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Low Protein Natural Rubber Latices

MA'ZAM MD SAID*#, K.P. NG*, H. HASMA*, K.L. MOK*,
M. ASRUL*, P.F. LAI* AND S. SAADIAH**

A comparative study of the latex concentrate properties and properties of latex dipped films prepared from low protein (LP) latices was carried out. Besides the basic latex properties, the extractable protein (EP), antigenic and allergenic protein (AP) contents of the latex concentrates and latex dipped films were also examined. In addition, the physical properties such as tensile, tear and cuff rupture strength and coefficients of friction of the latex dipped films were compared. The biocompatibility and barrier performance of these films were also evaluated. The majority of the coagulant dipped films prepared from LP latices, that were wet-gel leached for 5 min at 50°C, showed low levels of allergenic and antigenic protein (AgP) contents. However, only a few of these films showed EP content of less than 200 µg/dm². There was a considerable variation in the nitrogen contents of LP latices (0.04% – 0.21%) and prevulcanised LP latices (0.09% – 0.24%). In view of the relatively wide range of nitrogen contents and the expectation that product prepared from a LP latex ought to contain low levels of EP, AP and AgP contents, it was proposed that maximum limits for nitrogen content of the latex and maximum limits for EP, AP and AgP contents of the dipped vulcanised latex films prepared under standard conditions be established in order to characterise and define the term 'low protein latices'. The determinations of dry rubber contents and mechanical stabilities of some of the LP latex concentrates were found to be problematic due to the difficulty with coagulation and excessive foaming, respectively. For a majority of LP latex concentrates, extended maturation times were found to be necessary to achieve precure and tensile properties comparable to a normal high-ammonia centrifuged latex. Minimal problems were observed during the preparation of dipped films from the LP latices. The biocompatibility and barrier characteristics of dipped films prepared from LP latices were rather similar to those prepared from normal latex concentrate.

Key words: NR; latex concentrate; latex dipped films; low protein; extractable protein; antigenic protein; allergenic protein; physical properties; biocompatibility; barrier performance; mechanical stability; high-ammonia; centrifuged latex; DRC; deproteinisation; latex allergy

Latex protein allergy, of Type 1 (immediate) hypersensitivity, has emerged as a serious health-related issue in the natural rubber latex industry since the late 1980s[1–3]. The anti-latex lobby in the U.S.A. has attempted to portray NR latex as 'a strong senstiser'[4] and advocate that its use be curtailed. More recently, the call to ban on the use of latex gloves has been

*Rubber Research Institute, Malaysian Rubber Board, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia
**Department of Medicine, Hospital Universiti Kebangsaan Malaysia, Bandar Tun Razak, Cheras, 56000 Kuala Lumpur
#Corresponding author (e-mail: ma'zam@lgm.gov.my)

extended to food handling as a result of claims on the transfer of latex allergen to foods[5] The anti-latex campaign has been going on despite the fact that NR latex glove has been proven to be the glove of choice for medical use with its unsurpassed barrier performance, comfort and fit, tensile properties, environmental friendliness and low cost[6] Nonetheless, the latex industry has responded positively to the challenges posed by latex protein allergy These include intensified R & D on latex allergy, promotion of positive attributes of latex gloves and quality improvement through the production of low powder and low protein (LP) and powder free latex gloves As a means to guarantee the quality of latex gloves, the Standard Malaysian Glove (SMG) Scheme has been initiated[7,8] by the Malaysian Government The R & D efforts carried out at the Rubber Research Institute of Malaysia (RRIM), a research unit of Malaysian Rubber Board (MRB), have brought about significant technological innovations in addressing the latex protein issues Some examples of these are improved leaching protocol for protein reduction[9], formulation for improved heat resistance of chlorinated gloves[10], polymer-coating for latex gloves[11] and production of LP latices[12-14]

The production of LP latices has long been recognised as one of the means to tackle the latex protein issues at its source In recent years, both commercial[15-20] and experimental[12-14] LP latices have been developed though the commercial uptake has been extremely slow LP latices can be produced, in general, by either mechanical or chemical means The mechanical process involves multiple centrifugation or membrane filtration of dilute latex On the other hand, the chemical treatment involves a combination of digestion with a proteolytic enzyme or displacement of adsorbed proteins using a surfactant and the subsequent purification of the treated latex by centrifugation or possibly through creaming The starting materials can be field latex, latex concentrate or prevulcanised latex

It has been established that latex glove of extractable protein (EP) content of below 100 μg/g and 50 μg/g, as determined by the RRIM modified Lowry assay and *ASTM D5712-95*, respectively, would tend to induce low incidence of allergic reactions[21] Such an observation was subsequently confirmed by IgE latex specific ELISA-inhibition test that gloves with EP_{RRIM} of <100 μg/g had low allergen levels of <10 AU/mL[22] The experience of Finland on market surveillance to guarantee the import of low allergen gloves further confirmed that with a stringent control on protein level of gloves, the incidence of protein allergy would be, to a large extent, minimised[23]

It is the purpose of this study to compare the technical attributes of various LP latices and present an overview of the current status of these latices

EXPERIMENTAL

Latex Samples

Commercial LP latices, coded as CLP1, CLP2, CLP3, CLP4, CLP5 and CLP6, were obtained from the various suppliers A commercial prevulcanised low protein latex (CPVLP) was also included in the study Experimental low protein latices (MRB2 and MRB6) and prevulcanised latices (LPPVL and LAPPVL) were prepared by the RRIM A commercial HA latex concentrate was used as a control for preparation of a prevulcanised latex (HAPVL) and post-vulcanisable latex compound

Determination of Latex Properties

The latex properties were determined in accordance to the relevant *ISO* test methods for NR centrifuged latex concentrates.

Determination of Foaming Behaviour of Latex

A latex sample was diluted to 20% DRC using distilled water. A portion of the diluted latex (200 g) was placed into a 500 mL beaker. The sample was stirred at 390 r.p.m. for 1 min using a 44 mm diameter cross-stirrer blade of Δ shape. The stirrer shaft was set at zero degree to the vertical axis. After 1 min of stirring, a sample of the foamed latex (100 g) was immediately placed into a 200 mL measuring cylinder. The initial volume of the foamed latex was recorded. Its volume after 5 min, 30 min and 1 h of standing was also recorded.

Preparation of Latex Cast Films

Latex films of nominal thickness of 1 mm were prepared by casting approximately 100 g of sieved (180 μm stainless steel sieve) latex concentrate or prevulcanised latex without dilution onto glass plates (240 mm length × 240 mm width) and drying at ambient temperature for a period of at least 5 days.

Preparation of Post-vulcanisable Latex Compound

The following standard formulation (*Table 1*) was employed throughout the study for preparation of post-vulcanisable latex compounds.

Preparation of Coagulant Dipped Latex Films

Coagulant dipped films were prepared from matured (for 1 day and 3 days at 30°C) post-vulcanisable latex mixes or prevulcanised latices under conditions shown in *Table 2*. Films prepared from post-vulcanisable latex mixes were dried and cured at 100°C for 35 min. Films prepared from prevulcanised latices were dried at 70°C for 45 min.

Determination of Chloroform Number

Chloroform number of latex compound was determined by mixing equal amount of latex compound and chloroform. The coagulum formed was broken using a glass rod. The nature of the coagulum was graded as follows: tacky lump – chloroform no. 1; tender lumps, breaks short – chloroform no. 2; non-tacky crumbs – chloroform no. 3; fine dry crumb – chloroform no. 4. The bigger the chloroform number the higher would be the degree of vulcanisation.

