Guayule (NRG) Yulex® Latex Product Performance

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Abstract

Guayule, *Parthenium argentatum,* latex is commercially available as an alternate rubber source (Yulex® Latex) and is currently the sole natural rubber of U.S. domestic origin. It is the world's first natural rubber latex that is safe for Type 1 latex allergy sufferers due to its lack of proteins that cross-react with Hevea latex antigenic proteins, and is the only natural rubber latex to meet the current requirements of ASTM D1076 Category 4 [1]. Finished products from traditional Hevea latex retain natural proteins that are inherent to the Brazilian (or Para) Rubber Tree. These proteins are the cause of immediate (Type 1) allergy, and can precipitate symptoms ranging from rhinitis and conjunctivitis, to severer asthma and anaphylaxis [9, 11-13]. In this paper, a wide array of medical applications and the superior product performance and physical properties of guayule latex will be described and discussed and then compared to Hevea NRL and various synthetics.

Background

In 2005, Yulex Corporation commercially introduced the first domestic natural rubber latex source from guayule, known as Yulex® Latex [6]. Over the years, several publications and articles have indicated that guayule latex can be used for a wide variety of medical device applications and also has performance that is comparable if not better than Hevea latex, synthetic poly-isoprene, nitrile, chloroprene and vinyl [3-4, 8, 10]. Recent publications and articles lack details in support of claims that the performance of commercially-available guayule latex is superior to that of natural and synthetic rubbers currently in the marketplace. This paper will elaborate on the performance of guayule latex and provide additional data to substantiate those claims.

Recently, the Research Staff at Yulex Corporation developed and established a novel base formulation for guayule latex. Optimal formulations then were derived and used for a variety of applications including dental dams, condoms, catheters, balloons, examination and surgical gloves. The formulation process and components as described above will be elaborated on further in this paper. Furthermore, the consistency and performance of the guayule latex will be compared to Hevea NRL and other synthetics.

Formulation Development

For most latex applications formulation development proves to be a time consuming and tedious process: guayule latex was no exception. The first stage of formulation development often starts with a design of experiment (DOE), where the results of physical property testing of unaged and aged films are analyzed and compounding components are adjusted accordingly.

Effect of Antioxidant and Accelerator

Initially, the effect of the accelerator (Vanax PIC) and antioxidant (Vanox SPL) on guayule latex was investigated. Vanax PIC and Vanox SPL were obtained from R.T. Vanderbilt. Table 1 lists the guayule latex compounding components at various levels of antioxidant and accelerator while keeping the sulfur level constant at 2.5 phr (parts per hundred rubber).

Compound	**GL1**	**GL2**	**GL3**	**GL4**	**GL5**	Add in order
Ingredient	dry-phr	dry-phr	dry-phr	dry-phr	dry-phr	
Guayule latex	100	100	100	100	100	1
Ammonia	0.5	0.5	0.5	0.5	0.5	2
Accelerator (ACC)	**2**	**1**	**1.5**	**1**	**2**	3
Antioxidant (AO)	**1**	**2**	**1.5**	**1**	**2**	4
TiO_2 - Optional	0.5	0.5	0.5	0.5	0.5	5
Sulfur	2.5	2.5	2.5	2.5	2.5	6

Table 1: Antioxidant and accelerator optimization

All guayule latex compounding detailed in this paper was compounded and heated in an oven or water bath at 36°C (96.8°F) for 15 h. Following prevulcanization, the guayule latex compounds were cooled to 25°C± 2°C and a modified toluene swell index test was performed as outlined below [7].

<u>Modified toluene swell test methodology</u>

a. Pour 0.75ml of 5% aqueous $CaCO_3$ solution into either an aluminum or a polypropylene weighing dish and dry it either in a 65°C oven or air dry at ambient temperature
b. Cool to room temperature, if oven dried, and add 1.5 ml of compounded latex. Gently swirl latex to form a uniform layer and air dry. Complete dryness is indicated when the film turns from opaque white to translucent amber.
c. Coat the top surface of the film with $CaCO_3$ powder to prevent the surface of the film from sticking to itself. Peel the film out of the weighing dish.

d. Use a 25mm circle die to cut a 25mm film. Put it into a covered Petri dish containing toluene (10mm height from the base of the Petri dish) for 15 mins.
e. Hand swirl the Petri dish every 3-5 mins. to prevent the film from sticking to the Petri dish bottom.
f. After 15 mins. measure the final diameter of the film through the base of the dish.

Good precure of the mature guayule latex compound is indicated by a swell index of between 110% and 172% of the original film diameter (25mm). This contrasts with Hevea latex for which the swell index for good procure lies between 80 and 136%. This difference is most likely due to the greater linearity of the guayule polymer (lower branching and no gel) which permits greater swell due to fewer rubber polymer chain entanglements.

Guayule latex films were produced using the process described in Figure 1. The unaged articles were conditioned in a desiccator for 24 h prior to physical property testing. The aged articles were aged in the oven at 70 °C for 7 days as specified by ASTM D 573. Testing of both unaged and accelerated aged physical properties were performed in accordance with ASTM D 412.

