluble. Hydrocarbon fractions were prepared as reported by Buchanan.^{3,4} Samples of the dried hydrocarbon fractions were dispersed at room temperature in ACS-grade tetrahydrofuran (THF) containing a small amount of Irganox 1035 antioxidant. Gross amounts of gel (<30% w/w for Hevea and about 1% for the Midwestern plants) were removed by filtration through Whatman No. 1 filter paper, and most of the residual microgel was eliminated by forcing each sample through a 0.45- μm Teflon filter in a Swinney holder. Concentration of the rubber solutions was determined by residual weight after drying.

GPC Analyses

Chromatograms were prepared on an Ana-Prep chromatograph with the following operating conditions: solvent, THF; flow, 1 ml/min; oven temperature, 28°C; columns, 500, 5×10^3 – 1.5×10^4 , 5×10^4 – 1.5×10^5 , 7×10^5 – 5×10^6 , and $>5 \times 10^6$ Å Styragel; detector, differential refractive index; injection volume, 2 ml; and sample concentrations, 0.2–1.7% (w/v). Narrow MWD polystyrene and poly(propylene glycol) standards were used for calibration. The log of the extended chain length (A) was a linear function of elution volume (v , in ml) with the equation

$$\log A = 11.60204 - 1.22260v$$

Molecular weights were calculated by the method of Harmon using a Q factor of 60.4, which is the average of the ratios of molecular weight and polymer chain length reported for Hevea and guayule by Campos Lo'pez.^{13,14} Molecular weight measurements were hampered by lack of baseline resolution between the rubber and the smaller molecules. To obtain molecular weights, the lower molecular weight ends of the rubber peaks were extrapolated to baseline in smooth reasonable-appearing curves (dotted lines, Figs. 1 and 2). This questionable area contributes less than 5% to the \bar{M}_w values in all cases and can have considerable error without significant effect on the result. However, this area affects the number-average molecular weight (\bar{M}_n) measurements greatly, so the polydispersity ratios given in this paper are considered very approximate.

TABLE I
Weight Average Molecular Weight (\bar{M}_w) and Molecular Weight Distribution (MWD) Values for Natural Rubbers

Genus and species	Family ^a	Common name	$\bar{M}_w \times 10^{-3}$	MWD (\bar{M}_w/\bar{M}_n)
<i>Hevea brasiliensis</i> Mull. arg.	EUP	rubber tree	1310	5.2
<i>Parthenium argentatum</i> A. Gray	COM	guayule	1280	6.1
<i>Pycnanthemum incanum</i> (L.) Michx. ^b	LAB	mountain mint	495	4.0
<i>Lamium galeobdolon</i> (L.) Ehrend. and Polatsch.	LAB	yellow archangel	423	4.5
<i>Monarda fistulosa</i> L.	LAB	wild bergamot	419	3.1
<i>Vernonia fasciculata</i> Michx.	COM	iron weed	417	3.7
<i>Symphoricarpos orbiculatus</i> Moench	CAP	coral berry	367	6.1
<i>Melissa officinalis</i> L.	LAB	balm	316	4.2
<i>Lonicera tatarica</i> L.	CAP	tartarian honeysuckle	248	3.8
<i>Silphium integrifolium</i> Michx.	COM	rosinweed	283	3.1
<i>Helianthus hirsutus</i> Raf.	COM	hirsute sunflower	279	3.1
<i>Cirsium vulgare</i> (Savy) Ten.	COM	bull thistle	266	3.1
<i>Cacalia atriplicifolia</i> L. ^b	COM	pale indian plantain	265	4.0
<i>Euphorbia glyptosperma</i> Engelm.	EUP	ridgeseed euphorbia	264	2.7
<i>Monarda didyma</i> L.	LAB	Oswego tea	263	3.2
<i>Solidago altissima</i> L.	COM	tall goldenrod	239	3.0
<i>Cirsium discolor</i> (Muhl.) Spreng.	COM	field thistle	238	3.1
<i>Solidago graminifolia</i> (L.) Salisb.	COM	grass-leafed goldenrod	231	3.4
<i>Gnaphalium obtusifolium</i> L.	COM	fragrant cudweed	206	2.8
<i>Silphium terebinthinaceum</i> Jacq.	COM	prairie dock	197	3.6
<i>Elymus canadensis</i> L. ^c	GRA	Canada wild ryegrass	176	2.8
<i>Solidago rigida</i> L. ^b	COM	stiff goldenrod	164	3.1
<i>Euphorbia corollata</i> L.	EUP	flowering spurge	163	3.3
<i>Helianthus grosseserratus</i> Martens	COM	sawtooth sunflower	160	3.8
<i>Campsis radicans</i> (L.) Seem. ex Bur.	BIG	trumpet creeper	146	4.4
<i>Chenopodium album</i> L.	CHE	lambsquarter	145	3.5
<i>Monarda punctata</i> L.	LAB	horsemint	143	4.0
<i>Nepeta Cataria</i> L.	LAB	catnip	132	2.9
<i>Teucrium canadense</i> L. ^b	LAB	American germander	130	3.8
<i>Phalaris canariensis</i> L. ^c	GRA	canary grass	123	3.5
<i>Asclepias syriaca</i> L.	ASC	common milkweed	120	3.1
<i>Artemisia abrotanum</i> L.	COM	southernwood	120	2.4
<i>Campanula americana</i> L. ^b	CAM	tall bellflower	113	2.4
<i>Verbena urticifolia</i> L.	VER	white vervain	109	2.2
<i>Phyla lanceolata</i> (Michx.) Greene	VER	frog fruit	97.2	2.2

^a ASC, Asclepiadaceae; BIG, Bignoniaceae; CAM, Campanulaceae; CAP, Caprifoliaceae; CHE, Chenopodiaceae; COM, Compositae; EUP, Euphorbiaceae; GRA, Gramineae; LAB, Labiateae; VER, Verbenaceae.

