The Non Enzymatic Deproteinization of Natural Rubber Latex (DPNRL) Enabling the Greater Versatility in End Product Applications

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ABSTRACT

Natural Rubber Latex (NRL) is a constant and preferred raw material for latex end product manufacturers around the globe with its ready availability, ease of processing, and the excellent performance of latex end products in critical environments. However, the presence of non-rubbers, especially certain allergenic proteins, has inhibited its continued use in several existing products and entry into new applications. The introduction of a patented process in 2009, which uses specially treated aluminum hydroxide, to target the surface and bound proteins of both the extractable (EP) and Rubber Bound (AP) proteins has met success with a variety of latex product end users, as the superior performance attributes of these Deproteinized Natural Rubber Latex (DPNRL) materials becomes better characterized. These improvements extend beyond the ultra low allergenicity of the DPNRL and include improved color, absence of rubber odor, and improved physicochemical attributes. Improved air and helium retentions results are reported. The potential to extend applications into other non-conventional areas other than latex end products is discussed.

INTRODUCTION

Natural Rubber Latex (NRL) contains a small amount of non-rubbers, which include a variety of protein and have played a role in the biosynthesis and stabilization of rubber latex within the vessels of the tree. The latex of *Hevea brasiliensis* is a complex colloidal dispersion of biochemical components consisting of polyisoprene latex rubber particles and non-rubber components in an aqueous serum phase. Some adverse effects of these non-rubbers are well documented. These non-rubbers continue to play a role in the subsequent processing behavior of the NRL, its long-term stability, and catalyzing crosslinking reactions through free radical and ionic mechanisms resulting in covalent bonds. The protein sheath, which may be amphoteric in nature, around the latex particle is conjectured to facilitate the movement of curatives, usually carbon-, sulfur-, and nitrogen-containing materials, into the latex particles by providing an intermediate transport mechanism from the water phase to the rubber phase. The removal of the non-rubbers in treated NRL slows down the maturation process, hence translating into a longer “pot life.”

The crosslinking process of inserting poly-, di- and mono-sulfidic connections between separate elastomer chains increases the engineering utility of most elastomers, including treated NRL.

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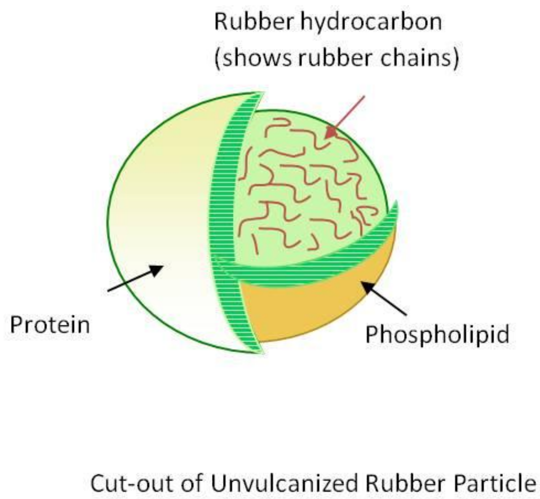

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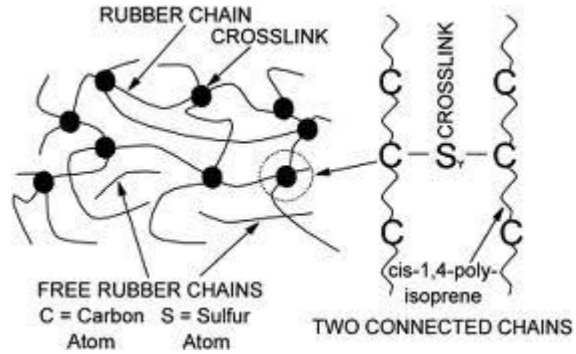


Figure 1. A) model of rubber latex particle, B) depiction of rubber polyisoprene chains crosslinked by sulfur. [1,2]

Aluminum Hydroxide-Treated Natural Rubber Latex

Aluminum hydroxide-treated NRL is a form of natural rubber latex that has undergone a patented process to remove proteins found in regular or untreated natural rubber latex. A slurry of aluminum hydroxide is introduced at the processing stage. The aluminum hydroxide mixture binds with the non-rubber particles, which are subsequently removed during centrifugation. The process was originally intended to remove the antigenic proteins associated with latex allergies, but work with treated NRL reveals that not only are antigenic proteins virtually eliminated, but some of the less desirable non-rubber content is greatly reduced. The resulting treated NRL is a cleaner and very stable form of NRL and has been found to impart a number of different benefits outlined here.