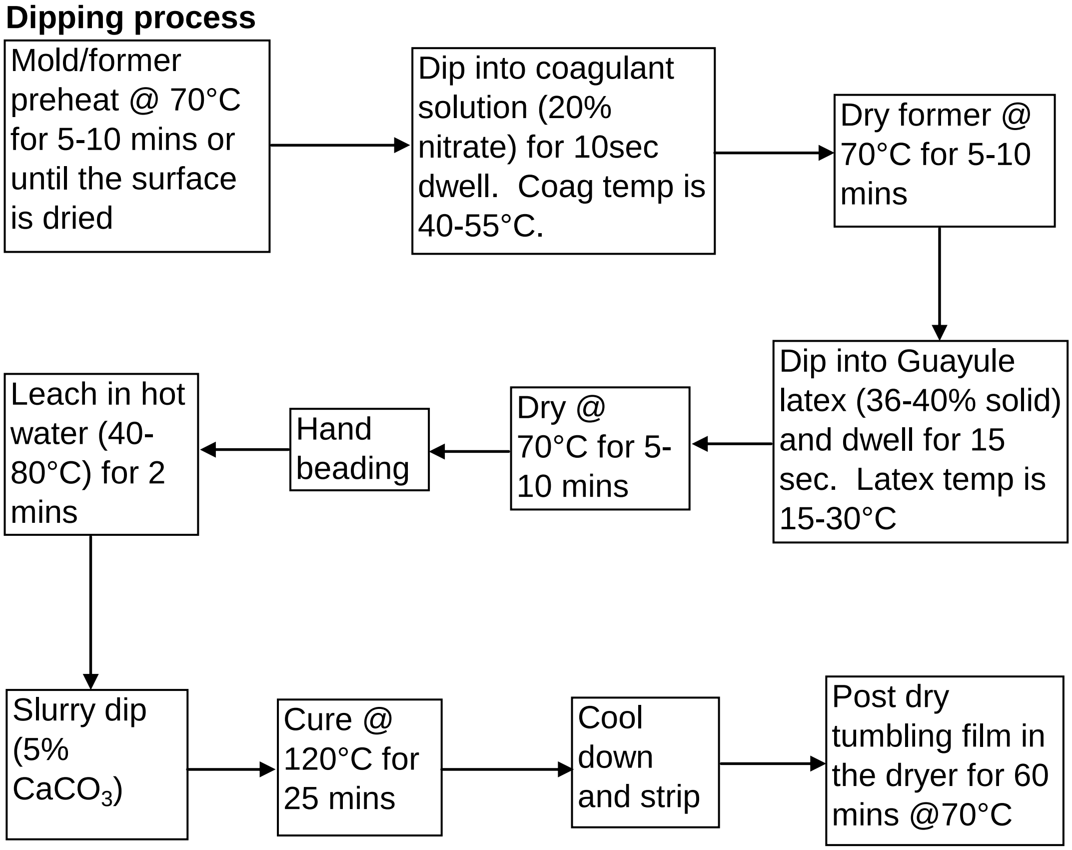

Figure 1 – Guayule Latex film making process

Due to the limitations of our tensiometer (Instron 3343 model, vertical test space 1067mm) and the naturally high elongation of the guayule latex, ASTM D412 die “D” was selected to cut the dumbbells for the physical properties testing. ASTM D412 die “C” dumbbells may be used but require a 3345 model with a vertical test space greater than 1123mm.

As outlined in Figure 2 and Table 2, formula GL2 yielded both unaged and heated aged films with excellent physical properties, which met or exceeded the ASTM 3577 requirement for NRL surgical gloves. This DOE shows that in order to maintain high unaged and heated aged physical properties, the concentration of the accelerator must be on the low side and the level of the antioxidant must be on the high side.

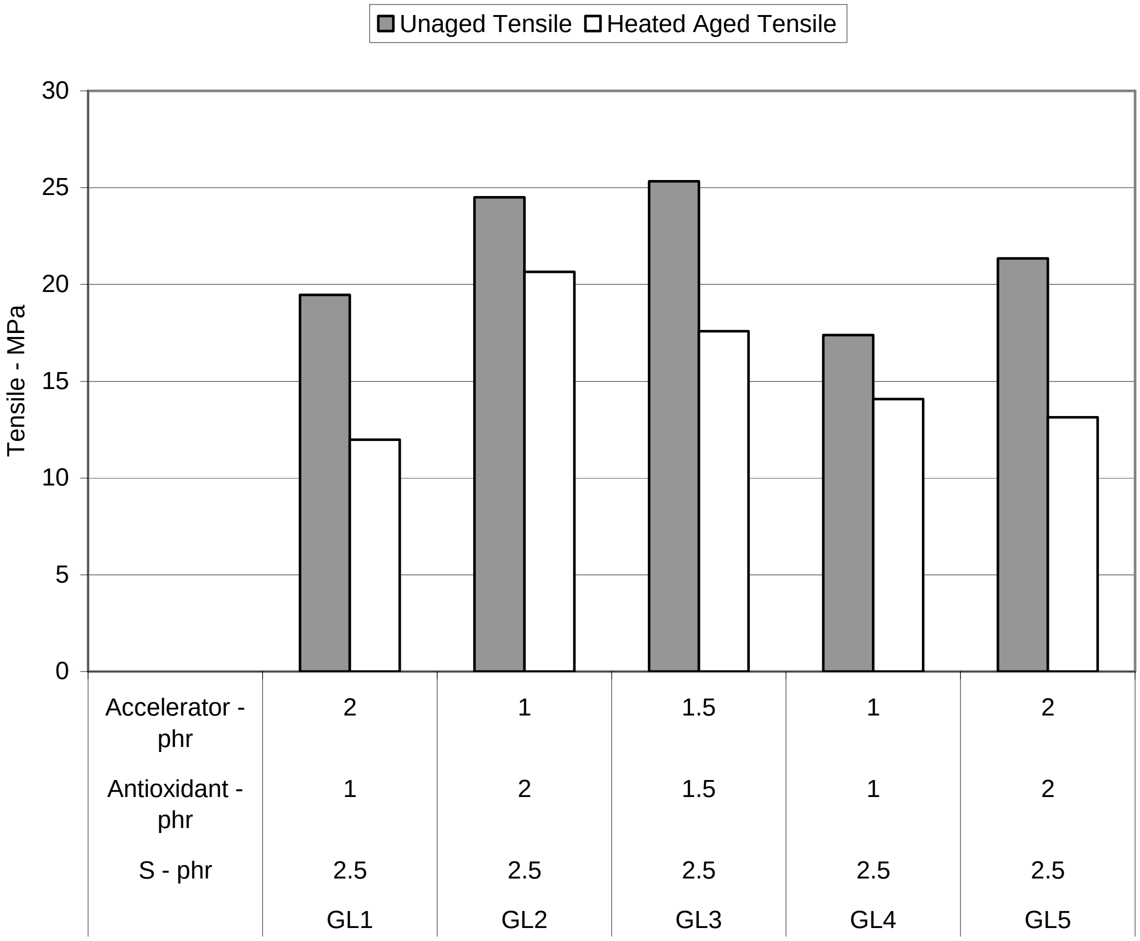

Figure 2 – Tensile results of various combinations of Antioxidant & Accelerator at constant Sulfur

