Guayule resin detection and influence on guayule rubber

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Abstract

Guayule (*Parthenium argentatum Gray*) is a natural rubber (*cis*-1,4-polyisoprene) producing crop, native to North America. Guayule also produces organic resins, complex mixtures of terpenes, triglycerides, guayulins, triterpenoids and other components. During natural rubber extraction, guayule resins can be co-extracted with the polymer, sometimes leading to a significant fraction of low molecular weight extractables in the rubber. Resin present in guayule rubber can affect viscosity, thermal stability and mechanical properties of rubber compounds. The objectives of this study were: 1) quantify the extractable content of guayule rubber and other polymers, 2) evaluate the use of Gel Permeation Chromatography (GPC) to characterize the resin in rubber, 3) measure the effect of the resin addition on physical properties of cast polymer films.

The four polymers investigated were: 1) solvent extracted Guayule rubber (Sacaton simultaneous extraction process) 2) dried Guayule latex (aqueous process), 3) synthetic Polyisoprene (Natsyn™), 4) dried Hevea latex (RRIM 600 Campinas, Brazil). Acetone soluble extracts were quantified as function of temperature by Accelerated Solvent Extraction (ASE). GPC was used to characterize the polymers before and after extraction, and the extracts. Guayule resin (Sacaton simultaneous extraction process) was added at +5% and +10% to a solution of guayule rubber in THF, and films cast for physical property testing. The evaluations included bulk viscosity, thermal stability (by Plasticity Retention Index (PRI)), and green strength of cast polymer films.

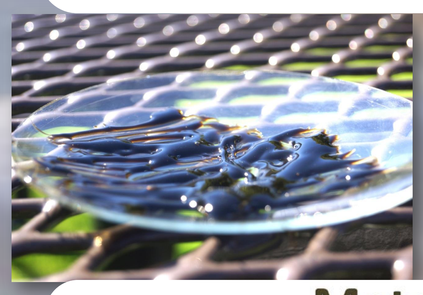
Resin addition and subtraction was readily quantified by the GPC UV detector at 254 nm and by Refractive Index; over a range of molecular weight from ~75 to ~500 g/mol. This demonstrated the potential of the GPC to measure rubber molecular weight and resin content simultaneously. The correlation between resin quantified by GPC and by ASE extractables was determined for all four polymers. Addition of Sacaton resin to guayule rubber led to decreased bulk viscosity, and softening of green tensile properties due to plasticization, in agreement with other published results. However, thermal stability (PRI) was improved, possibility due to antioxidant present in the Sacaton guayule resin.

Objectives:

- Evaluate the use of Gel Permeation Chromatography (GPC) to characterize the resin in rubber.
- Quantify the extractable resin content of guayule rubber and other polymers.
- Measure the effect of the resin addition on physical properties of cast polymer films.

Background:

- Guayule (*Parthenium argentatum* Gray) is a natural rubber (cis-1,4-polyisoprene) producing crop, native to North America.
- Guayule produces organic resins: complex mixtures of terpenes, triglycerides, guayulins, triterpenoids and other components. Resins allow guayule to resist many diseases and pests.
- Resin present in guayule rubber can affect viscosity, thermal stability and mechanical properties of rubber compounds.
- The naturally growing guayule shrub contains about 5-10% rubber and 7-12% resin.
- Guayule containing high levels of resin (low-molecular weight, acetone-extractable material) can degrade the physical properties of the raw rubber.
- It is the production process that ultimately determines guayule rubber's molecular weight and distribution and its content of non-rubber components.



Materials:

4 polyisoprene polymers:

→ Guayule Natural Rubber Sacaton (solvent extraction)
→ Guayule Natural Rubber latex (aqueous extracted)
→ Synthetic Polyisoprene (Natsyn) + synthetic PI latex (IR-401)
→ Hevea Natural Rubber RRIM 600 (made in Brazil)
+ commercial SIR20 Hevea + Hevea latex

Guayule Sacaton Resin

THF (Tetrahydrofuran), Acetone

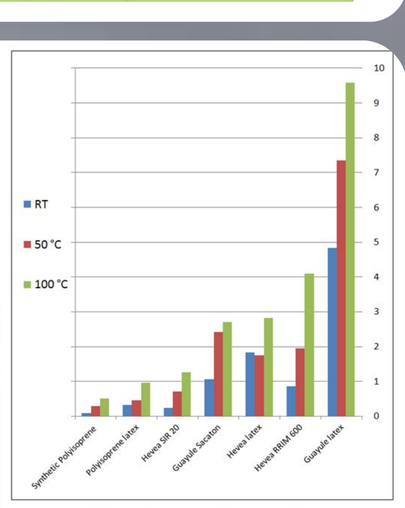
Methods:

	METHOD	PARAMETER	INSTRUMENTION
Acetone extracts	Liquid-solid extraction	% soluble	Dionex ASE 200
Polymer molecular weight/distribution	GPC SEC-MALS	Mw(g/mole) Mw/Mn	Agilient Life Sciences HPLC, Dawn Helios, Wyatt Technology
Plasticity and PRI	ASTM D3194-04	Po, PRI	Wallace Instruments
Dynamic viscolastic properties	ASTM D6204B APA	Ⴖ* (complex viscosity)	Advanced Polymer Analyzer, Alpha Technology
Film green strength	ASTM D412-06a	Green strength, elongation	Instron

Results:

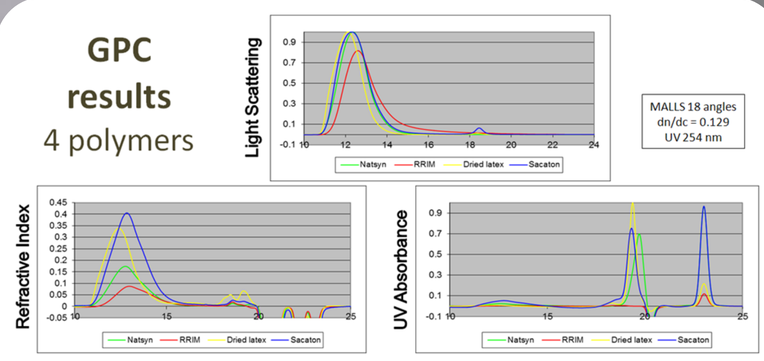
Rubber Acetone Extract:

Bale rubber as received and air-dried latex films



- Guayule > Hevea > Synthetic PI
- Latex > Solvent prepared/extracted

GPC results
4 polymers



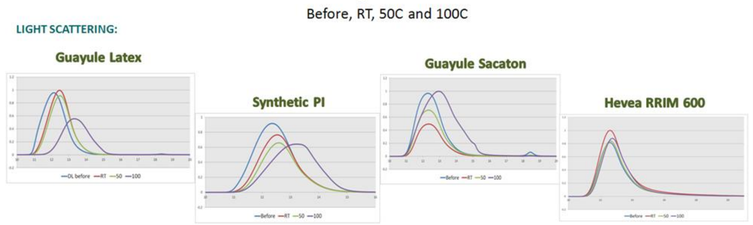
MALLS 18 angles
dn/dc = 0.129
UV 254 nm

Polymer	Mw (rubber)	Mw/Mn	Calc mass, low Mw	Calc mass all	% of low Mw
Synthetic Polyisoprene	1,461,333	2.590	1.06E-6	3.56E-5	2.48
Hevea RRIM 600	1,546,000	1.665	1.17E-6	2.32E-5	7.51
Guayule latex	2,027,500	2.390	4.47E-6	4.29E-5	11.15
Guayule Sacaton	1,965,333	2.158	1.09E-6	3.45E-5	1.62

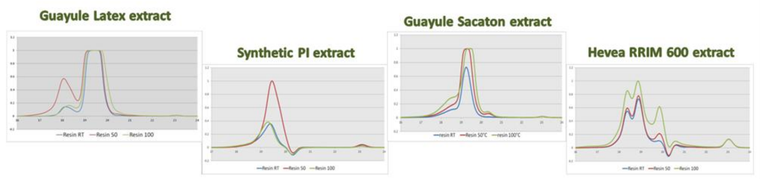
GPC results post-extraction

Before, RT, 50C and 100C

LIGHT SCATTERING:



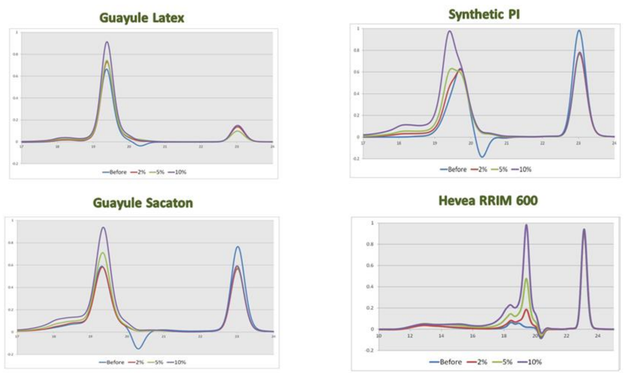
UV ABSORBANCE:



✓Extraction lowers Mw, esp. at elevated temperatures

GPC results following Sacaton resin addition

Sacaton resin added (+2%, +5%, +10%) in THF solution – **Refractive Index**



✓RI quantifies low Mw extractables + degraded rubber
✓Only in case of synthetic PI was resin addition detected by RI

Guayule resin measurement

- Is the RI peak useful to quantify extractables?
- Extraction lowers Mw, esp. at elevated temperatures
- Sacaton resin added in THF solution, films air-dried

- RI quantifies low Mw extractables + degraded rubber
- Only in case of synthetic PI was resin addition detected by RI

	Guayule Latex	Mw (rubber) (from LS) Avg 3 det.	% low Mw (from RI)	Theorical total – ASE (RT) added resin
Extracted	Before	2,027,500	11.15	4.84
	RT	1,307,500	5.49	4.84
	50 °C	1,236,500	3.86	7.34
	100°C	508,500	4.18	9.58
added	2% resin	2,120,333	12.15	6.84
	5% resin	1,949,100	16.18	9.84
	10% resin	2,316,333	13.77	14.84

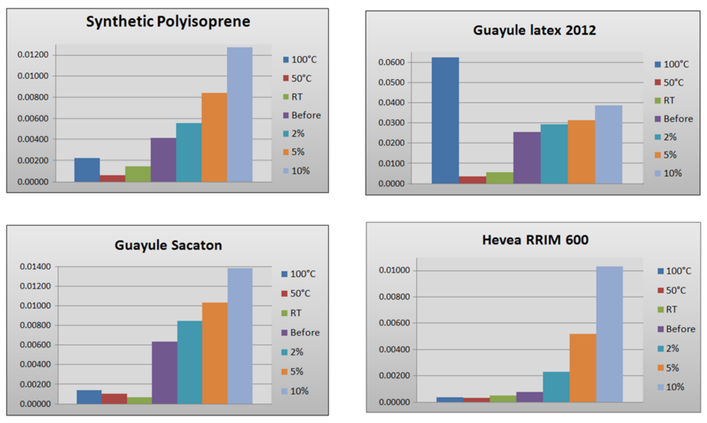
	RRIM 600	Mw (rubber) (from LS) Avg 3 det.	% low Mw (from RI)	Theorical total – ASE (RT) added resin
Extracted	Before	1,546,000	7.51	0.85
	RT	1,341,000	2.64	0.81
	50 °C	1,261,000	5.94	1.77
	100°C	1,065,000	1.65	4.16
added	2% resin	1,408,667	8.39	2.85
	5% resin	1,445,667	7.89	5.85
	10% resin	1,579,667	11.98	10.85

	Guayule Sacaton	Mw (rubber) (from LS) Avg 3 det.	% low Mw (from RI)	Theorical total – ASE (RT) added resin
Extracted	Before	1,965,333	1.62	1.06
	RT	1,759,500	2.56	1.06
	50 °C	1,821,000	3.06	2.42
	100°C	1,388,000	1.01	2.71
added	2% resin	1,800,333	7.05	3.06
	5% resin	1,822,667	6.35	6.06
	10% resin	1,761,667	8.51	11.06

	Synthetic Polyisoprene	Mw (rubber) (from LS) Avg 3 det.	% low Mw (from RI)	Theorical total – ASE (RT) added resin
Extracted	Before	1,461,333	2.48	0.09
	RT	1,153,500	1.19	0.09
	50 °C	1,065,500	1.94	0.29
	100°C	748,250	0.90	0.50
added	2% resin	1,508,667	2.69	2.09
	5% resin	1,475,333	4.21	5.09
	10% resin	1,520,667	6.45	10.09