Determination of Linear Swelling Index of Latex Films

The linear swelling index was determined by swelling a sample of air-dried latex dipped film (in the form of a disc, diameter 23 mm) in cyclohexane for a period of 30 min at ambient temperature and measuring the swollen diameter. The linear swelling index was calculated using the ratio of swollen diameter to that of the original sample diameter. The smaller the ratio the higher would be the degree of vulcanisation.

Determination of Weight Swelling Index of Latex Films

The weight swelling index was determined by swelling a sample of dipped film in toluene.

TABLE 1. FORMULATION FOR POST-VULCANISABLE LATEX COMPOUNDS

Ingredients	Parts by weight (dry)
Latex	100
Potassium hydroxide (20%)	0.3
Potassium laurate (20%)	0.15
Zinc diethyl dithiocarbamate (50%)	0.5
Zinc dibutyl dithiocarbamate (33.3%)	0.2
Sulphur (50%)	0.7
Zinc oxide (50%)	0.5
Wingstay L® (40%)	1.0
Distilled water	to 50% total solids

TABLE 2. PREPARATION OF COAGULANT DIPPED FILMS

Item	Conditions
Formers used	Glass plates (152 mm × 102 mm)
Total solids content of compound	50%
Calcium nitrate in industrial methylated spirit	10%
Dwell time	30 seconds
Wet-gel leach	50°C/5 mins
Post-leach	50°C/30 seconds
Cornstarch slurry (10%) dip	10 seconds

About 0.5 g of vulcanised latex film was immersed in 20 mL – 30 mL of toluene in a stoppered bottle. A change of solvent after one day of immersion was made in order to remove the soluble fraction of the rubber. The swollen vulcanisate was lightly blotted with filter paper in order to remove excess solvent. The weight, W_1, of the swollen vulcanisate was determined by difference, using a stoppered weighing bottle. The vulcanisate was then immersed in acetone for 30 min in order to extract the toluene, and then dried at room temperature to a constant weight, W_2. The determination was carried out in duplicates. The weight-swelling index, Q, was calculated using the following equation:

$$Q = \text{Weight of solvent in vulcanisate}/\text{Weight of de-swollen vulcanisate} = (W_1 - W_2)/W_2 \qquad \ldots 1$$

The smaller the Q-value, the higher would be the degree of vulcanisation.

Determination of Physical Properties of Latex Dipped Films

The tensile properties (modulus, tensile strength and elongation at break), tear strength (trouser and crescent) and cuff rupture were determined by *ISO 37, ISO 34* and *AS 4011* methods, respectively. The coefficient of friction (COF) of latex dipped films was tested by means of a friction tester made by Plint and Partners Ltd, (UK)[24].

Determination of Total Extractable (EP), Allergenic (AgP) and Antigenic (AP) Protein Contents of Latex Films

A test specimen measuring 6 cm × 6 cm was extracted with 25 mL phosphate-buffered saline (PBS) (1 g/5 mL) at 25°C for 2 h. The total extractable protein (EP) and antigenic protein (AP) contents in the extracts were determined respectively in accordance with *ASTM D5712-99* and *ASTM D6499-00*. The allergen content was determined by the IgE-ELISA inhibition method adapted from the test method described by Palosuo[25].

Determination of Biocompatibility of Dipped Latex Films

a) Delayed contact dermal sensitisation – modified Buehler Method (Animal study).

Induction phase

A test article (measuring 2.54 cm × 2.54 cm, backed by a 2.54 cm × 2.54 cm gauze pad) was applied to mid-back area (clipped of hair) of 10 healthy guinea pigs (5 guinea pigs for each side of the dipped latex film) and occluded with non-reactive adhesive tape wrapped with an elastic bandage to secure the tape. Test article was removed after 6 h and the animals were evaluated for erythema and oedema reactions. The test article application procedure was repeated 3 times each week for 3 weeks until 9 applications were made to the test area. An additional five guinea pigs were used as positive controls (tested with control substance, 0.06% 1-chloro-2,4-dinitrobenzene in 80% ethyl alcohol).

Challenge phase

Twelve days after the final induction dose, all animals including the positive controls and an additional 5 untreated animals as negative controls, were subjected to a challenge dose using similar procedures described above. Test articles were removed after 24 h of exposure. The test sites were evaluated for erythema and oedema reactions at 1 h, 24 h and 48 h after removal of the test article.

b) Primary skin irritation (Animal study). The dorsal area of 6 healthy New Zealand albino rabbits (3 for each side of the dipped latex film) was clipped free of hair and abraded in one side and left intact in the other. Test article measuring 2.54 cm × 2.54 cm each (backed by surgical gauze) was applied to both sites, and occluded with non-reactive adhesive tape wrapped with an impervious cloth. The test article was removed after 24 h of exposure, and sites were assessed immediately for erythema and oedema reactions. The animal was examined again after 72 h for similar reactions.

Determination of Virus Permeability of Latex Dipped Films

A piece of latex dipped film with a drawn circle of 28 mm diameter was stretched over an open top of glass cylinder (110 mm height and 60 mm diameter) such that the circle covered the entire mouth of the cylinder, resulting in the sample being stretched 4 times its original area.

The latex film was fastened in place with a tight-fitting rubber band and the fastened area wrapped with parafilm. A 50 mL virus ΦX 174 suspension of titre 1.24×10^6 plaque-forming unit (pfu)/mL was then introduced in the cylinder through the remaining opened end. The cylinder containing the virus suspension was placed onto a filter paper to check for any gross, visual leak. On passing the leak test, the cylinder was partially submerged in a 100 mm petri dish containing 5 mL of 0.1% Tween-80 for 12 min. Then 1 mL of the submersion solution exposed to the latex film was assayed for the virus using host bacterium *E. coli C*[26].

The compatibility of the virus with the latex sample was determined by the fraction of virus survived on contact with the sample in relation to the virus present in the original concentration. The amount of virus leak or permeated was calculated from the number of virus plague-forming units collected in the buffer.

RESULTS AND DISCUSSION

Properties of Low Protein Latices

Latex properties. The properties of low protein latex concentrates and low protein prevulcanised latices are summarised in *Tables 3a* and *Table 3b*, respectively.

Low protein latex concentrates and low protein prevulcanised latices were found to have nitrogen contents in the ranges 0.04% – 0.22% and 0.09% – 0.24%, respectively. Although CLP3 and CLP6 latices showed lower nitrogen contents than that of HA latex, their nitrogen contents were relatively high for them to be classified as low protein latex, since the nitrogen content gives a measure of the total proteins in latex. Amongst the low protein latices evaluated, CLP2, CLP4, CLP5 and MRB6 showed very low levels of nitrogen content of less than 0.07%. The nitrogen content of prevulcanised latex is expected to be higher than that of the unvulcanised latex, due to the addition of nitrogeneous compounds.

Low protein latex concentrates were found to have total solids, pH and ammonia content in the ranges 54.9% – 65.7%, 9.2% – 11.4% and 0.07% – 0.79% respectively (*Table 3a*). The ammonia content of CLP2 and CLP4 latices, ca. 0.3%, was relatively low in comparison to standard high ammoniated latex. The ammonia content of CLP1 latex was even lower, at 0.07%. It is doubtful if the low levels of ammonia could preserve these latices for a long time, unless a potent secondary preservative is also added in the latex. The total solids, pH and ammonia content of low protein prevulcanised latices were found to be in the ranges 58.5% – 59.1%, 10.9% – 11.3% and 0.59% – 0.68% (*Table 3b*).