				Unaged Article			Aged Article		
Run #	S - phr	AO - phr	ACC - phr	Elongation - %	Modulus @ 500% - MPa	Tensile - MPa	Elongation - %	Modulus @ 500% - MPa	Tensile - MPa
GL1	3	1	2	795	2.2	19.5	761	2.3	12.0
GL2	3	2	1	953	1.6	24.5	948	1.7	20.7
GL3	3	1.5	1.5	1011	1.8	25.3	710	3.3	17.6
GL4	3	1	1	866	1.9	17.4	925	1.4	14.1
GL5	3	2	2	919	1.7	21.3	633	2.5	13.1

Table 2 – Physical properties of guayule latex films made with various combinations of Antioxidant, Accelerator & Sulfur

Effect of Sulfur

After analyzing the results generated from the formulations in Table 1, additional DOE's (Table 3) were carried out to further optimize the physical properties of the guayule latex films. The effect of varying sulfur levels was tested at the constant accelerator and antioxidant concentrations of 1 and 2 phr, respectively.

Compound	**GL6**	**GL7**	**GL8**	**GL9**	**GL10**	Add in order
Ingredient	dry-phr	dry-phr	dry-phr	dry-phr	dry-phr	
Guayule latex	100	100	100	100	100	1
Ammonia	0.5	0.5	0.5	0.5	0.5	2
Accelerator (ACC)	1	1	1	1	1	3
Antioxidant (AO)	2	2	2	2	2	4
TiO_2 - Optional	0.5	0.5	0.5	0.5	0.5	5
Sulfur	**2**	**2.3**	**2.5**	**3**	**3.5**	6

Table 3 - Sulfur optimization at constant accelerator and antioxidant concentrations.

Table 4 and Figure 3 indicate that unaged tensile properties improve with increasing sulfur concentration. However, the heat-aged tensile properties decline with increasing sulfur concentration. A sulfur concentration of 2.5 – 3.0 phr maximizes both the unaged and heat-aged physical properties.

				Unaged Article			Aged Article		
Run #	S - phr	AO - phr	ACC - phr	Elongation - %	Modulus @ 500% - MPa	Tensile - MPa	Elongation - %	Modulus @ 500% - MPa	Tensile - MPa
GL6	2.0	2	1	923	2.0	22.9	962	1.9	25.4
GL7	2.3	2	1	947	1.9	23.3	924	1.9	24.0
GL8	2.5	2	1	961	1.8	25.2	898	1.8	22.0
GL9	3.0	2	1	1019	1.5	25.3	803	2.5	21.5
Gl10	3.5	2	1	963	1.7	26.4	876	2.2	21.3

Table 4 – The effect of varying sulfur concentrations on physical properties of guayule latex films.