BACKGROUND

The company is the exclusive creator of aluminum hydroxide-treated Natural Rubber Latex (NRL), a multi-patented, all-natural raw material that contains significantly reduced levels of non-rubber particles and proteins found in natural rubber latex. Since conception, the company has been dedicated to one cause: creating a natural rubber latex (NRL) with all the properties of NRL but without the allergy-causing proteins. Early operations focused on the research, development, testing, and commercialization of the product that is now patented and trademarked as Vytex® NRL, a revolutionary all-natural raw material that significantly reduces antigenic proteins found in natural rubber latex. Commercially available end products continue to be introduced into the marketplace. Pioneer Balloon Company, the largest US producer of balloons, has upgraded to using treated NRL for use in the high-end, jewel-tone color balloons. Several adhesive and foam manufacturers have also upgraded to the use of treated NRL, including Islatex which launched high-end foam pillows made from aluminum hydroxide-treated latex. The company continues to work with manufacturers across a broad range of consumer and medical products, such as Tamicare and their Cosyflex product. The company's mission is to develop products and processes that will provide economic, health, and safety benefits throughout the end-to-end cycle—from processors to manufacturers to end users.

When Vytex NRL was originally invented, it was thought that the most compelling benefit to reducing latex protein in the *Hevea* latex raw material would be to reduce the risk of exposure to antigenic protein. It has generally been accepted that latex allergies can be developed through repeated exposure to the antigenic proteins that naturally occur in latex.[3] It is believed that by greatly reducing these antigenic proteins in the raw material, a person's risk can be reduced. However, the experience of the past two years is that removing the non-rubber components of latex along with the proteins results in a superior NRL. This is advantageous in a number of different product applications.[4]

Natural Rubber Latex as a Physical Barrier

The widespread use of barrier NRL articles, such as gloves and condoms, increased tremendously in the 1980s primarily due to the "universal precautions" policy outlined by the US Centers for Disease Control.[5] NRL's popularity and longevity can be attributed to several factors, including the superior physical properties of NRL over the synthetic lattices and the excellent barrier properties of NRL compared to synthetic options which are due to differences in physical properties. Many studies highlight the superior barrier protection of natural rubber latex: less likely to fail during surgery;[6] decreased perforation rate than synthetic products;[7] and copolymer decreased barrier protection than NRL.[8] NRL is made up of long cis-1, 4-polyisoprene chains, and when cross-linked, the NRL films are flexible and extendible.[9] Flexibility is related to chain lengths, the stereochemistry, bond angle, rotation of the single C-C chains, while the covalent double bonds remain rigid. The impermeability of the films is related to the film thickness, extension, constituents of the polymer chain, presence of barrier additives, and the size of the gaseous molecules.

Certain chemicals can permeate rapidly through intact surgical gloves.[8] While there are synthetic alternatives available for gloves and other medical devices, many of their physical properties are not ideal, and there does not appear to be any alternative material that can fully match the characteristics, including safety with respect to resistance to the transmission of pathogens compared to natural rubber latex.[9]

Natural rubber latex is universally agreed to be superior in barrier protection against such organisms as deadly viruses and antimicrobial resistant micro-organisms.[10]

CHEMISTRY OF NON-RUBBER PARTICLES

Latex is the cytoplasm of highly specialized laticifer cells lining the inner bark of the rubber tree, *Hevea brasiliensis*. Field latex obtained from *Hevea brasiliensis* trees is composed of about 36 wt% of rubber fraction; 5 wt% of non-rubber components, such as proteins, lipids, sugars, amino acids, and soluble salts of calcium, magnesium, potassium, and copper; and 59 wt% of water (Fig. 1, Table 1). Much of the non-rubber components are dissolved in the aqueous phase of the latex, while others are absorbed at the surface of the rubber particles and still some are suspended in the latex. Field latex is converted into various commercial forms of natural rubber including latex, sheet, block, and crepe.