^b Previously selected as a promising source of natural rubber on the basis of botanical characteristics and yield of rubber and hydrocarbons.^{3,4}

^c Produces *trans*-1,4-polyisoprene.

RESULTS AND DISCUSSION

Chromatograms of hydrocarbon extracts from *Pycnanthemum incanum* (mountain mint) and *Asclepias syriaca* (common milkweed) are typical for the plants we studied and are shown in Figure 1. The leading higher molecular weight peaks represent rubber, while the following lower molecular weight peaks are believed to represent oligomeric polyisoprenes, waxes, terpenoids, and antioxidants. Differences in refractive indexes of the smaller species as well as the variability in Irganox contents prohibit other than very qualitative comparison

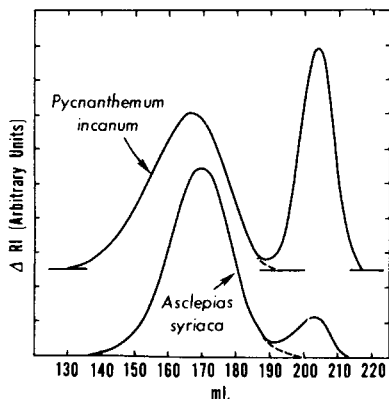


Fig. 1. Gel permeation chromatograms of typical natural rubbers from north temperate zone plants.

of the relative amounts of rubber and other hydrocarbons by measurements of peak areas. However, samples with the most rubber-like IR spectra had the smallest low molecular weight peaks.

For comparison, our GPC curves for milled SMR 5L and guayule rubbers are in Figure 2. The low-molecular-weight peaks primarily represent antioxidants. High molecular weight rubbers from these plants and the higher molecular weight rubbers from temperate zone plants, such as that from *Pycnanthemum incanum*, cover about the same molecular weight range. However, differences in distribution over this range cause widely different average molecular weights. Should higher average molecular weight rubber be desirable in the temperate zone plants, selective breeding might be easier with these plants that already produce some rubber in the high molecular weight range.

We stress that our data are from no more than a few specimens of each species that were collected at only one or two locations. Consequently, we have no measure of the intraspecies variability of yields and properties that probably results from differences in genetic heritage, maturity, and growing conditions. In addition, the particular solvents used for fractionation have great effect on the molecular weights observed. Changing from a 2:3 volume ratio of benzene:hexane for extracting the hydrocarbon fraction to straight cyclohexane extractant increased the molecular weight of the recovered rubber with little effect on yield.

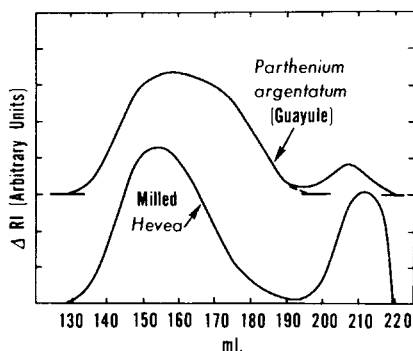


Fig. 2. Gel permeation chromatograms of commercial (Hevea, SMR 5L) and guayule natural rubbers.

\bar{M}_w and MWD values for rubbers from all 33 temperate zone plants, guayule, and Hevea are given in Table I. Plants producing rubbers in the higher molecular weight range ($>2 \times 10^5$, the upper limit of \bar{M}_w on the marginally useful goldenrod rubbers) hold promise as direct sources of rubber if they can be bred to produce high enough yields. Those producing lower molecular weight rubbers are preferred by Calvin as feedstocks for production of synthetic petroleum from plant sources—"gasoline trees."¹⁵ The MWDs for all these rubbers fall within the range of those possessed by commercial rubbers and should not limit their utility.

It is interesting that plants selected as promising sources of natural rubber on the basis of botanical characteristics and yields (superscript b, Table I) cover the complete range of average molecular weights. One of these, *Pycnanthum incanum*, is the most promising of the temperate zone plants studied since its rubber had the highest molecular weight.

CONCLUSIONS

Natural rubbers isolated from 17 of 33 plants native to the north temperate zone had molecular weights lower than those of Hevea and guayule natural rubbers but greater than those of the marginally processable goldenrod rubber. They should be easily processable on standard rubber-making equipment. One of the most promising rubber sources was *Pycnanthum incanum*, which produced more than 1% on a weight basis of rubber having a \bar{M}_w of 4.95×10^5 and a \bar{M}_w/\bar{M}_n ratio of 4.0. Other species producing rubbers having a \bar{M}_w greater than 4×10^5 were *Lamiastrum galeobdolon*, *Monarda fistulosa*, and *Vernonia fasciculata*. MWDs for all 33 rubbers were within the range used in commercial rubber production. The species producing lower molecular weight rubbers might provide feedstocks for a synthetic petroleum industry.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

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Received November 3, 1977

Revised December 20, 1977