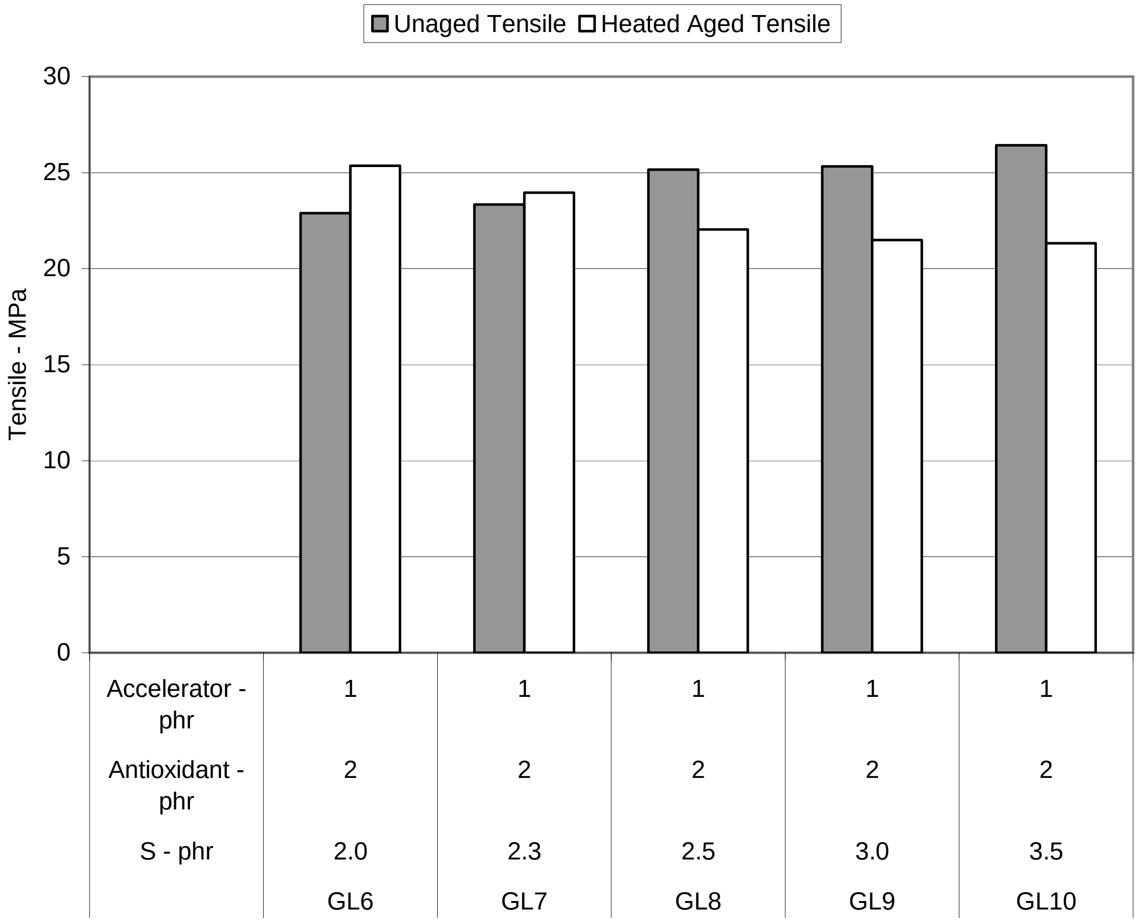

Figure 3 – Tensile properties of guayule latex films cured at various levels of antioxidant, accelerator and sulfur

Master Batch Development and Testing

The effect of a master batch (MB) dispersion on guayule latex also was investigated. The Yulex© MB was developed by Yulex staff and then produced by Akron Dispersions. As shown in Table 5, there was no significant difference between the MB compound method, in which the ingredients were pre-mixed before compounding, and the semi-continuous method, where individual components were added separately and mixed between each addition. Thus, the MB method provides an alternate way to compound guayule latex while simplifying and shortening the compounding process. The MB method also may reduce the total amount of compounding materials used.

				Unaged Article			Aged Article		
Run #	S - phr	AO - phr	ACC - phr	Elongation - %	Modulus @ 500% - MPa	Tensile - MPa	Elongation - %	Modulus @ 500% - MPa	Tensile - MPa
GL11	3.0	2	1	1027	1.5	24.1	789	2.6	23.3
GL12	Yulex® master batch			1022	1.6	25.1	836	2.3	22.8

Table 5 – Comparison of physical properties resulting from semi-continuous and Master Batch compounding methods.

Effect of ZnO

The effect of the ZnO also was examined to further maximize the performance of the guayule latex films. There was no significant impact on physical properties when ZnO was incorporated into the guayule latex formulation at 3phr sulfur (Table 6). However, additional studies demonstrated that the ZnO (0.5-2.0phr) yielded higher physical properties in the guayule latex when low amount of sulfur (1.0-2.5phr) was used in the compounding. On the contrary, the use of ZnO (0.5-2.0phr) yielded inferior physical properties, particularly of aged physical properties, when a high concentration of sulfur (2.5-3.5phr) was used.

		Unaged Article			Aged Article		
Run #	ZnO - phr	Elongation - %	Modulus @ 500% - MPa	Tensile - MPa	Elongation - %	Modulus @ 500% - MPa	Tensile - MPa
GL12	0	1022	1.6	25.1	836	2.3	22.8
GL13	0.5	1021	1.5	23.6	824	2.5	23.5
GL14	1	1014	1.6	24.4	830	2.6	23.1

Table 6 – Effect of ZnO on the physical properties of guayule latex films using Yulex® MB at 3phr sulfur

Raw Latex Maturation versus Compounded Latex Physical Properties

Different raw latex batches at various stages of maturation were used for the study. After the desired storage time, all batches were compounded using Formulation GL9 from Table 4. We have determined that guayule latex can be dipped as early as 20 days post-manufacture as compared to the typical 30 day minimum for Hevea latex (Figure 4 and Table 7). Furthermore, the physical property results for the different latex batches after different storage periods beyond 20 days of age showed no statistically significant differences. Currently, our data demonstrates that raw guayule latex is stable under good storage conditions for at least 16 months.

		Unaged Article			Heated Aged Article		
# of day maturity	Raw latex batch #	Elongation - %	Modulus @ 500% - MPa	Tensile - MPa	Elongation - %	Modulus @ 500% - MPa	Tensile – MPa
12	061221	991	1.5	19.4	892	2.2	21.8
20	061221	976	2.0	24.9	813	2.5	22.5
36	061221	1022	1.8	25.7	915	2.3	24.9
56	060918	928	2.1	24.3	880	2.2	21.4
59	060918	978	2.0	24.1	820	2.5	20.6
63	060626	969	1.9	26.6	768	2.8	23.1
74	060824	1025	1.5	24.9	740	3.2	22.7
171	060626	1019	1.5	24.2	847	1.9	18.4
266	Composite* (266-343)	1061	1.5	26.5	848	1.9	20.8
297	Composite* (297-374)	1032	1.5	24.3	857	2.5	23.1
505	051715	1008	1.6	24.0	758	3.0	21.2
* Composite latex - Mixture of Latex produced form Jan 09, 2006 to Mar 27, 2006							

Table 7 – Effect of raw latex storage time on compounded film physical properties using the GL9 formulation (see Table 4).