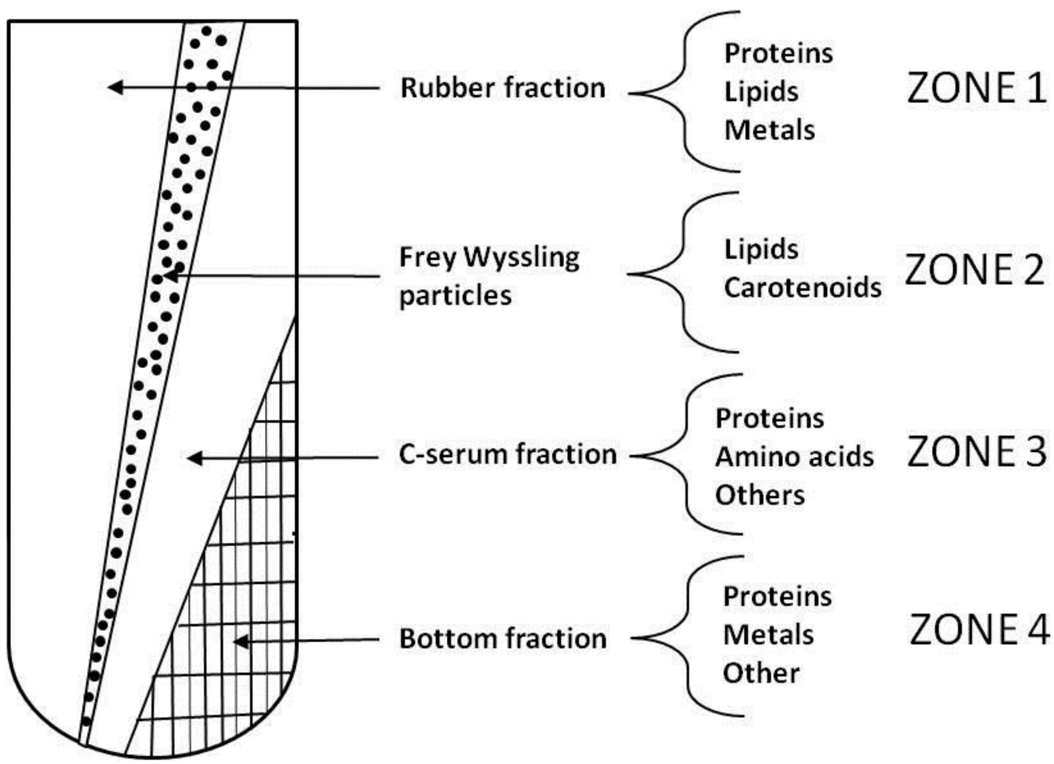


Figure 2. Fractions of Natural Rubber Latex after Centrifugation[11]

Table 1. The Four Major Zones in Natural Rubber and Their Function

No.	Zone	Major Components	Function
1	Rubber Particle	cis-1,4-polyisoprene Phospholipids	Elastomer
2	Frey Wyssling particles	Clusters of carotenoids and lutoids	affects viscosity, yellow color of latex
3	Clear serum	water soluble proteins, free amino acids, quebrachitol, potassium and phosphate ions, carbohydrates	• protein hydrolysis for stabilization, • buffers pH for stabilization, bioactive components for micro-organism consumptions
4	Bottom fraction	water soluble lipids, choline compounds, ash, inorganic constituents	• degrade on storage to form high fatty acids for stabilization, vulcanization accelerators, and natural anti-oxidants • forms sludge and removed during centrifugation, oxidizes rubber particles

The major rubber particle membrane protein is a 14kD polypeptide known as the rubber elongation factor. However, this protein along with a 30kD protein has been reported to be an important allergen in Type 1 allergic reaction.

Although the aluminium hydroxide-treated latex has lower content of non-rubbers and hence lower quantities of both 14kD and choline compounds, manufacturers still follow normal compounding formulation and practices. Some supplementation of antioxidants is done for long storage and reusable products from treated latex. Vulcanization in aluminium hydroxide-treated latex is not effected by reduction of amount of choline and 14kD protein.

It is as equally as important to highlight the reduced non-rubber content which could help in producing less rubber odor and a whiter color.

THE PROPERTIES OF TREATED LATEX

Table 2 illustrates the property difference between the treated and standard NRL. Treated NRL withstands mechanical shear and is more stable than standard NRL.