Some difficulties were encountered in the determination of DRC, volatile fatty acid numbers, mechanical stability times and on one occasion the potassium hydroxide number (experimental prevulcanised latex, LAPPVL). The difficulties arose as a result of the inability to respond to complete coagulation by the latices (DRC, volatile fatty acid numbers), excessive foaming of the latices (mechanical stability time) and premature coagulation (potassium hydroxide number). One of the important factors that contributed to the above difficulties in testing was likely to be the type and level of surfactants present in the low protein latices. Clearly the current test *ISO* methods for normal natural rubber latex concentrates may not be entirely suitable for low protein latices and some modifications may be required, possibly along the line for synthetic latices.

TABLE 3A PROPERTIES OF HA LATEX AND LOW PROTEIN LATICES

Property	HA	CLP1[a]	CLP2[a]	CLP3[a]	CLP4[a]	CLP5[a]	CLP6[a]	MRB2[b]	MRB6[b]
Dry rubber content (%)	60.04	UC	UC	52.91	UC	65.64	60.21	62.05	62.55
Total solid content (%)	61.52	63.35	59.87	54.87	56.64	65.68	61.61	63.59	63.25
Non-rubber solids (%)	1.48	–	–	1.96	–	0.04	1.40	1.54	0.70
Ammonia (%)	0.69	0.07	0.29	0.65	0.30	0.61	0.67	0.79	0.73
pH	10.80	9.21	10.49	11.35	10.30	10.39	10.58	10.66	10.67
KOH No.	0.53	0.34	0.15	0.71	0.31	0.31	0.60	0.48	0.27
MST (sec)	1510	OVF (120)	OVF (120)	OVF (240)	OVF (120)	OVF (140)	1090	OVF (120)	OVF (120)
VFA No.	0.02	NA	NA	NA	NA	0.01	0.03	NA	NA
Coagulum content (%)	0.001	0.001	<0.001	<0.001	<0.001	0.001	NA[c]	0.009	0.002
Sludge content (%)	0.013	0.002	0.002	0.007	0.001	0.004	NA[c]	0.005	0.002
Nitrogen (%)	0.26	0.094	0.056	0.21	0.068	0.04	0.22	0.14	0.06
Acetone extract (%)	2.56	3.05	2.63	3.88	2.51	3.02	NA[c]	3.60	2.95
Ash (%)	0.38	0.22	0.17	0.62	0.13	0.12	NA[c]	0.28	0.09

HA: Commercial high-ammonia latex concentrate (as control)
[a]Commercial LP latex concentrates
[b]Experimental LP latex concentrates
UC: Unable to coagulate
OVF: Sample overflowed after the time (in seconds) shown in brackets
KOH No.: Potassium hydroxide number
VFA No.: Volatile fatty acid number
NA: Test result could not be obtained because the sample could not be coagulated or serum could not be obtained
NA[c] Not available due to insufficient sample
MST: Mechanical stability time.

TABLE 3B PROPERTIES OF PREVULCANISED HA AND PREVULCANISED LP LATICES

Property	HAPVL	CPVLP[a]	LPPVL[b]	LAPPVL[b]
Dry rubber content (%)	58 18	UC	57 99	56 47
Total solid content (%)	60 25	58 46	58 51	59 05
Non-rubber solids (%)	2 07	–	0 52	2 58
Ammonia (%)	0 71	0 68	0 59	0 60
pH	11 62	10 86	11 72	11 29
KOH No	0 43	0 41	0 21	NAT
MST (sec)	515	OVF (120)	695	OVF (120)
VFA No	0 05	NA	0 02	NA
Coagulum content (%)	0 015	0 004	0 001	0 099
Sludge content (%)	0 16	0 74	0 005	0 273
Nitrogen (%)	0 25	0 092	0 11	0 24
Acetone extract (%)	4 34	5 55	2 68	5 35
Ash (%)	1 59	1 19	0 63	1 70

HAPVL Experimental prevulcanised latex prepared from HA latex (as control)
[a]Commercial low protein prevulcanised latex
[b]Experimental low protein prevulcanised latex
NAT Not able to test because sample coagulated after addition of 3 mL of KOH
OVF Sample overflowed after the time (in sec) shown in brackets
NA Test result could not be obtained because the sample could not be coagulated or serum could not be obtained
UC Unable to coagulate

Foaming tendency Surfactants are invariably employed in the production of low protein latices The presence of a high level of surfactant may promote foaming in latex and latex compound during agitation or transfer of latex or latex compound The bubbles formed could promote formation of pinholes in dipped products unless appropriate measures are taken to minimise the problem *Table 4* shows that most of the low protein latices had a greater tendency to foam compared to HA latex, except for CLP6 latex However, analysis of the results in the following section does not indicate that CLP6 latex can be considered as a low protein latex Most of the low protein latices showed a rather similar rate of reduction of foam volume compared to HA latex, except for CLP3 and MRB2 latices Amongst the low protein prevulcanised latices investigated, LPPVL latex showed a high tendency to foam during stirring

Extractable Protein Contents of Low Protein Latex films

Latex cast films *Table 5* shows that all of the air-dried cast films from low protein latex concentrates, except those prepared from CLP6 latex, had low total EP, allergenic protein (AgP) and AP of <50 μg/dm^2, <10 AU/mL (except CLP4 latex) and <10 μg/dm^2, respectively The films prepared from the CLP6 latex, rather unexpectedly, showed EP (2458 μg/ dm^2), AgP

TABLE 4. FOAMING BEHAVIOUR OF LATICES

Type of latex		Initial	Volume of latex foam (mL)		
			After 5 min	After 30 min	After 60 min
Unvulcanised	HA	118	114	111	110
	CLP1	132	116	114	114
	CLP2	122	118	114	114
	CLP3	132	128	119	116
	CLP4	122	118	114	114
	CLP5	124	116	110	110
	CLP6	108	107	107	107
	MRB2	140	136	128	120
	MRB6	140	113	110	109
Prevulcanised	HAPV	110	108	108	108
	CPVLP	114	110	108	108
	LPPVL	132	128	119	116
	LAPPVL	118	109	109	109

TABLE 5. PROTEIN CONTENTS OF CAST FILMS PREPARED FROM HA LATEX, LP LATICES, PREVULCANISED HA LATEX AND PREVULCANISED LP LATICES

Type of latex film, latex used for cast film preparation and nitrogen content of latex			EP (µg/dm2)	AgP (AU/mL)	AP (µg/dm2)
Latex film	Latex	Nitrogen (%)			
Unvulcanised latex film	HA	0.26	702	62	17
	CLP1	0.094	<50	2	3
	CLP2	0.056	<50	2	3
	CLP3	0.21	<50	2	3
	CLP4	0.066	<50	20	8
	CLP5	0.040	<50	2	5
	CLP6	0.22	2458	550	43
	MRB2	0.14	<50	2	7
	MRB6	0.060	<50	2	8
Prevulcanised latex film	HAPVL	0.25	1116	69	225
	CPVLP	0.092	<50	6	9
	LPPVL	0.11	110	5	14
	LAPPVL	0.24	533	2	5

EP: Total extractable protein
AgP: Allergenic protein
AP: Antigenic protein.

