

Semisynthetic guayule latex with reduced allergenicity

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Abstract

Semisynthetic latices were prepared batchwise using solvent-swollen rubber extracted from guayule (*Parthenium argentatum*). Emulsification of the extracted rubber with anionic surfactants followed by vacuum desolventization yielded stable, low-resin products. The swollen guayule rubber had a low protein content (2.3 $\mu\text{g/g}$ dry rubber). As a consequence, the semisynthetic latices had protein contents (11–20 $\mu\text{g/g}$ dry rubber) significantly lower than that of native guayule latex (129 $\mu\text{g/g}$ dry rubber) isolated directly from the shrub. More importantly, these semisynthetic latices and the dipped films prepared from compounded latices contained none of the protein allergens associated with either *Hevea brasiliensis* latex or native guayule latex. © 1997 Elsevier Science B.V.

Keywords: Guayule; *Hevea brasiliensis*; Latex allergy; Latex protein; Natural rubber; *Parthenium argentatum*; *cis*-1,4-polyisoprene

1. Introduction

Cis-1,4-polyisoprene latex (GR latex) isolated from the guayule shrub (*Parthenium argentatum* Gray), and dipped films produced from compounded latex, contain none of the allergens known to elicit Type I systemic allergic reactions

in individuals sensitized to latex from *Hevea brasiliensis* Muell. Arg. (NR latex) (Siler and Cornish, 1994; Schloman et al., 1996). However, native GR latex does contain low levels of other proteins which elicit an allergic response in sensitized subjects (Siler et al., 1996). The polymer phase of native GR latex has a lower bulk viscosity and a higher resin content than that of NR latex. Native GR latex, therefore, cures more slowly and reaches a lower state of cure than NR latex. As a result, the unaged stress-strain proper-

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ties of cured dipped films prepared from native GR latex are inferior to those prepared from NR latex.

Factors contributing to the lower bulk viscosity of GR include a lower average molecular weight and a lower level of gel than are found in NR (Angulo-Sanchez and Quero-Gutierrez, 1985). When guayule is processed to recover bulk polymer rather than latex, the rubber is first extracted from ground shrub with a low-polarity solvent or solvent mixture such as the acetone-pentane azeotrope, then a polar solvent such as methanol or acetone is added to coagulate a high-molecular weight fraction (Wagner and Schloman, 1991). The immediate product of this fractionation is a solvent-swollen mass, which is subsequently desolventized and extruded into solid bales. This fractionated polymer has a desirably high bulk viscosity and low resin content (Wagner and Schloman, 1991). Could the polymer phase in a guayule latex be tailored in a similar way?

Latices, including those of synthetic polyisoprene (Kostin et al., 1970), have been prepared by the initial emulsification of polymer cements in aqueous surfactant solutions. Careful desolventization of the emulsions yield stable latex products. Crucial control factors include the composition of the cement phase, the ratio of cement to aqueous phase, the choice of surfactant, and the nature and extent of phase mixing. A natural rubber latex prepared from bulk polymer may be characterized as 'semisynthetic', in contrast to a 'native' latex, which is a dispersion formed as the result of biosynthetic processes. While there is a production cost associated with manufacturing a semisynthetic latex, there is one very attractive benefit. By starting from a polymer of known composition and physical properties, the composition of the product could be controlled in an appropriate processing environment. We report here the evaluation of solvent-swollen GR as a feedstock for the production of low-allergen semisynthetic GR latices. We report further the production of low-allergen dipped films from compounded semisynthetic GR latex.

2. Materials and methods

2.1. Bulk GR

Samples were taken from a single bale produced at the Sacaton, Arizona, pilot plant operated by Bridgestone/Firestone.

2.2. Swollen GR

Ground guayule shrub was charged to a pilot-scale extraction apparatus and exhaustively extracted with a mixture of 22% by weight of acetone and 78% by weight of pentane. An antioxidant (AgeRite Superlite, R.T. Vanderbilt) was added at a level equivalent to 1% w/w based on rubber content (1 phr). Solvent was removed on a rotary evaporator to adjust the extract solids content to about 10% by weight. Sufficient acetone was then added to adjust the acetone-pentane ratio to 52:48 parts by weight. As the acetone was added, *cis*-1,4-polyisoprene separated from the solution as a solvent-swollen mass containing about 35–50 parts by weight of dry rubber. The compositions and bulk viscosities of the swollen GR samples used in this study are listed in Table 1.