Table 2. Property Comparison between Treated NRL and Standard NRL

Characteristic	Treated NRL	Standard NRL
Dry Rubber Content, % (m/m)	60.03	60.08
Total Solids Content % (m/m)	60.94	61.21
Non Rubber Solids, % (m/m)	0.91	1.13
pH	10.05	10.55
Alkalinity (as NH3), % (m/m)	0.25	0.62
Volatile Fatty Acid Number (VFA)	0.02	0.03
KOH Number	0.56	0.4
Mechanical Stability (MST) seconds	960	586
Viscosity (sp2/60), cP	70	79.5
Coagulum content, % (m/m)	0.002	

BENEFITS OF TREATED LATEX IN PRODUCT APPLICATIONS

1) Condoms/Gloves

Condoms manufactured from treated NRL show improved performance exhibited in Table 3, burst analysis. Additionally, reduced appearance of number of pinholes is suggestive of improved quality. These results have been confirmed by several manufacturers currently using treated NRL. Below, treated NRL performs within the acceptable limits of the ISO 4074 standards, exhibiting parity with standard NRL.

Table 3. Burst Analysis of Treated NRL Performed by Company A

ISO 4074	Burst Pressure [kPa]	Burst Volume [L]	Pinhole
Treated NRL (Average 315 pieces)	2.19 ± 0.28	35.4 ± 4.7	0
	pass	pass	pass

The improved rubber to non-rubber ratio in treated NRL results in improved dynamic properties (resilience and rebound),[12] translating into improved quality hence better products.

The physical properties of modified NRL were compared to those of standard NRL manufactured by company B. The removal of the non-rubbers correlates with the treated NRL increase in stability as compared to the manufactured glove.

Table 4. Physical Properties of Examination Gloves Made from Treated NRL and Standard NRL

SET	Formulation	Tensile Strength (MPa)					
		BEFORE AGING (ASTM STD: Min. 14MPa)			AFTER AGING (ASTM STD: Min. 14MPa)		
		Highest	Lowest	Average	Highest	Lowest	Average
A	treated latex	33.3	30.1	31.5	23.2	19.4	20.9
Control	L9D	31.3	27.9	29.6	25.6	17.8	20.8
SET	**Formulation**	**Elongation %**					
		BEFORE AGING (ASTM STD: Min. 550 %)			**AFTER AGING (ASTM STD: Min. 400 %)**		
		Highest	**Lowest**	**Average**	**Highest**	**Lowest**	**Average**
A	treated latex	966.9	884.0	927.8	999.3	867.7	932.5
Control	L9D	845.8	770.2	808.7	893.3	782.8	831.6
SET	**Formulation**	**Modulus at 300% (MPa)**					
		BEFORE AGING (ASTM STD: Not Stated)			**AFTER AGING (ASTM STD: Not Stated)**		
		Highest	**Lowest**	**Average**	**Highest**	**Lowest**	**Average**
A	treated latex	3.85	3.43	3.63	2.71	1.95	2.34
Control	L9D	7.05	5.83	6.37	5.50	3.20	4.20

The modified NRL is slightly more expensive than standard NRL but less expensive than nitrile, chloroprene, and other synthetic alternative materials. To this, the modified NRL provides a significant cost value when compared to other synthetic lattices. Previously, we have described that the increased price for the modified NRL can be offset by reducing the number of manufacturing steps required to achieve acceptable protein levels.[4] Here, we further present that the stability of the modified NRL has greater flexibility, allowing for a longer shelf life and a greater filler load, which results in a significantly reduced cost.

Table 5. Cost Analysis

Latex Used	**Common Latex**				**Vytex**											
	Price (RM/kg)		**7.5**	**(MRB)**	**Price (RM/kg)**		**8.25**	**(10% more)**	**Price (RM/kg)**		**8.625**	**(15% more)**	**Price (RM/kg)**		**9**	**(20% more)**
Latex Portion, phr	67.5	62.5	57.5	51.5	67.5	62.5	57.5	51.5	67.5	62.5	57.5	51.5	67.5	62.5	57.5	51.5
Filler Amount, phr	30	35	40	46	30	35	40	46	30	35	40	46	30	35	40	46
	Price (RM/kg)		**0.5**		**Price (RM/kg)**		**0.5**		**Price (RM/kg)**		**0.5**		**Price (RM/kg)**		**0.5**	
Compounding Curative Portion, phr	2.5	(fixed for all level of fillers)			2.5	(fixed for all level of fillers)			2.5	(fixed for all level of fillers)			2.5	(fixed for all level of fillers)		
Total Cost Comparison, (RM/kg)	**5.213**	**4.863**	**4.513**	**4.093**	**5.719**	**5.331**	**4.944**	**4.479**	**5.972**	**5.566**	**5.159**	**4.672**	**6.225**	**5.8**	**5.375**	**4.865**

