



A Novel “Protein-Free” Natural Rubber Latex: Properties and Applications

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Abstract

It is well known that liquid natural rubber latex from the *Hevea brasiliensis* tree contains a number of proteins that cause minor to serious allergic reactions. Many prior authors have studied these proteins extensively and have isolated what are believed to be the most allergenic. Estimates run as high as 17% of healthcare workers affected by latex allergies due to the various targeted proteins within a relatively short range of rubber elongation factors. Vystar Corporation has developed a novel, patented method for the deactivation of the antigenic proteins (AP) in liquid natural rubber latex that involves the quasi-sequestration of these proteins. The authors believe that this method “denatures” the proteins by altering the stereochemistry of their structures thus reducing the ability to generate an immune response. It appears that the deactivation method has no adverse effects on the physical and chemical properties of natural rubber latex as it is used in the manufacture of dipped products. Further studies are planned to determine if barrier properties may be slightly improved over untreated natural rubber latex. Dipped product manufacturing techniques may be enhanced by greatly reducing the antigenic protein levels prior to production; costs may be positively impacted due to a reduced need for post treatment such as excessive washing and leaching. Processability studies and pilot plant runs are in the early stages, but show promise. Applications include the production of medical devices such as gloves, condoms, catheters, etc. End unit pricing will be in line with the alternatives currently in the market while providing the positive properties of natural rubber latex.

Introduction

Although latex as a protectant has a long history of usage dating back to the 1800s, the use of barrier goods like gloves and condoms increased tremendously in the 1980s. Due to its complex mechanical and chemical properties, latex is considered to have the best broad range of desirable properties. Allergic reactions for human skin in contact with latex have grown tremendously in the previous two decades. Naturally occurring antigenic protein in raw latex has been identified as the problem as they migrate from the finished latex product to the skin.¹

The first description of allergic reaction to latex gloves appeared in the American literature in 1933, yet more than 20 billion gloves from latex are used annually in the

United States.^{2,3} It has been published that in 2003, 16.7% of the cases of intra-operative shock were attributed to latex allergies.⁴ Similarly, it is estimated that 17% of American healthcare workers and 73% of frequently exposed patients have become sensitized to the antigenic latex proteins.^{5,6}

The amount of protein in natural rubber latex (NRL) has remained fairly constant at 1.6-2.0 wt % (16,000- 20,000 _g/g), but the final concentration varies between 3 to > 600 _g/g depending on the manufacturing technique used.⁷ In March 1995, the United States Food and Drug Administration issued interim labelling guidance on permissible levels of protein in medical latex gloves that set the upper limit at 50 _g/g for low protein claims. Most experts argue that the level should be lower since the probability of an allergic reaction decreases with the protein level and should be around 1 _g/g.⁸ Achieving this lower number plus preserving the superior properties of latex, such as elasticity, has proven to be elusive.

Since there are 240 potentially antigenic proteins in processed latex, and due to the complex nature of the latex extract, accurate protein measurement presented a challenge. Some believe that the optimal estimation of antigenic protein levels are determined by the ELISA Inhibition Assay Method, ASTM D6499-03, while the Modified Lowry Test, ASTM D5712 quantitatively shows the total protein content that includes the potentially allergenic proteins.^{9, 10}

Many efforts have been made to remove protein from NRL by physical and /or chemical methods that affect the complex acid-base behavior of proteins. Also, protein content can be decreased to such levels as 200-300 _g/g through successive centrifugations of NRL or by enzymatic decomposition however, appearance and physical and chemical properties usually suffer. AP levels were decreased to 20mg/g through the use of proteolytic enzymes and surfactants.¹¹ Ultrasonic leaching or irradiation by cobalt also showed promise to reduce AP levels in the literature.^{12,13}

Most of the above methods are complex and offer limited effectiveness resulting in the inadequate removal of allergenic protein. More promising could be a treatment of NRL in the liquid phase by using selected inorganic and/or organic chemicals prior to processing and manufacturing the end product. Absorbents, such as fumed silica, have offered considerable protein removal.¹⁴ Little research exists in this field and there has not been a blueprint for methodological or technological advancement. The solution to lowering the antigenic protein to those levels generally accepted is complicated due to the complex chemical nature of protein.