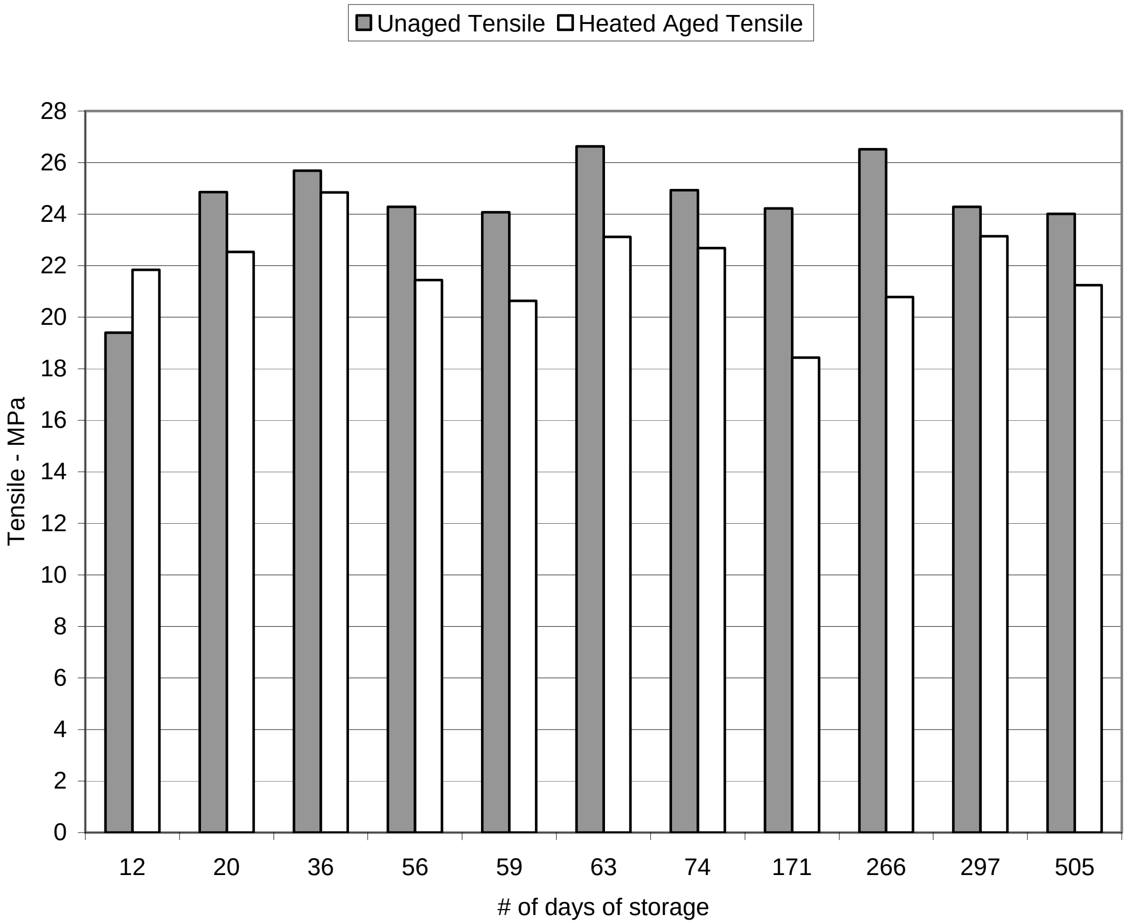

Figure 4 – Effect of raw latex storage time at ambient temperature on compounded film tensile strength using the GL9 formulation (see Table 4).

Compounded latex pot-life determination

Based on the results established above, Formulation GL9 from Table V (3phr of sulfur, 1phr of accelerator and 2phr of antioxidant) was selected to perform a pot life study of compounded latex. Compounded guayule latex was used to produce glove films over a 13-day period. Glove films were collected after 1, 2, 3, 7 and 13 days. The compounded latex was kept at ambient temperature (25-30°C) with continuous mixing during dipping. However, there was no agitation or mixing at night. As seen in Figure 5, the tensile and elongation trended down over time, while modulus trended up over time. The stability was excellent during the first 7 days, which indicates the pot life of this particular compounded latex batch is approximately between 7-13 days. In fact, both unaged and heated aged physical properties met the surgical latex ASTM D3577 standard comfortably. The swell index established for this study ranged from 102-172%.