The slower rate of cross linking in modified NRL would benefit the glove manufacturers in terms of longer shelf life of the compounds for longer span of dipping hours. The softer feel of the modified gloves and the comparable physical properties even at the increased filler, 45 phr, makes the modified NRL a better choice for cost saving approach. The addition of high load of filler on the modified NRL gloves can be done without any quality deterioration as seen in Table 6 below. The extra from more filler in the modified NRL is due to the absence of non-rubbers. Overall, lower price for modified NRL (Table 5) is due to good-quality gloves as seen in the physical testing (above table) at 46% as compared to standard NRL at 35%. This translates into a reduced phr Latex portion of compounded modified NRL with an increased filler load, thus adding to the reduction in manufacturing costs.

Modified NRL or standard *Hevea* NRL were compounded for production of gloves (Table 6).

Table 6. Compounding of Treated and Standard NRL

Ingredients	**Level of Addition (phr)**		
	Treated/G45	**Treated G/40**	**Common/G40**
Treated NRL	100	100	-
Common Hevea CL60	-	-	100
20% Potassium Hydroxide	0.1	0.1	0.1
20% Potassium Laurate	0.15	0.15	0.15
60% Sulfur	1.2	1.2	1.2
50% Zinc Oxide	0.6	0.6	0.6
50% ZDEC	0.4	0.4	0.4
50% BZ	0.2	0.2	0.2
50% Wingstay L	0.5	0.5	0.5
70% Calcium Carbonate (filler)	45	40	40

Using the Toluene Swell Index, both the compounded modified NRL and standard NRL were assessed for pre-cure state without heat vulcanized before release into the production line where the compounds were subject to heat for drying and vulcanization.

Table 7. Toluene Swell Analysis

Days	Hours	Toluene Swell Results (%)		
		Treated G/45	Treated G/40	Common G/40
1	6	136	134	132
	12	120	118	116
	18	116	112	112
	24	108	106	102
2	30	100	98	94
	36	96	94	88
	42	92	90	82
	48	88	88	78 (overcured)
3	54	84	82	78
	60	80	80	-
	66	78 (overcured)	78 (overcured)	-
	72	78	78	-
4	78	-	-	-
	84	-	-	-
	90	-	-	-
	96	-	-	-

Once the toluene swell reached the manufacture-acceptable limit of 90%, the compounds were used to dip films of 0.1 mm thickness, mimicking the thickness of examination gloves. Significantly, both treated NRL compounds had similar toluene swell indexes to standard NRL. However, the treated NRL has a slower maturation as compared to standard NRL. Treated NRL needed to be dipped within 42 hours after compounding and used within 12 hours of compounding, while standard NRL required being dipped within 30 hours after compounding and being used within 6-8 hours. This translates into greater time flexibility on the production line when using treated NRL as source material.

The physical properties of the dipped films were assessed. The modified and standard NRL with 40 phr filler have comparable tensile strength (Table 8). Significantly, the modified NRL gloves have a softer feel than the standard NRL glove due to the higher elongation at break. This translates into more room in the compounding formula for extra filler. The modified NRL with the extra 5 phr filler had a higher elongation break than the standard NRL at 40 phr filler. The 700% elongation values of the modified NRL compounds, 40phr and 45 phr filler, still are softer than the standard *Hevea* NRL CL60.

Table 8. Physical Properties of Different Compounded Treated NRL and Standard NRL

Physical Properties	Treated G/45			Treated G/40			Standard G/40		
	Before Aging	After Aging	% Retention	Before Aging	After Aging	% Retention	Before Aging	After Aging	% Retention
Tensile Strength Mpa	22.9	16.3	71.2	24.1	17.2	71.4	24.9	15.7	63.1
Elongation %	712	705	99.0	751	720	104.3	640	697	108.9
Modulus at 300%, MPa	3.26	3.07	94.2	3.72	3.1	83.3	3.93	3.02	76.8
Modulus at 500%, MPa	10.0	7.96	79.6	11.3	7.99	70.7	13.3	7.99	70.7
Modulus at 700%, MPa	19.7	14.5	73.6	20.3	14.7	72.4	-	14.7	-

The results presented in Table 8 illustrate that treated NRL has significantly lower modulus or require less force as compared to standard NRL. This attribute makes treated NRL particularly attractive for the application of surgical and examination gloves due to less hand fatigue.