The aim of this current work is to present a selection of chemicals that might be useful for protein removal as shown in the results discussion of treated NRL and laboratory produced films. The protein removal occurs without losing the very important physical and chemical properties of latex. Prior studies show that lowering total protein lowers the antigenic protein also.

Experimental

Two different types of NRL have been used for experimental testing.

1. Field latex from South East Asia containing 1,123.7 $\mu\text{g}/\text{ml}$ of antigenic protein (AP) and a pH of 9. (Total solids not reported but assumed to be ~30%.)
2. Field latex from South East Asia, with 26 % wt. total solids (TS); 636.3 $\mu\text{g}/\text{ml}$ of AP and a pH of 10.92.

(Additional tests are ongoing to determine the effect of antigenic protein removal using centrifuged latex.)

One hundred grams of NRL were used as the sample size for laboratory experiments. Each sample was poured into a glass flask followed by the introduction of specific additives mixed into latex. When necessary, the pH of latex was adjusted to 11 by adding NaOH to the solution. Different concentrations of additives (0.01 - 1.0 %¹) were added to the latex to determine their influence on AP content. Depending on the combination of additives, as described below, the insertion methods were different.

Several types of chemicals were used as additives to NRL to deactivate AP in latex by absorption or binding it chemically. ALDRICH, SIGMA, SIGMA-ALDRICH, ALFA AESAR, BASF and ZEOLYST supplied all the chemicals as either powders or standard solutions with known concentrations and technical grades.

The first group included inorganic salts: aluminium chloride (AlCl_3), aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$), magnesium chloride (MgCl_2), silver nitrate (AgNO_3), zinc iodide (ZnI_2). These salts were preliminary dissolved in distilled water and calculated amounts of solutions were added to NRL.

The second group of additives included inorganic oxides and hydroxides: aluminium hydroxide ($\text{Al}(\text{OH})_3$), titanium dioxide (TiO_2), fumed silica (SiO_2) and zeolytes. Because these compounds are insoluble in water, $\text{Al}(\text{OH})_3$ was added as a solution in 45-50 % NaOH or KOH. However, TiO_2 , which is practically insoluble in alkali, was added as a suspension of TiO_2 in 50% NaOH. In some tests TiO_2 , and $\text{Al}(\text{OH})_3$ were added to latex in their powder form as was done with zeolytes and silica.

Four types of zeolytes were used for latex treatment: (1) Zeolyte (ZSM-5), containing NH_4^+ on active sites; (2) Zeolyte with H^+ , obtained after a heat treatment (550°C for 3 hours) for the removal of NH_3 ; (3) Zeolyte with Fe^{2+} ; (4) Zeolyte with Al^{3+} . An ion exchange was performed by a heat treatment of Zeolyte (ZSM-5) followed by treatment in solutions of AlCl_3 and FeCl_3 for 2 hours, filtration and drying at 110°C. The Zeolyte supplier recommended the ion exchange procedure.

The third group of additives included metal powders aluminium (Al) and silver (Ag), and aluminium wire (Al-wire). The powders were added directly to NRL, however the Al-wire was immersed into the latex and exposed for a set period of time to get the aluminium ions into the latex as the wire corroded.

¹ Here and further % means wt. %

The fourth group included organic compounds: formaldehyde, sodium salts of benzenesulfonic and benzenesulfinic acids, sodium decylsulfate, acrylamide, zinc gluconate, zinc acetate, copper(2) acetate. They were added to latex as liquids, solutions or solids.

The fifth group included polymeric absorbents: lupamin 9010, lupamin 1595, lupasol FG, lupasol G20, lignins.

After the addition of chemicals and thoroughly mixing with a magnetic stirrer, the pH was evaluated using a digital pH meter. Next, the latex with additives was agitated for 72 hours. This time was chosen as optimal after some preliminary estimation. Ten gram samples of treated latex were taken to determine the AP content. Additional 10g samples of treated latex were taken after centrifuging the treated latex for 1 hour at 3,000 rpm using a DIMON/IEC HN-SII centrifuge.