(550 AU/mL) and AP (43 μg/dm^2) contents that were significantly higher than those prepared from the control HA sample

The air-dried cast films prepared from prevulcanised CPVLP latex were found to have low EP (<50 μg/dm^2), AgP (<10 AU/mL) and AP (<10 μg/dm^2) contents The films prepared from prevulcanised LPPVL and LAPPVL showed relatively high levels of EP content of 110 μg/dm^2 and 533 μg/dm^2, respectively However, the AgP and AP contents of these films were relatively low

There was no simple relationship between EP content of air-dried cast film and nitrogen content of LP latex concentrates that were used to prepare the films The low protein CLP3 latex for instance, had high nitrogen content of 0 21% and yet the EP (<50 μg/dm^2), AgP (2 AU/mL) and AP (3 μg/dm^2) contents of its cast films were very low On the other hand, the low protein CLP4 latex had a low nitrogen content of 0 066%, but its cast film had a relatively high AgP content of 20 AU/mL

Latex dipped films The EP contents of unleached dipped films (*Table 6*), except for film prepared from CLP6 latex, were higher than those of unleached cast films (*Table 5*) Unleached dipped films prepared from CLP2 and CPVLP latices showed EP content of <100 μg/dm^2 However, when these films were wet-gel leached, only film prepared from CLP2 latex showed EP content of <100 μg/dm^2 Thus, wet-gel leaching alone appeared to be inadequate to bring down the EP content of low protein latex vulcanisates to very low values of <100 μg/dm^2

In general, EP content of <200 μg/dm^2 and AgP content of <10 AU/mL could only be obtained from dipped vulcanised films of low protein latex concentrates when they were subjected to both wet-gel and post-cure leach (*Table 5*) The exceptions were films prepared from CLP3 latex (an enzyme treated latex), which had EP content of 404 μg/dm^2 and CLP6 latex with AgP of 132 AU/mL However, the AP values of all these low protein latex dipped films, with or without post-cure leach, were <10 μg/dm^2 The vulcanised film prepared from CLP6 latex, despite having very high levels of EP and AgP contents, the AP content of its film that was subjected to wet-gel and post-cure leach, however, was found to be less than 10 μg/dm^2

Similarly dipped films from the commercial and experimental low protein prevulcanised latex were found to contain EP <200 μg/dm^2 (except for LAPPL) and AgP of <10 AU/mL when subjected to both wet-gel and post-cure leach (*Table 6*) Combined treatment of wet-gel and post-cure leaching also ensured that the AP of the samples to be <10 μg/dm^2

It is noteworthy that for vulcanised films prepared from HA latex concentrate and prevulcanised HA latex, the combination of wet-gel leach and post-cure leached used in this study could not bring down EP, AgP and AP contents to figures that are considered low levels

Correlations between Nitrogen, EP and AgP Contents of Dipped Films

Figures 1–9 show the correlations between nitrogen content of latices and EP and AgP contents of vulcanised latex films prepared from all the latices used in this study

The nitrogen content of latex was found to have a strong correlation with the EP content of film, especially with unleached and wet-gel leached films, with linear correlation coefficient (r) in the range 0 934 – 0 941

(*Figures 1–2*). For wet-gel leached + post leached films, a slightly smaller correlation coefficient of 0.744 was observed (*Figure 3*).

The correlations between nitrogen content of latices and the AgP content of films, or between EP content and AgP content of films, under the various film leaching conditions were found to be poor (*Figures 4 – 9*).

Proposed Criteria for Low Protein Latex

There is a wide range of nitrogen contents, hence total protein contents, found in the so-called low protein lattices. It appears that unleached, air-dried cast film is not suitable for characterising low protein latices. There is absence of clear correlations observed between nitrogen contents of latex concentrates and the EP, AgP and AP contents of unleached, air-dried cast films prepared from these latices.

A study by Hasma *et al.*[27] has shown that gloves with EP_{RRIM} content of <100 μg/g and $EP_{ASTM-00}$ content of <60 μg/dm^2 would tend to have low to moderate allergen level of <10 to 10 AU/mL – 100 AU/mL, respectively and AP content of <10 μg/dm^2. Results obtained in the present study showed that the majority of the coagulant dipped LP latex vulcanisates that were subjected to both wet-gel and post-cure leach showed AgP of <10 AU/mL and AP of <10 μg/dm^2 despite having EP values as high as 633 μg/dm^2 (LAPPVL film, *Table 6*). This would imply that AgP or AP, in particular, would be a suitable parameter for characterising the LP latex dipped film rather than EP. It is for practical purpose, that the EP, AgP and AP content of coagulant dipped latex vulcanisates prepared under a standardised condition be included in the characterisation of LP latex concentrates as well as LP prevulcanised latices. It is proposed that a LP latex should meet the criteria as shown in *Table 7*.

Biocompatibility of Coagulant Dipped Low Protein Latex Vulcanisates

All of the low protein latex vulcanisates shown in *Table 8* did not give positive reactions in primary skin irritation and delayed contact dermal sensitisation tests. Similar results were obtained with the HA latex vulcanisate, despite having a relatively high AgP content of 184 AU/mL. The type and level of chemicals added in the latex compound and the leaching protocol used were important factors for the excellent biocompatibility characteristics of NR latex vulcanisates.

Maturation of Post-vulcanisable Low Protein Latex Compounds

LP latices were observed to require a maturation time of 3 days at 30°C to achieve satisfactory degree of precure (chloroform number of 3 and linear swelling index of in the range 1.78–1.87) when compared with normal HA latex concentrate which could achieve similar degree of precure after 1 day at 30°C of maturation (*Table 9*). Films that were prepared from low protein latices containing low nitrogen content generally showed lower degree of precure compared to those films prepared from latices of higher nitrogen content. The viscosity of the post-vulcanisable LP latex compounds remained stable during 3 days storage at 30°C.

Physical Properties of Coagulant Dipped LP Latex Vulcanisates

Tensile properties. The tensile properties of unaged and aged (70°C/7 days and 100°C/22 h)

TABLE 6. PROTEIN CONTENTS OF COAGULANT DIPPED VULCANISED LATEX FILMS PREPARED FROM POST-VULCANISABLE LATEX COMPOUNDS AND PREVULCANISED LATICES

Type of latex vulcanisate, latex used for dipped film preparation and nitrogen content of latex			EP ($\mu g/dm^2$)			AgP (AU/mL)			AP ($\mu g/dm^2$)		
Latex vulcanisate	Latex	Nitrogen (%)	UL	WL	WL+ PL	UL	WL	WL+ PL	UL	WL	WL+ PL
Post-vulcanised	HA	0.260	2083	1256	240	>1000	918	184	34	91	19
	CLP1	0.094	159	172	44	4	4	4	3	2	2
	CLP2	0.056	37	67	85	3	2	3	2	2	3
	CLP3	0.210	1564	627	404	4	3	4	5	6	5
	CLP4	0.066	204	205	57	44	56	8	7	8	3
	CLP5	0.040	202	223	69	7	7	3	7	6	3
	CLP6	0.220	975	824	151	893	>1000	132	32	44	9
	MRB2	0.140	558	463	54	24	22	5	8	7	3
	MRB6	0.060	307	179	24	8	6	3	5	4	2
Prevulcanised	HAPVL	0.250	1606	1332	287	315	296	74	101	101	48
	CPVLP	0.092	61	166	88	16	41	8	5	10	4
	LPPVL	0.110	416	464	48	78	108	10	28	35	5
	LAPPVL	0.240	1267	1330	633	6	5	4	6	6	4

Note: Post-vulcanisable latex mixes were matured for 3 days at 30°C
UL: Unleached
WL: Wet-gel leached for 5 min at 50°C
PL: Post-cure leached for 30 sec at 50°C.