2) Balloons

The manufacturing of balloons is a growing use of treated NRL. Treated NRL produces a very high quality, more translucent balloon that has better barrier properties than ordinary NRL. No doubt this is due to removal of the lutoids and Frey-Wyssling particles to reduce discoloring by removing the opportunity of PPO browning, higher rubber to non-rubber ratio, and reduction of odorous low molecular weight acids.

To demonstrate the true color nature of treated NRL over standard NRL manufactured balloons, a comparison study was performed between colored balloons made with either treated or standard NRL. The data support that treated NRL is brighter in color. More significantly, for each color of balloon tested, the treated NRL results in a truer color than that of the standard NRL. These data confirm the removal of the contaminating inherent colors.

Table 9. Quantitative Color Determination

	Treated NRL			Standard NRL			Difference		
	L	a	b	L	a	b	ΔL	Δa	Δb
Orange	39.31	61.17	49.73	35.96	57.37	48.22	3.35	3.8	1.51
Red	-21.07	85.13	0.09	-37.11	80.17	0.03	16.04	4.96	0.06
Green	-31.76	-79.89	-0.15	-39.45	-72.13	-0.08	7.69	-7.76	0.13
Yellow	79.02	0.11	85.13	71.77	0.21	76.19	7.25	-0.1	8.94
Plain	69.86	0.04	3.54	45.87	0.08	10.43	23.99	-0.04	-6.89

L (lightness) axis - positive values are more white; negative values are more black and 0 is transparent

a (red-green) axis - positive values are red; negative values are green and 0 is neutral

b (blue-yellow) axis - positive values are yellow; negative values are blue and 0 is neutral

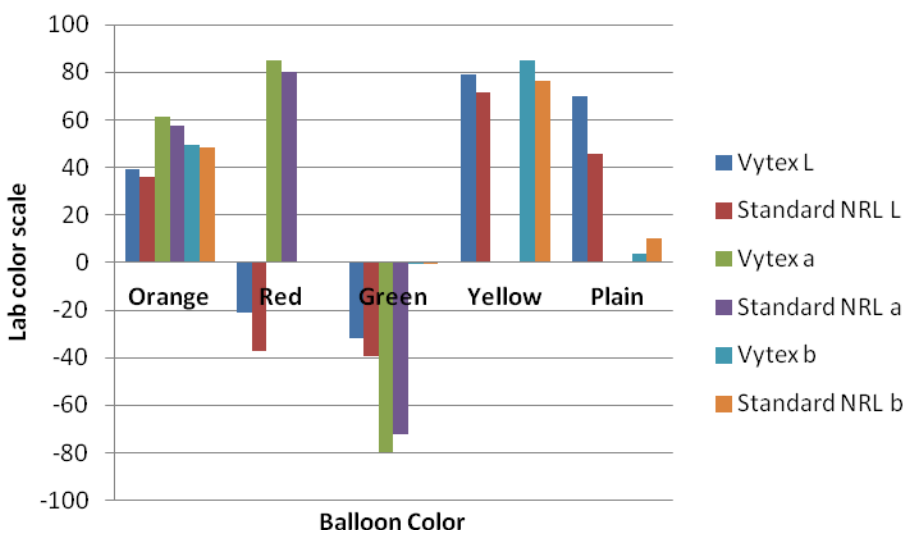
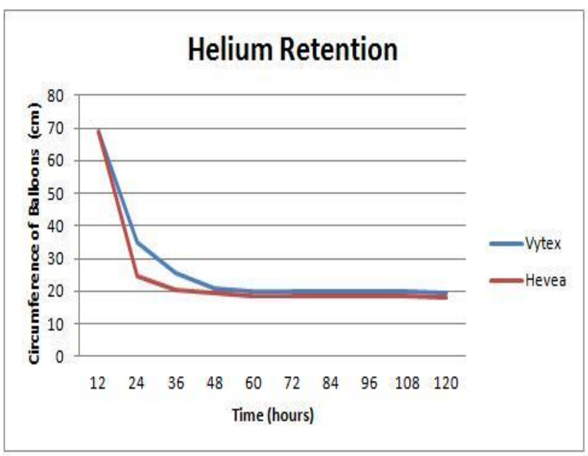


Figure 3. Lab Color Analysis of Balloons

Complementing earlier success for the modified NRL balloon studies, which revealed brighter and truer colors along with better air (N_2 and O_2) and helium (He) retention, here we report similar results of modified NRL compared to a common balloon by manufacturer C.