The mix was then compounded by standard additives, which are commonly used to produce latex goods. Added compounds and concentrations used are:

Additive	PHR	Additive	PHR
Potassium hydroxide	0.05	2-mercaptobenzothiazole, zinc salt	0.25
Sodium polynaphthalenesulfonate	1.00	Zinc oxide	0.70
Sulfur	0.70	Butylated hydroxytoluene	0.50
Zinc dimethyldithiocarbamate	0.45		

The compounded latex was agitated for 48 hours in a covered glass flask. The mix was then used to produce films. About 40g of liquid latex were poured on a levelled glass plate, drawn by an adhesive spreader and then dried for 8 to 10 hours in air. Next, the glass plate and film were placed in an oven at 70°C for 10 minutes, and then placed into a bath with distilled water. The film was detached from glass and then leached in distilled water at 100°C for 2 minutes. The rubber film was then mounted on metal frame and placed into an oven for vulcanization at 130°C for 25 minutes. Next, samples were cut from the treated latex film to analyze AP.

All samples, both liquid and film, were analyzed using ELISA Inhibition Assay method (ASTM D6499-03) at LEAP Testing Service Laboratory (Donald Guthrie Foundation Education Research) to determine AP content. Certain selected films were tested to determine elongation, and samples with a 20mm width and a 70mm length were cut from the film. One end of the sample was attached to a metal crossbeam frame and the sample was examined by loading weights at the lower end. The measurement for each sample (20mm) was recorded after loading and release.

Results and Discussion

Influence of pH and method of pH adjustment on antigenic protein content

Maintaining a desirable pH in latex is important for latex processing. The pH can be adjusted by using potassium hydroxide (KOH) and/or potassium hydroxide + ammonium hydroxide (NH₄OH). The reactive functional groups of protein are acids or bases, thus

their reactivity must vary with the pH of latex.¹³ Therefore, the total protein content would be changed as the pH changes.

Table 1 below illustrates the results of AP value in latex after a pH adjustment. Because an initial pH of latex used for these tests was 9, the pH had to be increased to 11 before adding additional chemicals. The adjustment was made by adding NaOH to the latex followed by the introduction of other chemicals. The addition of chemicals also changed the pH because of the alkalinity of the added chemicals (solutions).

Table 1. Influence of pH at different methods of adjustment on the AP content

#	Additives			Test conditions			AP, $\mu\text{g/ml}$	Notes
	Chemical	Formula	Wt. %	pH	Exposition after Introduction of additives, hours	Centrifuging + yes - no		
1	Sodium Hydroxide	NaOH	-	11	72	-	14,700.0	
	Sodium Hydroxide	NaOH	-	11	72	+	30,365.4	
2	Sodium Hydroxide + Ammonium Hydroxide	NaOH	-	11	72	-	31,487.4	Double treatment
		NH ₄ OH	1.0	11+	-	+		
		NaOH	-	11	72	-	-	
NH ₄ OH	1.0	11+	-	+	-			
3	Sodium Hydroxide + Formaldehyde	NaOH	-	11	72	-	3,758.6	Treatment by NaOH then HCHO
		HCHO	0.01	11	24	+		
		NaOH	-	11	72	-	5,203.4	
		HCHO	0.10	11	24	+		
NaOH	-	11	72	-	7,328.6			
HCHO	0.50	11	24	+				
4	Formaldehyde	HCHO	0.01	9	24	+	314.9	
		HCHO	0.10	9	24	+	379.2	
		HCHO	0.50	9	24	+	555.2	
5	Sodium Hydroxide + Aluminum Hydroxide	NaOH	-	11	72	-	243.1	Treatment by NaOH then Al(OH) ₃
		Al(OH) ₃	0.01	11+	24	+		
		NaOH	-	11	72	-	22.8	
		Al(OH) ₃	0.05	12	24	+		
NaOH	-	11	72	-	14.5			
Al(OH) ₃	0.10	13	24	+				