TABLE 7. PROPOSED CRITERIA OF LOW PROTEIN LATEX

Parameter	Proposed limit (max)
Nitrogen content of latex concentrate	0.10%
Nitrogen content of prevulcanised latex	0.15 %
EP of prevulcanised and post-vulcanised film[a]	[b]100 μg/ dm^2
AgP of prevulcanised and post-vulcanised film[a]	10 AU/mL
AP of prevulcanised and post-vulcanised film[a]	10 μg/dm^2

[a]The post-vulcanised film was prepared using compound formulation and conditions used in the present study, with a compound storage condition of 3 days at 30°C, film leaching of wet-gel for 5 min at 50°C and post-cure leached for 30 sec at 50°C.
[b]*60 μg/dm^2 + 2 (standard deviation) to allow for poor reproducibility of the method.*

TABLE 8. BIOCOMPATIBILITY DATA FOR COAGULANT DIPPED VULCANISED LATEX FILMS PREPARED FROM POST-VULCANISABLE LATEX COMPOUNDS AND PREVULCANISED LATICES

Type of latex vulcanisate and latex used for dipped film preparation		Primary skin irritation test	Delayed contact dermal sensitisation test
Latex vulcanisate	Latex		
Post-vulcanised	HA	X	X
	CLP1	X	X
	CLP4	X	X
	MRB6	X	X
Prevulcanised	LPPVL	X	X

Note: Post-vulcanisable latex mixes were matured for 3 days at 30°C. Films were wet-gel leached for 5 min at 50°C and post-cure leached for 30 sec at 50°C
X: No positive reaction.

post-vulcanised latex dipped films, subjected to a combination of wet-gel and post-cure leaching, are summarised in *Table 10a*. In general, post-vulcanised LP latex vulcanisates showed satisfactory unaged tensile strength values in the range 22.9 MPa – 30.6 MPa. The aged tensile strength values of 22.9 MPa – 30.0 MPa and 19.6 MPa – 28.9 MPa, respectively, for ageing at 70°C and 100°C were also considered as satisfactory. However, the latex dipped films prepared from LP latices appeared to give lower tensile modulus than the control HA latex. The differences in the modulus of the latex vulcanisates were very much reflected by the differences in the weight-swelling index of these latex vulcanisates. Amongst the low protein latices evaluated, the vulcanisates prepared from CLP3 and CLP6 latices showed relatively high modulus values. This could be partly because these latices contain relatively high levels of

TABLE 9. PROPERTIES OF POST-VULCANISABLE HA AND LP LATEX COMPOUNDS ON MATURATION

Properties	HA	CLP1	CLP2	CLP3	CLP4	CLP5	CLP6	MRB2	MRB6
	Matured for 1 day at 30°C								
pH	11.1	10.4	11.8	12.1	11.3	12.8	11.4	11.9	11.8
Brookfield viscosity (cps)	16	13	14	17	15	16	17	15	14
Chloroform number	2+	2+	2+	2+	2+	2+	3	2+	2+
Linear swelling index	1.87	2.04	2.04	2.04	2.04	2.04	1.96	2.09	2.09
Total solid content (%)	51.5	50.2	50.6	50.6	50.8	50.7	49.7	50.0	50.0
MST (sec)	1340	Overflow	Overflow	Overflow	Overflow	Overflow	NA	Overflow	Overflow
	Matured for 3 days at 30°C								
pH	11.0	10.4	11.7	12.1	11.3	12.8	11.4	11.9	11.8
Brookfield viscosity (cps)	16	13	14	17	15	16	17	15	14
Chloroform number	3	3	3	3	3	3	3	3	3
Linear swelling index	1.74	1.87	1.87	1.83	1.87	1.83	1.78	1.87	1.87
Total solid content (%)	51.5	50.3	50.4	50.5	50.6	50.6	49.8	50.1	50.0
MST (sec)	1470	Overflow	Overflow	Overflow	Overflow	Overflow	NA	Overflow	Overflow

NA: Not available due to insufficient sample.

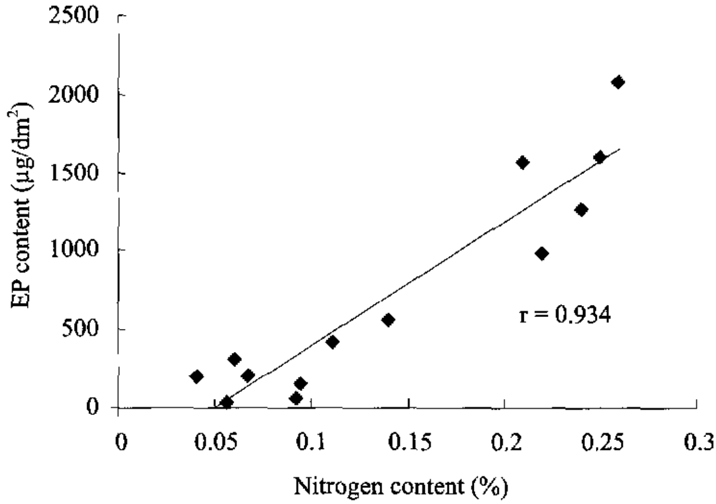

Figure 1. Correlation between nitrogen content of latex and EP content of unleached vulcanised latex films.

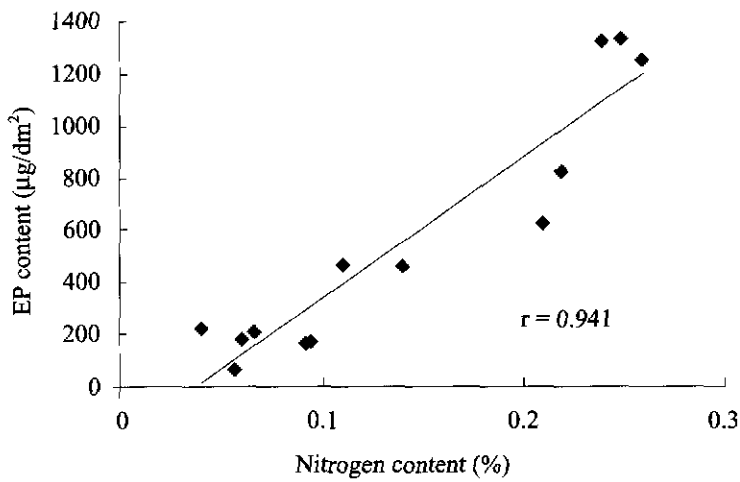

Figure 2. Correlation between nitrogen content of latex and EP content of wet-gel leached vulcanised latex films.