Table 10: Gas Retention of Treated NRL vs Standard NRL

Days	Hours	Circumference Measurement of Balloons at Intervals (cm)							
		Helium Retention				Normal Air Retention			
		Vytex 1	Vytex 2	Hevea 1	Hevea 2	Vytex 1	Vytex 2	Hevea 1	Hevea 2
1	12	69	69	69	69	69	69	69	69
	24	34.9	35.2	22.4	26.9	59.5	58.3	48	49.7
2	36	25.4	26	20.1	20.4	53	58	35.5	32.8
	48	21	20.5	19.5	19.6	52.5	57.3	29.4	28.1
3	60	20.2	19.4	18.9	18.5	49.4	52.6	20.4	22
	72	20.1	19.4	18.9	18.5	48.9	50.2	19.5	19.9
4	84	20.1	19.4	18.6	18.5	45.2	47.4	19.1	18.2
	96	20.1	19.4	18.6	18.5	44	44.2	19	18.2
5	108	20.1	19.4	18.1	18.4	42.5	41.4	19	18.2
	120	20	19.1	18	18.4	40.8	39.4	18.9	18.2



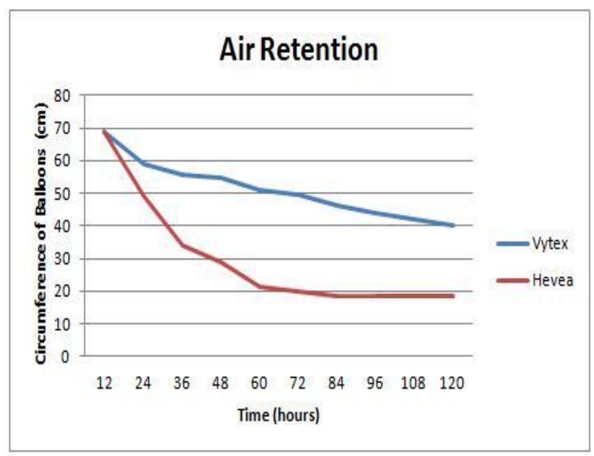


Figure 4. Gas Retention for Helium and Air

Gas retention was assessed as a function of tightly packed rubber particle matrix. Using either helium gas or normal air, balloons made of either modified NRL or the standard NRL balloons were inflated to a specified circumference with gas. The circumferences were measured at intervals of 12 hours. The modified NRL demonstrate about a 30% greater retention of helium as compared to the standard NRL. Additionally, modified NRL maintained air retention at 58.1% on the fifth day as compared to standard NRL which completely deflated by 60 hours. The removal of non-rubbers is believed to lead to the tighter rubber particle integration, preventing the 'wicking' loss of gas from within the balloons. The helium molecules being lighter and smaller are able to permeate out faster than normal air molecules of nitrogen and oxygen.

CONCLUSIONS

Aluminum hydroxide-treated NRL is the exclusive material of choice by the largest US manufacturer of latex balloons due to the radiant colors quantified by independent test methods. Glove manufacturers continue to differentiate their products and upgrade to Vytex due to the softness/low modulus and are able to increase filler loading due to the absence of non-rubbers, reduce leaching processes and cost. The aluminum hydroxide-treated NRL has a longer "pot life" compared to regular NRL which benefits glove manufacturers in terms of longer shelf life of the compound allowing for more dipping flexibility. These attributes are attractive in other applications, such as foam, where less rubber odor and a whiter color are highly desirable. Aluminum hydroxide treated-NRL has a low non-rubber content compared to regular NRL and is virtually free of the 14kD and 30kD polypeptide proteins reported to be known Type 1 latex allergens. These characteristics make it the material of choice for applications seeking high-quality, safer end products.

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