Table 1 also indicates that increasing the pH from 9 to 11 by adding NaOH and NH₄OH resulted in a significant increase of AP in latex (from 1,123.7 $\mu\text{g/ml}$ initially at pH=9 up to more than 60,000 $\mu\text{g/ml}$). This AP increase suggests that strong alkalis provide an activation of proteins releasing AP. Formaldehyde with NaOH partially neutralizes this action and even reduces AP content 2-3 times, when used alone. This decrease in AP may not be enough to obtain the status “protein-free” latex. Better results were observed by the addition of aluminium hydroxide as a 2% solution in saturated NaOH. Table 1 demonstrates that this additive drastically reduces the AP in latex compared with the initial AP value, even at a slightly higher pH of the final product. The required pH of 11 can be achieved by introducing the appropriate amount of alkali in added solutions. This effort is ongoing but initial test results are encouraging. Also, additional tests are being conducted that use other additives containing aluminium ions as well as ions of other metals.

Influence of soluble inorganic and organic compounds

Table 2. Influence of soluble inorganic and organic additives on AP content in liquid latex

#	Additives			Test conditions		AP, µg/ml	Notes
	Chemical	Formula	Wt. %	pH	Centri- fuged		
Soluble inorganic compounds							
6	Magnesium chloride	MgCl ₂	0.24	9	+	156.0	Field Latex (pH = 9, AP = 1,123.7µg/ml)
			0.12	9	+	126.4	
			0.06	9	+	165.4	
7	Aluminium hydroxide	Al(OH) ₃	0.05	12	-	12.1	Field Latex (pH = 11, AP = 636.3µg/ml)
			0.04	11	-	39.5	
			0.04	11	+	41.6	
			0.02	11	+	147.3	
			0.01	11	+	403.9	
8	Aluminium chloride	AlCl ₃	0.1	11	-	487.6	
			0.05	11	-	520.2	
			0.01	11	-	562.4	
9	Silver nitrate	AgNO ₃	0.1	11	-	445.8	
			0.05	11	-	763.3	
			0.01	11	-	832.4	
10	Aluminium sulphate	Al ₂ (SO ₄) ₃	0.10	11	-	343.8	
			0.05	11	-	351.3	
			0.01	11	-	357.9	
11	Zinc iodide	ZnI ₂	0.20	11	-	416.0	
			0.10	11	-	287.3	
			0.05	11	-	417.4	
Soluble organic compounds							
12	Copper acetate	(CH ₃ COO) ₂ Cu	0.08	11	+	912.5	Field Latex (pH = 11, AP = 636.3µg/ml)
			0.08	11	-	1,163.1	
			0.02	11	+	575.2	
			0.02	11	-	607.0	
13	Zinc gluconate	Zn[CH ₂ (OH)(CHOH) ₄ CO ₂] ₂ ·3H ₂ O	0.20	11	-	384.3	
			0.10	11	-	475.4	
			0.05	11	-	470.0	
14	Zinc acetate	Zn(CH ₃ COO) ₂	0.20	11	-	331.0	
			0.10	11	-	338.8	
			0.05	11	-	379.7	
15	Sodium dodecyl sulphate	CH ₃ (CH ₂) ₁₁ SO ₃ Na	0.50	11	-	1,978.8	
			0.50	11	+	1,953.4	
			0.05	11	-	610.4	
			0.05	11	+	1,067.0	
16	Sodium salt of Benzenesulfinic acid	C ₆ H ₅ SO ₂ Na	0.50	11	-	447.3	
			0.50	11	+	559.5	
			0.05	11	-	490.2	
			0.05	11	+	262.4	
17	Sodium salt of Benzenesulfonic acid	C ₆ H ₅ SO ₃ Na	0.50	11	-	389.8	
			0.50	11	+	647.4	
			0.50	11	-	420.9	
			0.05	11	+	378.6	

Table 2 illustrates the AP content in liquid latex after treatment by soluble inorganic and organic compounds. Table 2 reveals the inorganic compounds are more effective for AP reduction than organic compounds. Also, it is evident that effectiveness of inorganic additives becomes higher with increased concentration. The most significant influence on AP removal is observed in tests with addition of $\text{Al}(\text{OH})_3$.