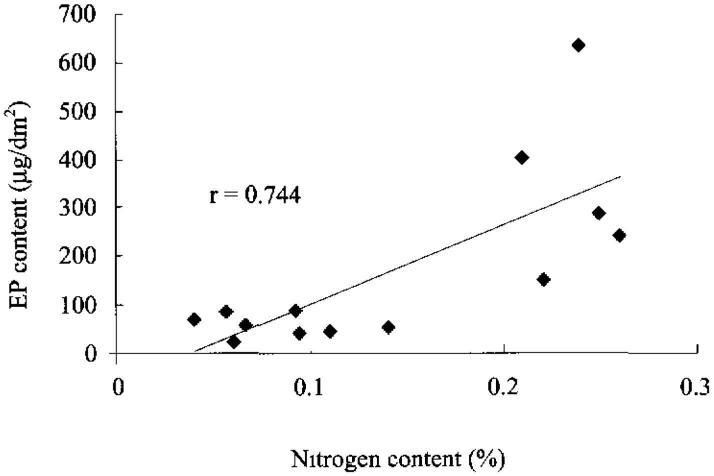

Figure 3. Correlation between nitrogen content of latex and EP content of wet-gel leached + post-leached vulcanised latex films.

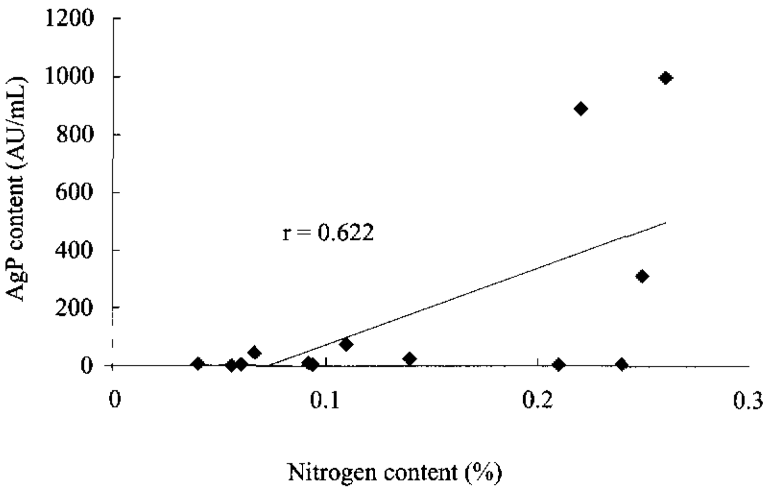

Figure 4. Correlation between nitrogen content of latex and AgP content of unleached vulcanised latex films

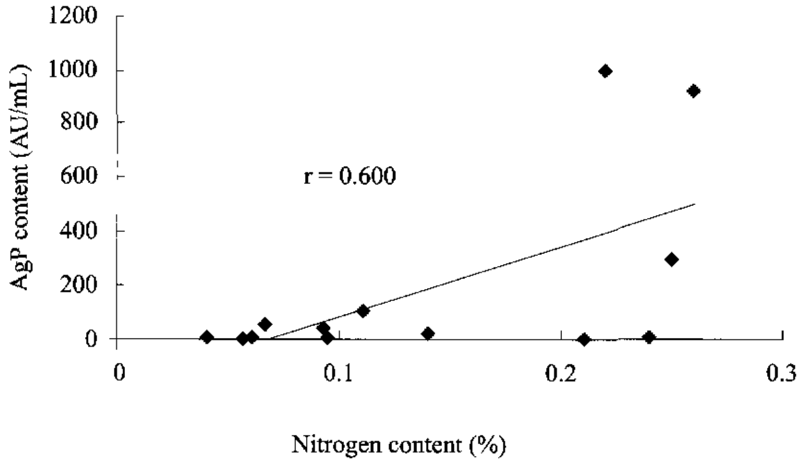

Figure 5. Correlation between nitrogen content of latex and AgP content of wet-gel leached vulcanised latex films.

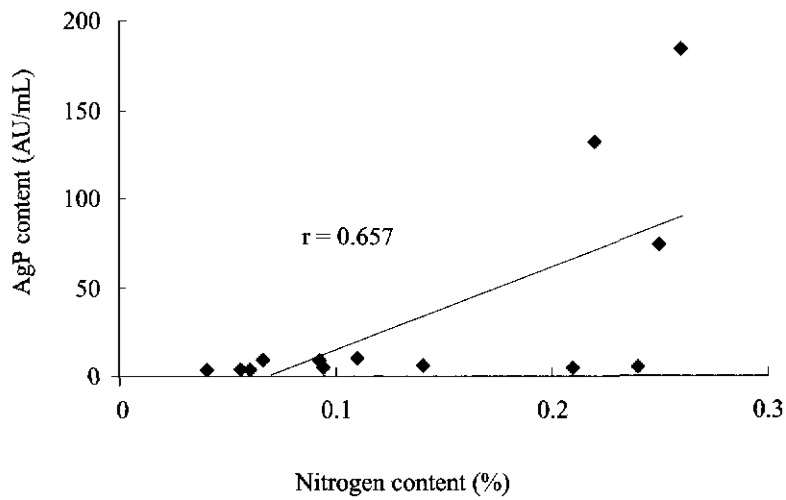

Figure 6. Correlation between nitrogen content of latex and AgP content of wet-gel leached + post-leached vulcanised latex films.

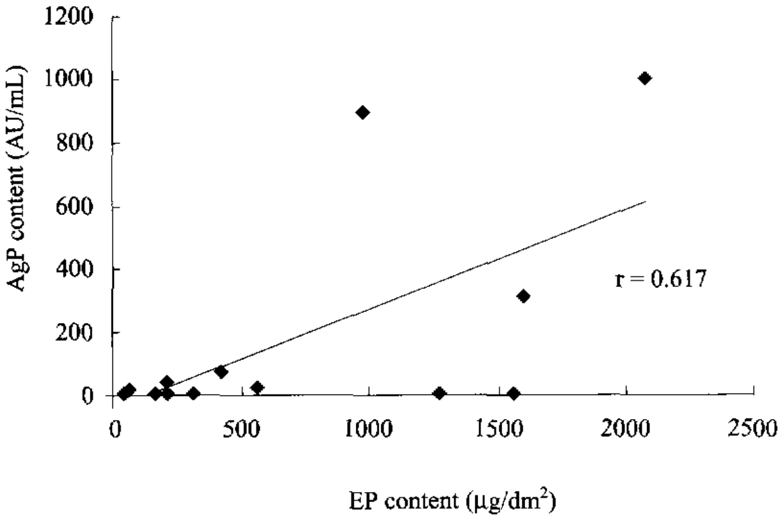

Figure 7. Correlation between EP content and AgP content of unleached vulcanised latex films.

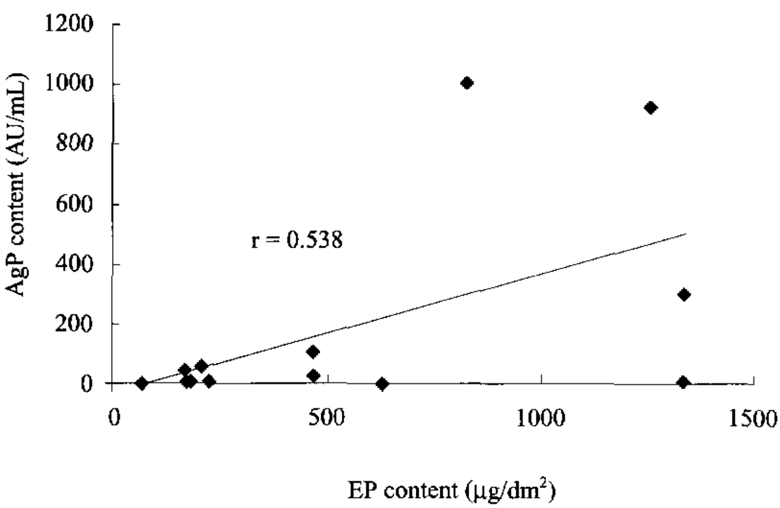

Figure 8. Correlation between EP content and AgP content of wet-gel leached vulcanised latex films.