2.3. Analysis and physical testing

Samples of native GR latex and semisynthetic GR latex were coagulated by the addition of 10% v/v acetic acid. The crude rubber samples were rinsed in water, then dried for 18 h under vacuum at 70°C. Swollen GR samples were vacuum dried directly. Mooney viscosities [ML1 + 4 (100°C)] were determined in accordance with ASTM

Table 1
Dry rubber contents and Mooney viscosities [ML1 + 4 (100°C)] of swollen GR samples

Date prepared	GR %	ML1 + 4 (100°C)
10/95	36	45.5
12/95	35	66.3
06/96	36	70.2
06/96	48	77.3

method D 1646-94. Resin contents were determined by exhaustive acetone extraction of sheeted rubber samples in a Soxhlet apparatus.

2.4. Cast GR film

A rubber cement prepared from 36.83 g of swollen GR (35% solids), 0.13 g of AgeRite Superlite, and sufficient pentane to adjust the total weight to 200.0 g was centrifuged at $150 \times g$ to bring down any entrained plant tissue. A film was cast by pouring 39.64 g of the cement into a $151 \times 151 \times 1.5$ mm steel-frame mold backed by PTFE. The film was air-dried, carefully peeled from the PTFE backing, and dusted front and back with USP/FCC CaCO_3 while still held in the mold. Two 0.11-mm PET sheets were placed on and under the mold. The film was then cut away while sandwiched between the sheets. The final thickness of the film was 0.21 ± 0.02 mm, based on an average of nine measurements over the film surface.

2.5. Semisynthetic GR latex from swollen GR

In a typical experiment, a cement was prepared from 36.83 g of swollen GR (35% solids), 0.13 g of AgeRite Superlite, and sufficient pentane to adjust the total weight to 200 g. The cement was centrifuged at $150 \times g$ to bring down any entrained plant tissue. Over a 5-min period, the cement was added to a 500-ml reactor containing 100 g of 1.035% w/w aqueous sodium lauryl sulfate. An ice bath was placed around the reactor to maintain a temperature below that of the boiling point of acetone-pentane azeotrope. To produce a cement-in-water emulsion in the course of addition, the water-cement mixture was agitated with a PowerGen homogenizer (Fisher Scientific) fitted with a 32-mm saw-tooth impeller run at 7500 rpm. Organic solvents were evaporated from the emulsion at ambient temperature in a rotary evaporator operating at about 27 kPa pressure. Desolventization after filtration through a 60-mesh filter cloth produced 105.62 g of a dilute latex which was concentrated by mixing with 10.48 g of 1% w/w aqueous ammonium alginate in a separatory funnel. On standing, the latex-ammonium

alginate mixture separated into two layers. The lower layer containing essentially no rubber was drawn off and replaced by 23 g of water. The latex and water were then mixed. On standing, the mixture separated into two layers. The lower layer was again drawn off. After filtration of the upper latex layer through a 60-mesh filter cloth, 24.97 g (75% based on GR recovery) of latex were obtained having a dry rubber content of 35%.

2.6. Semisynthetic GR latex from swollen GR, in-situ surfactant

A rubber cement was prepared from 45.10 g of swollen GR (47% solids), 0.21 g of AgeRite Superlite, 0.65 g of oleic acid, and sufficient pentane to adjust the total weight to 200.0 g. The centrifuged cement was emulsified on addition to 100 g of 0.20% w/w aqueous potassium hydroxide. Desolventization yielded 96.03 g of dilute latex, which was concentrated by mixing with 8.56 g of 1% w/w aqueous ammonium alginate, followed by 38.0 g of water. After final filtration, 47.49 g (100% based on GR recovery) of latex were obtained having a dry rubber content of 45%.

2.7. Semisynthetic GR latex from bulk GR

A rubber cement was prepared from 30.21 g of GR (Mooney viscosity 99.6), 0.30 g of AgeRite Superlite, 30.21 g of acetone, and 246.75 g of pentane. The cement was emulsified by addition to 195.17 g of 0.88% w/w aqueous potassium oleate. After desolventization and recovery of 10.15 g of coagulated GR, 216.80 g of dilute latex was concentrated by mixing with 10.0 g of 1% w/w aqueous ammonium alginate, followed by 172.18 g of 0.05% w/w aqueous ammonium alginate. After final filtration, 44.62 g (63% based on GR recovery) of latex were obtained having a dry rubber content of 43%. The dry GR had a Mooney viscosity of 43.4 and a resin content (including antioxidant) of 3.0%.