Influence of metallic additives and absorbents

The results of treating latex by metals, inorganic and organic absorbents are presented in Tables 3, 4. It is interesting to observe the effect of metal additives in dispersed but insoluble (or poorly soluble) form (Table 3). Field latex (AP = 636.3 $\mu\text{g}/\text{ml}$) was used in these tests and it was not centrifuged after treatment. It is concluded that metals can decrease antigenic protein content but not enough to be achieve the target levels.

Table 3. An effect of the metals on AP content in liquid latex

#	Additives			pH	AP, $\mu\text{g}/\text{ml}$	Notes	
	Chemical	Formula	Wt.%				
18	Silver	Ag	0.10	11	396.1	Powder	
			0.05	11	394.1		
19	Aluminium	Al	N/A	11	325.1	Immersed Al- wire at 20°C for 180 h.	
20	Aluminium	Al	N/A	11	359.4	Agitation in aluminium vessel for the period of time noted (hours)	1.0
				11	411.4		2.5
				11	369.5		5.0
				11	350.4		72

Table 4 displays the results of AP removal by adding some well-known inorganic and organic absorbents to the field latex (AP=636.3 $\mu\text{g}/\text{ml}$). It was noted that centrifuging the samples does not play an important role for AP removal in these cases. It is also clear that absorption alone is not enough to remove or deactivate AP in latex. Even when the most active absorbents were used, the AP reduction is minimal but experiments with TiO_2 suspension in a NaOH solution provided encouraging results. This result can be explained by the activation of the surface of titanium dioxide in strong alkali.

Table 4. Effectiveness of absorbents on AP content in liquid latex, inorganic

#	Additives		Test conditions			AP, $\mu\text{g}/\text{ml}$	Notes
	Chemical		Wt.%	pH	Centrifuged		
Inorganic compounds							
21	Titanium dioxide	TiO_2	0.1	11	-	376.0	Powder
			0.06	11	-	311.2	
			0.02	11	-	384.2	
			0.02	11	-	116.3	Suspended in NaOH
22	Fumed silica		0.1	11	-	347.9	Powder
			0.1	11	+	261.5	
			1.0	11	-	243.2	
			1.0	11	+	251.6	
23	Zeolyte – ZSM5 (molecular sieve)		0.5	11	-	605.1	Zeolyte (NH_4^+)
			0.5	11	-	485.2	Zeolyte (H^+)
			0.5	11	-	493.1	Zeolyte (Al^{3+})
			0.5	11	-	513.6	Zeolyte (Fe^{3+})

Table 4, cont. Effectiveness of absorbents on AP content in liquid latex, organic

#	Additives		Test conditions			AP, $\mu\text{g/ml}$	Notes
	Chemical		Wt. %	pH	Centrifuged		
Organic compounds							
24	Merrifield's Peptide resin		0.50	11	-	824.7	Powder
			0.50	11	+	645.0	
			0.10	11	-	756.8	
			0.10	11	+	787.2	
25	Acrylamide		1.0	11	-	296.0	Powder
			0.5	11	-	328.8	
			0.1	11	-	467.5	
26	Polyacrylamide		1.0	11	-	420.7	50% solution in H_2O
			0.1	11	-	443.5	
27	Vinylamine-vinylformamide polymer		0.5	11	-	361.7	Liquid
	Polyethylenimine with Mw 800g/mol		0.5	11	-	221.3	
	Polyethylenimine with Mw 1300g/mol		0.5	11	-	325.2	

Influence of mixed additives on AP content in liquid latex

Assuming that a combination of the most effective additives can improve AP removal, several combinations of $\text{Al}(\text{OH})_3$ with other chemicals were tested. The Table 5 results indicate that this assumption was only partially confirmed by tests. Latex which was treated with $\text{Al}(\text{OH})_3$ dissolved in NaOH in combination with absorbents (fumed silica and Lignin Curan 2711P), provided the best results. The AP levels in latex treated by these combined additives are similar to the results obtained from treating latex with $\text{Al}(\text{OH})_3$ alone dissolved in alkali.