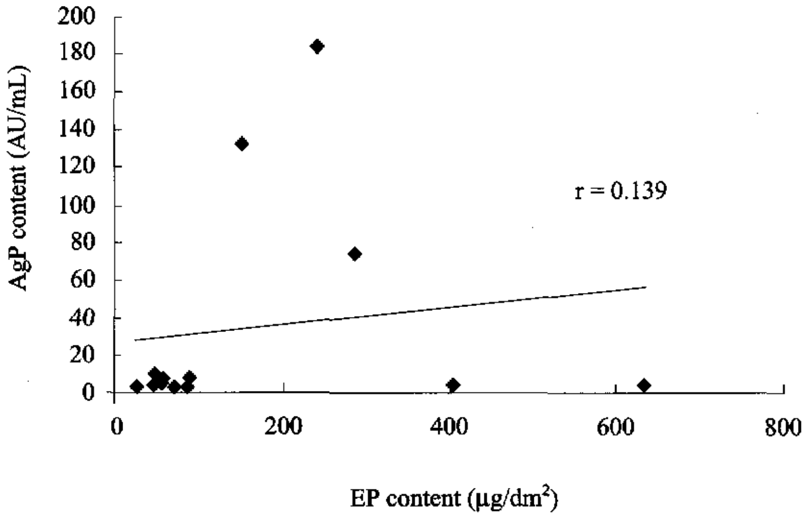

Figure 9. Correlation between nitrogen content of latex and AgP content of wet-gel leached + post-leached vulcanised latex films.

proteins. Vulcanisate prepared from CLP2 latex was observed to give the least satisfactory values for tensile properties.

The tensile properties of unaged and aged (70°C/7 days and 100°C/22 h) prevulcanised latex dipped films, subjected to a combination of wet and post-cure leaching, are summarised in *Table 10b*. In general, prevulcanisates prepared from LP latex showed satisfactory unaged and aged tensile properties. The prevulcanisates showed unaged tensile strength values in the range 25.6 MPa – 30.7 MPa. The aged tensile strength values were in the ranges 33.5 MPa – 34.9 MPa and 30.9 MPa – 33.8 MPa, respectively, for ageing at 70°C and 100°C. The tensile modulus of unaged prevulcanisates prepared from CPVLP latex appeared to be comparable with those prepared from HA latex. Prevulcanisates prepared from LAPPVL showed relatively low modulus values but these values were found to increase after ageing for 7 days at 70°C.

Tear strength and cuff rupture. The values for unaged tear strength of LP post-vulcanised latex dipped films were found to be in the range of 6 N/mm – 20 N/mm (trouser tear) and 68 N/mm –104 N/mm (crescent tear), with cuff rupture values in the range of 13.2 N – 20.0 N. In contrast, the normal latex concentrate gave tear value of 27 N/mm (trouser tear) and 113 N/mm (crescent tear), with a cuff rupture of 20.0 N (*Table 11*).

The values for unaged tear strength of low protein prevulcanised latex dipped films were found to be in the range 7 N/mm – 22 N/mm (trouser tear) and 96 N/mm – 107 N/mm (crescent tear), with cuff rupture values in the range 14.8 N – 19.8 N. By comparison, prevulcanised latex obtained from the normal

TABLE 10A. TENSILE PROPERTIES OF COAGULANT DIPPED VULCANISED FILMS PREPARED FROM POST-VULCANISABLE HA LATEX AND LP LATEX COMPOUNDS

Properties	HA	CLP1	CLP2	CLP3	CLP4	CLP5	CLP6	MRB2	MRB6
					Unaged				
M100 (MPa)	0.75	0.58	0.55	0.65	0.62	0.58	0.78	0.65	0.55
M300 (MPa)	1.45	1.05	0.98	1.19	1.14	1.06	1.55	1.21	0.99
M500 (MPa)	3.36	1.67	1.52	2.30	2.18	1.83	3.28	2.28	1.68
M700 (MPa)	14.6	7.6	7.1	10.8	10.2	8.8	14.6	11.2	7.6
Tensile strength (MPa)	32.8	28.0	22.9	26.8	30.6	29.0	30.2	30.0	25.9
Elongation at break (%)	870	950	930	880	920	950	870	900	930
Weight swelling index	4.24	4.93	5.10	4.74	4.79	5.16	4.18	4.52	5.00
					Aged for 7 days at 70°C				
M100 (MPa)	0.90	0.59	0.57	0.70	0.61	0.57	0.76	0.64	0.56
M300 (MPa)	1.80	1.07	1.06	1.29	1.20	1.06	1.52	1.21	1.04
M500 (MPa)	3.79	1.55	1.53	2.24	1.93	1.65	2.89	2.02	1.54
M700 (MPa)	17.3	6.7	5.4	10.5	8.6	6.9	13.0	10.2	6.7
Tensile strength (MPa)	32.8	25.5	22.6	27.2	30.0	26.6	28.9	26.1	29.5
Elongation at break (%)	830	920	920	870	920	930	850	870	950
					Aged for 22 h at 100°C				
M100 (MPa)	0.67	0.55	0.45	0.66	0.52	0.52	0.71	0.60	0.49
M300 (MPa)	1.40	0.95	0.80	1.18	0.98	0.94	1.44	1.12	0.85
M500 (MPa)	2.61	1.35	1.20	1.97	1.57	1.42	2.61	1.73	1.12
M700 (MPa)	10.6	4.0	2.4	8.3	4.8	4.9	10.8	6.9	3.6
Tensile strength (MPa)	26.2	24.3	19.6	27.9	26.5	25.6	28.9	27.1	21.8
Elongation at break (%)	850	970	980	920	970	950	890	930	970

Note: Post-vulcanisable latex mixes were matured for 3 days at 30°C. Films were wet-gel leached for 5 min at 50°C and post-cure leached for 30 sec at 50°C.
M100, M300, M500 and M700 are modulus or stress at 100%, 300%, 500% and 700% extension, respectively.

TABLE 10B. TENSILE PROPERTIES OF COAGULANT DIPPED FILMS PREPARED FROM PREVULCANISED HA LATEX AND LP LATICES

Property	HAPVL	CPVLP	LPPVL	LAPPVL
		Unaged		
M100 (MPa)	0.69	0.68	0.62	0.57
M300 (MPa)	1.27	1.22	1.15	0.97
M500 (MPa)	2.77	2.95	2.36	1.76
M700 (MPa)	11.4	13.0	9.9	7.6
Tensile strength (MPa)	29.4	30.7	30.0	25.6
Elongation at break (%)	920	900	960	950
		Aged for 7 days at 70°C		
M100 (MPa)	0.69	0.61	0.58	0.63
M300 (MPa)	1.32	1.12	1.07	1.12
M500 (MPa)	2.49	2.14	1.74	1.94
M700 (MPa)	10.2	9.27	7.3	8.8
Tensile strength (MPa)	33.5	33.8	33.5	34.9
Elongation at break (%)	930	970	1000	970
		Aged for 22 h at 100°C		
M100 (MPa)	0.62	0.52	0.54	0.55
M500 (MPa)	2.11	1.59	1.49	1.46
M700 (MPa)	7.9	5.3	5.4	5.4
Tensile strength (MPa)	34.8	32.5	33.8	30.9
Elongation at break (%)	1000	1070	1050	1030

Note: Films were wet-gel leached for 5 min at 50°C and post-cure leached for 30 sec at 50°C.

latex concentrate gave tear value of 10 N/mm (trouser tear) and 114 N/mm (crescent tear), with a cuff rupture of 16.2 N.