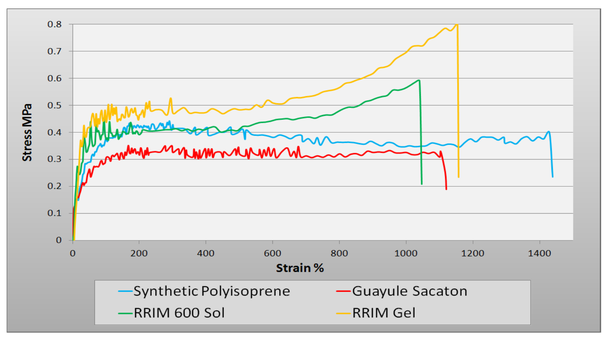
UV signal at low Mw from the rubber GPC test

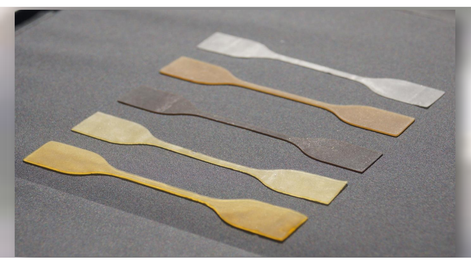
✓UV signal peak area



Films green strength

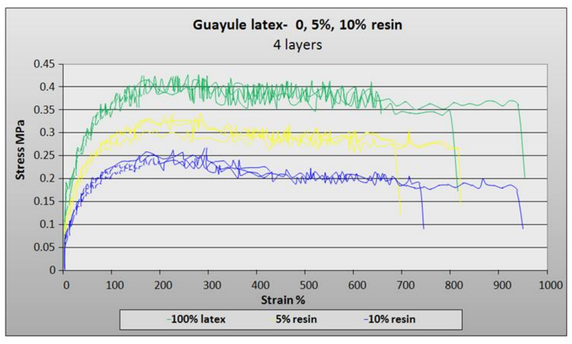
Polymer solubilized in THF solution, films air-dried – **3 Polymers**



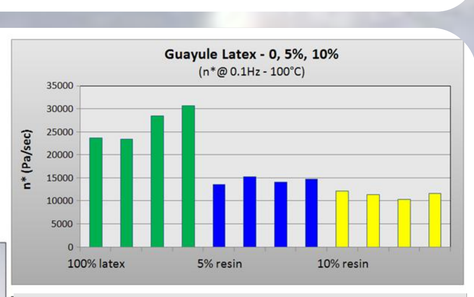


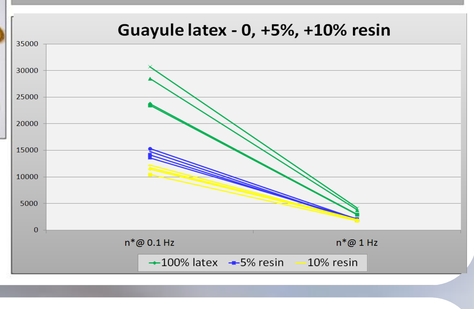
Effect of resin on films green strength

Sacaton resin added in THF solution, films air-dried



Bulk Viscosity



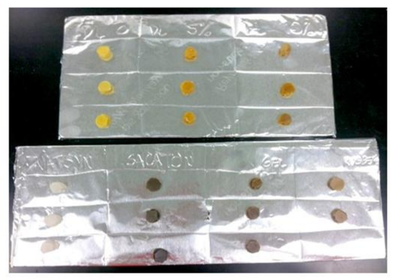


Effect of resin addition on PRI

Pa = 30 min at 140°C cooled down at RT for 45 minutes

Sample	Plasticity Po	Median PRI
Synthetic Polyisoprene	37.5	21.33
Guayule Sacaton	29.0	51.72
Hevea RRIM 600 Rubber	31.5	55.56
Hevea RRIM 600 Gel	37.0	50.00

Sample	Plasticity Po	Median PRI
Guayule latex	28.5	8.772
Guayule latex +5% Sacaton resin	21.5	13.953
Guayule latex + 10% Sacaton resin	15.5	32.258



✓Sacaton resin has AO?

Conclusions:

- ASE accurately quantified % extractable content of rubber.
- Low molecular weight peaks were detected in rubber GPC for all polymers.
- The GPC – UV detector (254 nm) best predicted the extractable/ resin content of the rubber.
- Addition of Sacaton resin to guayule rubber led to decreased bulk viscosity, and softening of green tensile properties due to plasticization.
- Thermal stability (PRI) was improved, possibly due to antioxidant present in the Sacaton Guayule resin.
- From a product applications standpoint, resin is an important component of guayule rubber. The low- molecular weight resin components act as plasticizers, so high-resin guayule rubber can be less firm and more easily deformed than Hevea NR.

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