Table 5. Effectiveness of combined additives on AP content

#	Additives		pH	AP, $\mu\text{g/ml}$	Notes
	Title	Wt. %			
28	Fumed silica + Aluminium hydroxide	0.50 0.04	11	22.2	$\text{Al}(\text{OH})_3$ dissolved in NaOH solution, Powder of SiO_2
		0.50 0.05	12	15.5	
29	Acrylamide Aluminium hydroxide	0.5 0.04	11	215.2	$\text{Al}(\text{OH})_3$ dissolved in NaOH solution, Powder of Acrylamide
30	Lignin + Aluminium hydroxide	0.5 0.04	11	48.0	Type of lignin: Curan 2711P
		0.5 0.05	11	12.3	Curan 2711P
		0.5 0.04	11	71.6	Norlig
		0.5 0.04	11	76.9	Lignosite 100
		0.5 0.04	11	68.0	Lignin alkali

The additives on the base of Al(OH)₃ in various combinations with alkali and other chemicals were chosen for further research to determine their influence on AP content in vulcanized NRL and on other physical properties of NRL.

Influence of additives on AP content in NRL film

NRL films were created from the treated liquid latex as previously described. A control film sample was made from the field latex that contains 636.3µg/ml of AP.

Table 6. Antigenic protein in latex films

#	Additives		Technological features			AP, µg/g
	Chemical or formula	Wt. %	Ageing before compounding, hours	Premixing before compounding additives, hours	Increase of + - viscosity C - conglomeration	
1	Control sample	-	0	0	not observed	33.0
2	Al(OH) ₃ in NaOH	0.04	432	0	+	23
	Al(OH) ₃ in NaOH	0.05	456	0	++	6.7
3	Fumed Silica Al(OH) ₃ in NaOH	0.5 0.04	312	0	not observed	46.5
	Fumed Silica Al(OH) ₃ in NaOH	0.5 0.05	360	0	++	10.8
	Fumed Silica Al(OH) ₃ in NaOH	0.25 0.05	504	0	+++ C	1.8
	Fumed Silica Al(OH) ₃ in NaOH	0.5 0.06	648	0	+++ C	1.1
	Fumed Silica Al(OH) ₃ in NaOH	0.5 0.1	0	0	not observed	37.3
4	Lignin Al(OH) ₃ in NaOH	0.5 0.05	528	0	++ C	4.5
	Lignin Al(OH) ₃ in NaOH	0.5 0.06	624	0	+++ C	0.4
	Lignin Al(OH) ₃ in NaOH	0.5 0.06	72	0	not observed	22.4
5	Lignin Al(OH) ₃ in KOH	0.5 0.06	72	0	not observed	112.0
	Lignin Al(OH) ₃ in KOH	0.5 0.06	0	0	not observed	53.8
	Lignin Al(OH) ₃ in KOH	0.5 0.1	72	0	not observed	31.0
	Lignin Al(OH) ₃ in KOH	0.5 0.1	0	0	not observed	7.2
	Lignin Al(OH) ₃ in KOH	0.5 0.1	0	72	not observed	1.9
	Lignin Al(OH) ₃ in KOH	0.5 0.15	0	72	not observed C	<0.2
	Lignin Al(OH) ₃ in KOH	0.5 0.20	0	72	not observed C	0.8

Potassium hydroxide (KOH) was substituted in some tests for NaOH because it is a typical component for compounding latex products. Table 6 illustrates that the AP value

is significantly reduced in vulcanized rubber film compared to the AP value in liquid latex. From this comparison we can initially conclude that the AP level in liquid latex is approximately 10-20 $\mu\text{g/ml}$ and the AP level in the vulcanized product is approximately $\leq 1\mu\text{g/ml}$.