There was a wide variation of tear strength values of LP latex vulcanisates in comparison to cuff rupture strength values. The comparatively low trouser tear strength (< 10 N/mm) for vulcanisates prepared from MRB2, MRB6, LPPVL and LAPPVL latices was rather peculiar. There was no clear relationship between tear strength and degree of cure of the latex vulcanisates or nitrogen content of the latices used to prepare these vulcanisates.

Coefficient of Friction

Table 12 shows that the powdered post-vulcanised latex dipped films obtained from most of the low protein latices were found to give lower COF (0.21–0.57) when compared to that of the HA latex dipped film (0.70). Post-vulcanised latex films prepared from CLP3 latex was found to give the highest COF amongst the LP latices. This latex also had the highest nitrogen content amongst the low protein latices evaluated.

Similarly, the COF values of prevulcanisates prepared from LP latices (0.23–0.36) were

TABLE 11. TEAR STRENGTH AND CUFF RUPTURE OF UNAGED COAGULANT DIPPED VULCANISED FILMS PREPARED FROM POST-VULCANISABLE LATEX COMPOUNDS AND PREVULCANISED LATICES

Type of latex vulcanisate and latex used for dipped film preparation		Tear strength (N/mm)		Cuff rupture (N)
Latex vulcanisate	Latex	Trouser	Crescent	
Post-vulcanised	HA	27	113	20.0
	CLP1	17	83	15.4
	CLP2	13	68	20.0
	CLP3	19	80	17.0
	CLP4	20	104	16.6
	CLP5	15	84	14.6
	CLP6	NA	NA	NA
	MRB2	7	84	16.0
	MRB6	6	83	13.2
Prevulcanised	HAPVL	10	114	16.2
	CPVLP	22	107	16.2
	LPPVL	8	96	19.8
	LAPPVL	7	99	14.8

Note: Post-vulcanisable latex mixes were matured for 3 days at 30°C. Films were wet-gel leached for 5 min at 50°C and post-cure leached for 30 sec at 50°C.
NA: Not available due to insufficient sample.

lower than that of film prepared from the normal prevulcanised latex (0.85) (*Table 12*). These results are very significant in that vulcanised films prepared from LP latices tend to show relatively low COF values, despite the tendency that these type of films contain relatively lower degree of crosslink density compared to the film prepared from normal HA latex.

Barrier Performance

The result of permeability test of selected latex dipped films against virus ΦX 174 was summarised in *Table 13*. The virus was found to be compatible with the latex dipped films (92% – 97% virus survived) prepared from both normal and LP latices and that the films were impermeable to the virus ΦX 174 (diameter 27 nm). The results clearly showed that intact dipped natural rubber latex films, irrespective of their protein level, would be impermeable to virus ΦX 174, which is approximately 5 times smaller than HIV (diameter 100 nm).

CONCLUSION

The current *ISO* test methods for normal latex concentrates was found to be inapplicable to LP latices for the determination of DRC, volatile fatty acid number, potassium hydroxide number

TABLE 12. COEFFICIENT OF FRICTION OF COAGULANT DIPPED VULCANISED FILMS PREPARED FROM POST-VULCANISABLE LATEX COMPOUNDS AND PREVULCANISED LATICES

Type of latex vulcanisate and latex used for dipped film preparation		Coefficient of friction[a]
Latex vulcanisate	Latex	
Post-vulcanised	HA	0.70
	CLP1	0.39
	CLP2	0.30
	CLP3	0.57
	CLP4	0.29
	CLP5	0.21
	CLP6	NA
	MRB2	0.21
	MRB6	0.29
Prevulcanised	HAPVL	0.85
	CPVLP	0.36
	LPPVL	0.30
	LAPPVL	0.23

Note: Post-vulcanisable latex mixes were matured for 3 days at 30°C. Films were wet-gel leached for 5 min at 50°C and post-cure leached for 30 sec at 50°C.

[a]Test conditions: Number of cycle: 1 ; Speed: 1 mm/s ; load: 20 N ; Relative humidity: 60% ; Temperature: 25°C.

NA: Not available due to insufficient sample.

TABLE 13 . PERMEABILITY OF COAGULANT DIPPED VULCANISED FILMS PREPARED FROM POST-VULCANISABLE LATEX COMPOUNDS AND A PREVULCANISED LP LATEX AGAINST VIRUS ΦX 174

Type of latex vulcanisate and latex used for dipped film preparation		Virus surviving fraction	Virus permeated	
Latex vulcanisate	Latex		Direct contact	In buffer
Post-vulcanised	HA	0.94	NP	<DL
	CLP1	0.95	NP	<DL
	CLP4	0.92	NP	<DL
	MRB6	0.94	NP	<DL
Prevulcanised	LAPPVL	0.97	NP	<DL

Note: Post-vulcanisable latex mixes were matured for 3 days at 30°C. Films were wet-gel leached for 5 min at 50°C and post-cure leached for 30 sec at 50°C.

NP: No plague formed

<DL: Below detection limit of 0.005 μL.

and mechanical stability times This is due to the fact that, among others, some latices could not be satisfactorily coagulated, some coagulated prematurely and some foamed excessively

There was a considerable variation in the nitrogen contents of LP latices (0 04% – 0 21% and 0 09% – 0 24% for latex concentrates and prevulcanised latices, respectively) and this might pose complications as to its suitability as a parameter to properly define LP latices It was suggested that in addition to nitrogen content of LP latex concentrate and LP prevulcanised latex, parameters such as total EP, AgP and AP contents of coagulant dipped latex vulcanisates that are prepared under a standard condition might be required to characterise and define the term 'LP latices' Suggested maximum limits for nitrogen content of LP latex concentrates and LP prevulanised latices are 0 10% and 0 15%, respectively Recommended EP, AgP and AP contents of coagulant dipped LP latex vulcanisates prepared under the conditions proposed in this paper are <100 $\mu g/dm^2$, <10 AU/mL and <10 $\mu g/dm^2$, respectively

A significant observation of LP latices is that, even if vulcanised film prepared from these latices might contain high levels of EP content, there was a great tendency for their AgP and AP contents to be at low levels For powdered vulcanised films made from normal latex concentrate, a very vigorous leaching protocol need to be carried out in order to bring AgP and AP contents to below 10 AU/mL and 10 $\mu g/dm^2$, respectively

Both LP latex vulcanisates and those prepared from normal HA latex exhibited excellent biocompatibility in primary skin irritation and delayed contact dermal sensitisation tests

The tensile properties of latex dipped films obtained from LP latices, both unaged and aged, were observed to be satisfactory in most cases (>25 MPa) The values for tensile modulus were in some cases lower than the dipped films obtained from normal HA latex concentrate There was also some indication of lower tear strength in some instances for LP latex dipped films but differences in cuff rupture values appeared to be minimal when compared against normal HA latex One notable feature of powdered latex dipped films was the low coefficient of friction *vis-a-vis* the latex dipped obtained from normal HA latex This might have some effect on the dry donning characteristics of the gloves made from LP latices

The vulcanised latex dipped films obtained from LP latices were found to be impermeable to virus ΦX 174 (diameter 27 nm) and should prove to be an effective barrier against virus

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