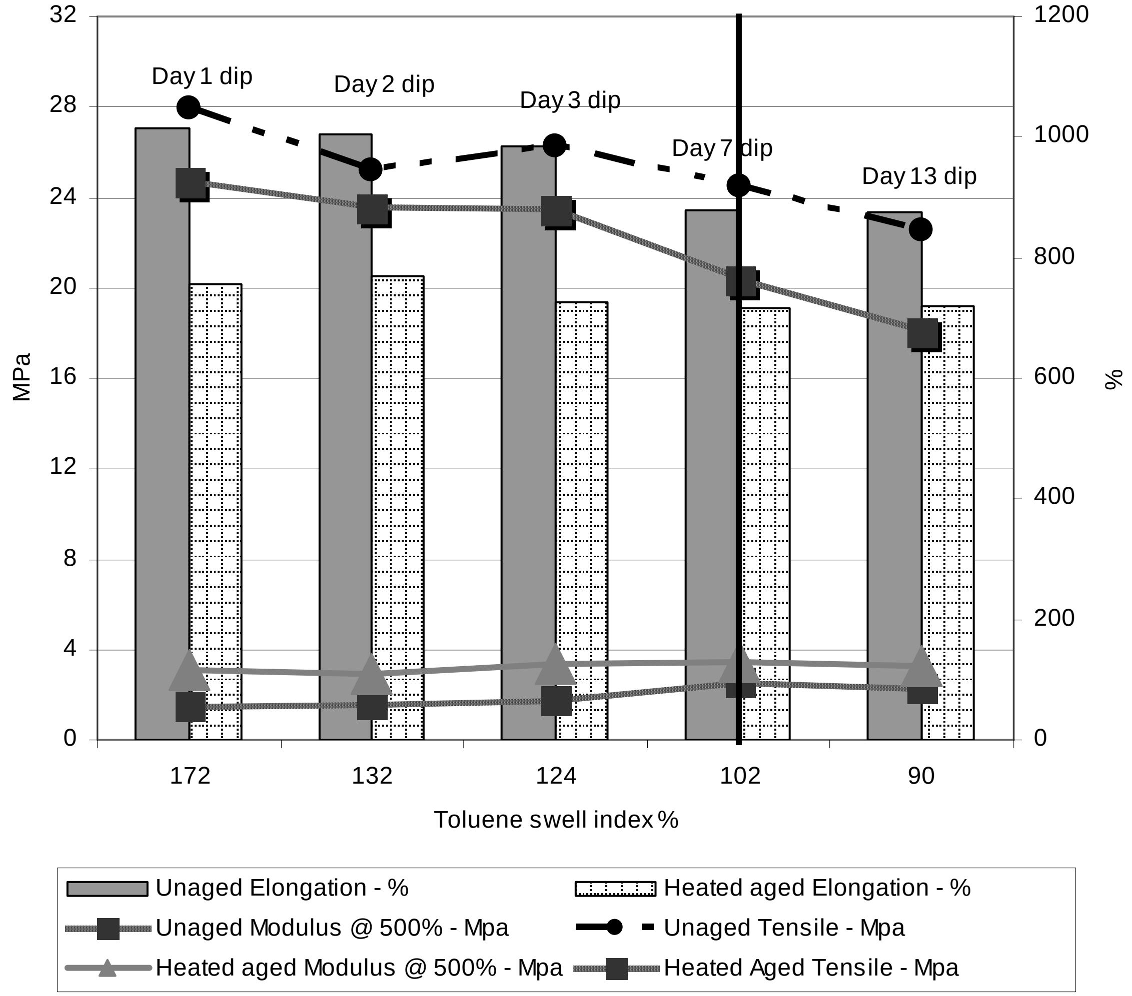

Figure 4 –Physical properties of films produced from compounded latex performance stored for different time periods before dipping.

Performance of Guayule Latex Films in comparison with NRL and Several Synthetic Elastomers

A comparative study of guayule latex, Hevea NRL and other synthetic elastomers was performed to substantiate the product performance of guayule latex among commercially available Hevea NRL and other synthetic elastomers. Guayule latex films were produced in-house using formulation GL9 from Table 4 while commercially available Hevea NRL and other synthetic elastomers were obtained from several glove distributor sources. Physical property, tear and puncture resistance tests were performed and compared among films of guayule latex, Hevea NRL, deproteinized NRL, chloroprene, synthetic poly-isoprene, vinyl and nitrile.

Tear resistance testing was performed in accordance with ASTM D624. The die C tear test was used. Puncture resistance testing was performed in accordance with ASTM F1342. A 23 gauge hypodermic needle was used because probe A did not puncture the rubber films and failed to yield usable data.

Guayule latex film puncture resistance was on par with the Hevea NRL and synthetic poly-isoprene films (Figure 5). Although nitrile latex displayed the most puncture resistance of all, it did not display a high level of tear resistance (Figure 6) and was the third lowest of all samples tested. Guayule latex tear resistance outperformed the synthetic materials, and was not significantly different to Hevea NRL.

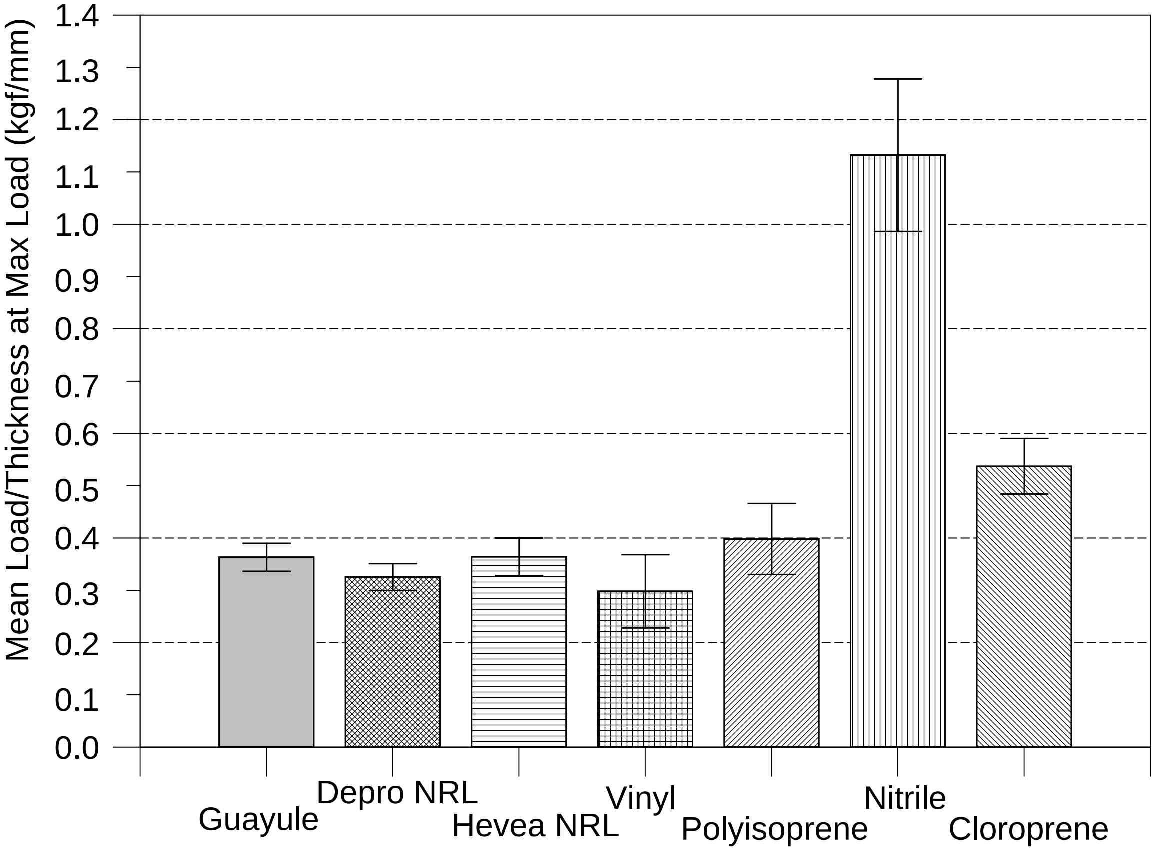

Figure 5 - Puncture test comparison of guayule latex films versus Hevea NRL and other synthetic elastomers using 23G hypodermic needle