It is important to note that an increase in viscosity and a coagulum formation was observed during extended agitation of the latex. Under these circumstances, water was added as needed (~10 to 15%) to the latex to reduce the viscosity in order to process the

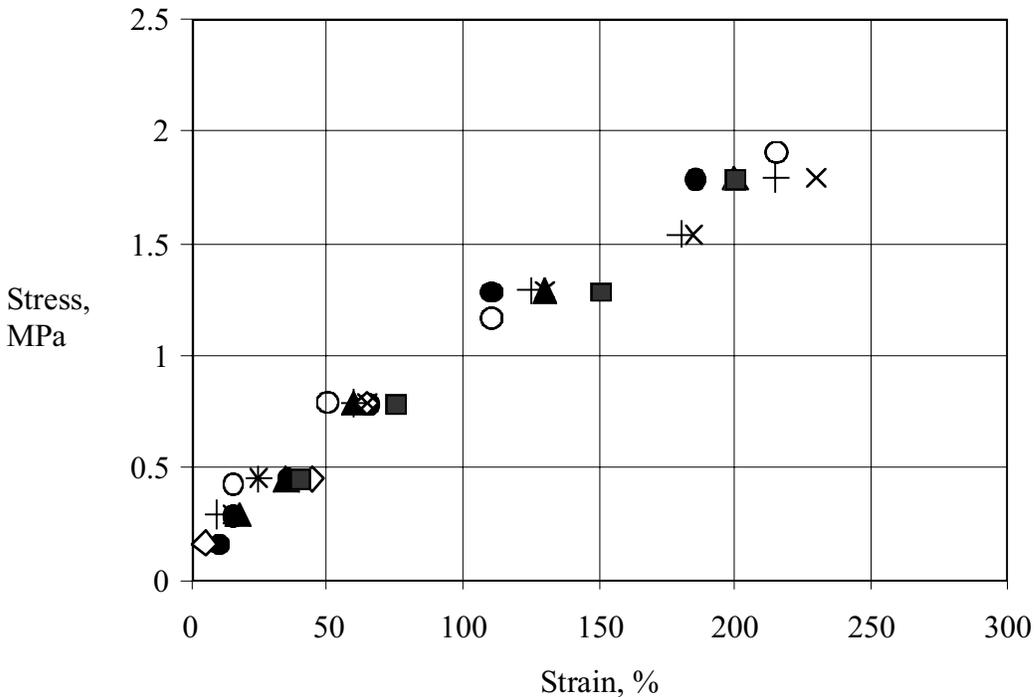


Figure 1. Elasticity of latex

- Industrial rubber (cut off from glove)
- ▲ Without anti-protein additives
- ◇ 0.25% SiO₂ + {0.05% Al(OH)₃ in saturated NaOH}
- 0.5% Lignin (Curan 2711P) + {0.05% Al(OH)₃ in saturated NaOH}
- × 0.5% Lignin (Curan 2711P) + {0.05% Al(OH)₃ in saturated NaOH} + 0.05% Al(OH)₃ in saturated NaOH
- 0.5% Lignin (Curan 2711P) + {0.1% Al(OH)₃ in saturated KOH}

latex into the film. The mixture was stirred for 1 hour by mixing with a magnetic stirrer. The coagulated particles were removed before the addition of compounding additives and before film creation. The formation of the large conglomerates occurred in some cases. It is believed that this could have occurred due to some coagulation of latex that happened prior to compounding. We can also assume that this process can facilitate the binding and deactivation of antigenic protein. It should be noted that we observed a

reverse correlation with the lowest levels of AP occurring in the cases when the highest coagulation took place.

Elasticity of NRL films

The elasticity of NRL films made from various types of latex are plotted together in Figure 1. It demonstrates that NRL films produced from latex treated with “anti-protein” additives have elasticity similar to industrial rubber films. Latex films made with anti-protein additives do not significantly alter the elasticity of NRL within the limits of measurement error, which was close to data available in the literature.¹⁴ The length of the samples after testing remained mostly unchanged.

The possible mechanism of influence of $Al(OH)_3$ on removal of AP

Fresh precipitated aluminium hydroxide is used in the purification of water because it can form a jelly-like structure suspending any unwanted materials in water, including most of bacteria.¹⁵ Furthermore, because of a high ionic strength (low ionic radius and high positive charge), aluminium can form a different kind of oxide-hydroxide complex ion, which can have a positive, neutral or negative total charge depending on the pH of a solution. Figure 2 shows the dependency of aluminium ionic composition on pH.¹⁶

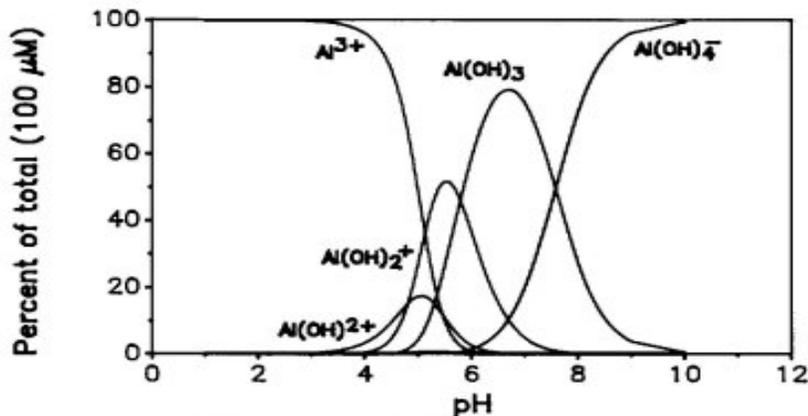
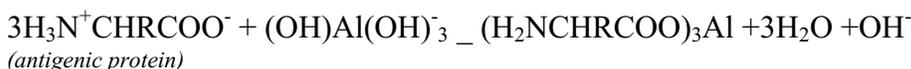
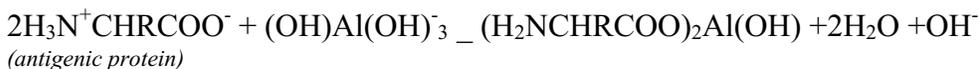
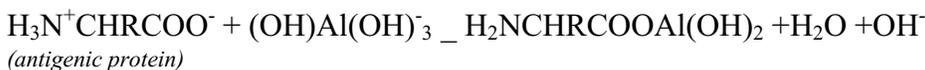
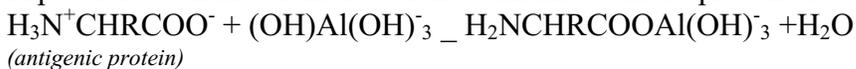


Figure 2. Aluminum ionic composition vs. pH

The effect of protein removal from natural latex can be contributed to the absorption of protein by a jelly-like freshly precipitated aluminium hydroxide. The precipitation of aluminium hydroxide occurs when an alkaline solution with a rather high concentration of aluminium ions is added to latex. The low alkalinity of natural latex emulsion allows the $Al(OH)_3$ to precipitate thus forming thin particles, which have very strong absorbing ability. Furthermore, aluminium ions can bind protein chemically. The ability to form complexes with carboxylic group (which is present in proteins) is well known from literature.¹⁷ These complexes can be rather stable in a solution with a high alkalinity. Therefore the proteins are capable of replacing the hydroxide group in the complex aluminium-hydroxide ion partially or completely. The formation of pure protein-

aluminium complex could form a soluble compound, but the partially replaced complex can be insoluble in the solution that would remove proteins from latex.

A possible scenario of the reactions with AP could be presented as:



The presence of an insoluble coagulum has been observed in latex emulsion after treatment in all of our successful tests. There is evidence of a formation of insoluble compounds, which can provoke crosslinking of latex and can contain bound protein.

Conclusion

It is quite apparent from the test data that dramatic reduction in protein levels is achieved by the relatively simple processes of denaturing protein found in natural rubber latex with aluminium hydroxide alone or with lignin and a fumed silica. All of these processes are employed prior to vulcanization¹⁸ of the natural rubber latex. In doing so, products can be produced while reducing risks imposed upon users of natural rubber latex products, including healthcare professionals, as a result of type I hypersensitivity. Most importantly, work to date indicates this can be accomplished without diminishing the physical properties of natural rubber latex that makes commercial products made from this material so desirable.

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