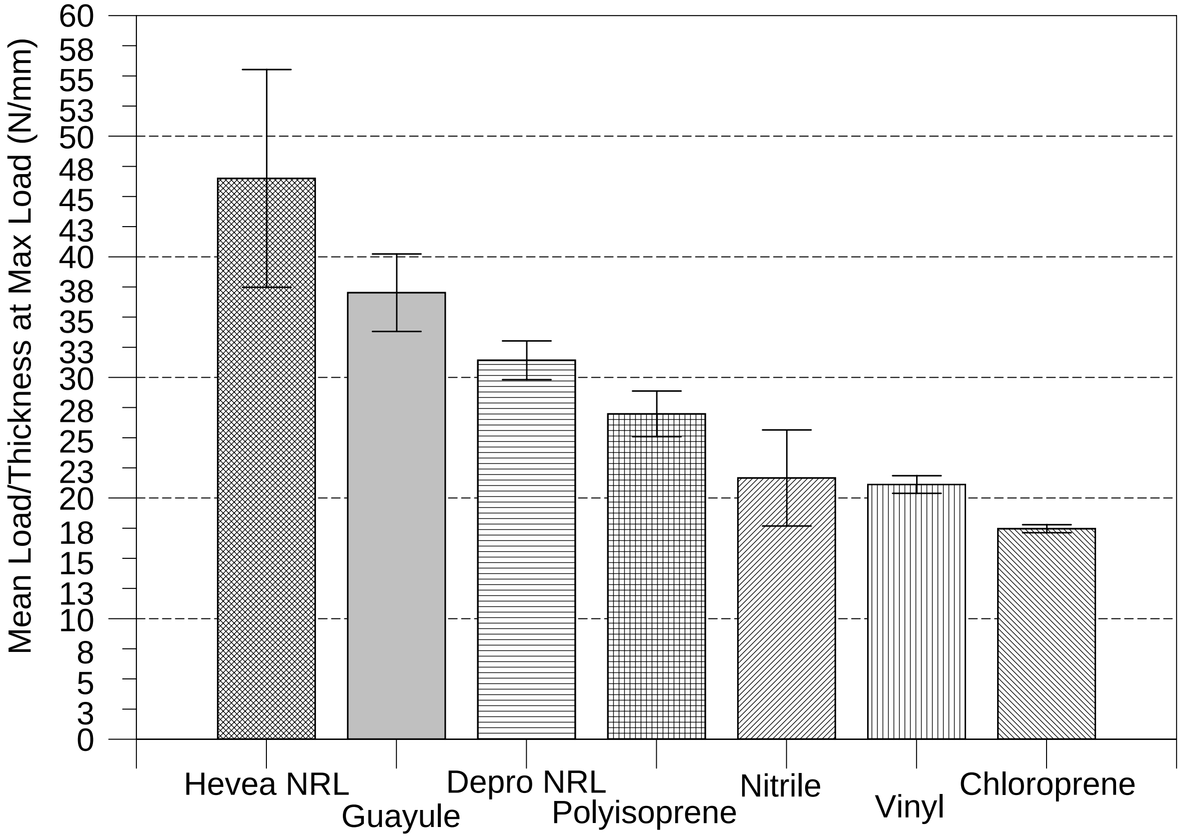

Figure 6 - Tear test results of guayule latex films versus Hevea NRL and other synthetic elastomers

Physical property testing was performed according to ASTM D 412. ASTM D412 die D was used to cut the dumbbells for physical property testing. Guayule latex film tensile strength (24.5 MPa) was on par with Hevea NRL, deproteinized NRL and synthetic poly-isoprene, and out performed the others (Figure 7). Guayule latex film elongation averaged 1015% which is much higher than all other materials tested. Furthermore, guayule latex film modulus at 500% was 1.6 MPa, much lower than the other materials tested. These results indicate that the guayule latex is not only strong, but is a very supple and soft material that enhances comfort during product wear.

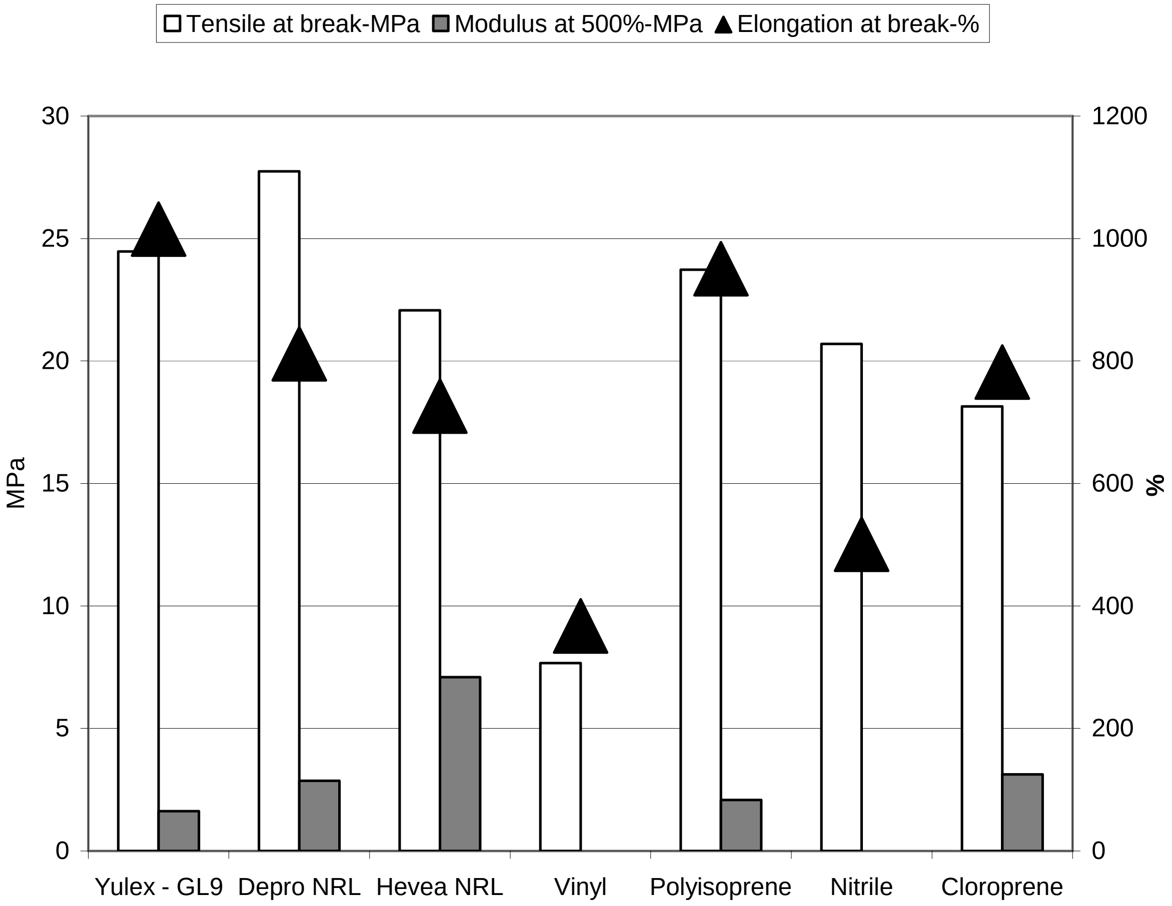

Figure 7 - Physical properties results of guayule latex films versus Hevea NRL and other synthetic elastomers

Conclusions

There are currently 40,000 consumer and industrial products that utilize natural rubber latex (NRL) and other synthetic rubbers. As demonstrated above, guayule latex performance is superior to NRL and other synthetic elastomers and can effectively be used as a substitute. Additionally, it provides a safe alternative material for Type 1 latex allergy sufferers [2, 5]. Finally, it provides cost leverage over synthetic poly-isoprene. In conclusion, guayule latex is a safe, domestic resource that is essential to the American economy.

References

1. Cornish, K., McMahan, C.M., Xie, W., Williams, J., Nguyen, K.C., Kostyal, D. Kelly Horton, K. and Marsh, D.T., ASTM D1076 Category 4 Latex and Quantifying Guayule (NRG) and Hevea (NR) Latex Protein, Proceedings 9th International Latex Conference, Charlotte, NC, July 25-26th, 2006.
2. Cornish K., Brichta, J.L., Chapman, M.H., Scott, D.J., Van Fleet, J.E., Xie, W. and Wood, D.F. Guayule latex: a clinically-proven, natural solution to Type I latex allergy. Proceedings of Latex 2002, December 4-5, 2002, Berlin, Germany.
3. Cornish, K., Brichta, J.L., Yu, P., Wood, D.F., McGlothlin, M.W. and Martin J.A. Guayule latex provides a solution for the critical demands of the non-allergenic medical products market. Agro-Food-Industry *hi-tech* 12 (6): 27-31, 2001. Selected as cover article.
4. Cornish, K. and Lytle, C.D. May 6, 1999. Viral impermeability of hypoallergenic, low protein, guayule latex films. J. Biomed. Mater. Res. 47, 434-437.
5. Cornish, K. and Williams, J. 2006 Guayule Latex: Effective substitute for natural rubber latex to produce medical goods. Global Handbook and Directory on NR and SR Lattices.
6. Cornish, K., Williams, J. and Martin, J.A. Commercialization of Yulex Natural Rubber Latex™: the improving margin structure of guayule latex products. 8th International Latex Conference, Charlotte, NC, July 26-27th, 2005.
7. Mausser, R.F., ed, The Vanderbilt Latex Handbook, Third Edition, Published by R.T. Venderbilt Company, Inc. Norwalk, CT (1987).
8. McMahan, C.M., Cornish, K., Pawlowski, H. and Williams, J. 2005 Dynamic mechanical properties of latex films. Presented at the spring 167th Technical Meeting of the Rubber Division, American Chemical Society, San Antonio, May 16-18, Paper 62.
9. Morales, C., Bascomba, A., Carriera, J. and Sastre, A. July 1989. Anaphylaxis produced by rubber glove contact. Case reports and immunological identification of the antigens involved. Clinical and Experimental Allergy 19(4): 425-430.
10. Scholman, W.W., Wyzgoski, F., McIntyre, D., Cornish, K. and Siler, D.J. 1996. Characterization and performance testing of guayule latex. Rubber Chem. Technol. 69: 215-222.
11. Slater, J.E. April 27, 1989. Rubber anaphylaxis, New England Journal of Medicine, 320:1126-1130.
12. Slater, J.E., Mostello, L.A., Shaer, C. and Honsinger, R.W. November 1990. Type I hypersensitivity to rubber. Annals of Allergy, 65(5): 411-414.
13. Tomazic, V.J., Withrow, T.J., Fisher, B.R. and Dillard, S.F. 1992. Latex associated allergies and anaphylactic reactions. Clinical Immunology and Immunopathology, 64(2): 89-97.