2.8. Semisynthetic GR latex from native GR latex

A 250-ml bottle was charged with 12.61 g of native GR latex (56% solids), 0.07 g of AgeRite

Superlite, and sufficient pentane to adjust the total weight of the contents to 105.61 g. A 5-cm PTFE-coated magnetic stirring bar was added to facilitate phase mixing. The bottle was then sealed with a polyethylene-lined cap and stirred overnight. After removal of the stirring bar, the bottle was centrifuged at $500 \times g$ for 1 h, 91.27 g of overhead cement phase then being decanted. A 89.70-g aliquot was emulsified on addition to 50.0 g of 0.70% w/w aqueous sodium dodecyl sulfate. Desolventization afforded 50.30 g of dilute latex. The latex was concentrated by mixing with 5.0 g of 1% w/w aqueous ammonium alginate, followed by 39.0 g of water. After final filtration, 10.39 g (53% based on GR recovery) of latex were obtained having a dry rubber content of 32%.

2.9. Control procedures

To prevent protein cross-contamination, several precautions were taken during compounding, dipping, and curing operations. Equipment and samples were handled with 100% nitrile gloves. Separate coagulant solutions, dusting powder, and leaching baths were used for each latex recipe. All glassware was washed in a 1% w/v aqueous detergent solution, then immersed in 10% v/v household bleach for a minimum of 2 h. Cured films were stored in sealable polyethylene bags.

2.10. Compounding and prevulcanization

Latex was filtered through a 200-mesh polyester cloth into a 50-ml vial. With the exception of antioxidant, compound components (Table 2) were then added. The vial was placed in an oil bath maintained at 65°C and its contents heated over a 30-min period with mixing by PTFE-coated magnetic stirring bar. The compound was then maintained at 65°C for a minimum of 2 h. Antioxidant was added at the conclusion of prevulcanization.

Table 2
Latex dipping compound formulation

Ingredients	Weight (parts)	
	Dry	Wet
Latex	100.0	250.0
10% Potassium hydroxide solution	0.5	5.0
33% Surfactant ^a	2.0	6.0
68% Sulfur dispersion	0.8	1.18
60% Zinc oxide dispersion	0.75	1.25
Dithiocarbamate solution ^b	—	2.25
Water	—	4.5
65% Antioxidant emulsion ^c	1.0	1.54

^a1:1 Darvan SMO+Darvan WAQ (R.T. Vanderbilt).

^bSetsit 104 (R.T. Vanderbilt).

^cAgeRite Superlite (R.T. Vanderbilt).

2.11. Dipped film preparation

Films were prepared as described in Schloman et al. (1996).

2.12. Protein contents

BCA assays were carried out as described in Siler and Cornish (1994) and Schloman et al. (1996).

2.13. Enzyme-linked immunosorbent assays (ELISA)

Hevea allergens in solubilized latex proteins were determined using rabbit anti-*Hevea* glove protein polyclonal antibodies (Guthrie Research) in accordance with the procedure of Siler and Cornish (1994), with final incubation of allergen-bound antibodies using anti-rabbit IgG conjugated to alkaline phosphatase. Allergenicity was determined by monitoring absorbance at 405 nm. Guayule allergens in solubilized latex proteins were determined using rabbit anti-guayule protein polyclonal antibodies prepared by injecting rabbits with proteins solubilized from guayule rubber particle suspensions. Assays were run by incubating allergen-bound antibodies with anti-rabbit IgG conjugated to alkaline phosphatase. As before, color development at 405 nm was monitored.

3. Results and discussion

3.1. Latex preparation

Solvent-swollen GR was chosen as the primary feedstock because the technology needed to prepare this material was successfully evaluated in 1987–1990 by the (then) Firestone Tire and Rubber Company as part of its operation of a pilot processing facility at Sacaton, Arizona. Typically, the swollen polymer contained about 34% GR, 32% pentane, and 34% acetone by weight (Cole et al., 1991). The viscosity of the swollen polymer was low enough that the material could be pumped through the processing system. An important advantage to using swollen GR of the type produced at Sacaton is that, under production conditions, the rubber would have been fractionated to remove low-molecular weight polymer (Beinor and Cole, 1986). Table 3 provides a comparison of the rubber bulk viscosities and resin contents of native NR latex, GR latex, and solvent-extracted GR of the type produced at Sacaton. During its period of continuous operation, the Sacaton processing facility produced GR with a Mooney viscosity of 92 ± 12 . None of the swollen GR samples used in this work contained polymer with a Mooney viscosity greater than 80 (Table 1), reflecting our inability to tailor polymer viscosity with the same flexibility of the pilot scale operation. While it was considered most desirable to use swollen GR of the same composition and physical characteristics as was produced at Sacaton, the experiments using swollen GR samples of

ambient viscosity were carried out as proofs-of-concept.

One control parameter for cement emulsification is the cement viscosity, a function of solids content and the polymer bulk viscosity. It was found that, with the mixing hardware used in these preparations, a cement viscosity of no more than 1000 cP allowed the most consistent control during addition and emulsification. Accordingly, swollen GR was diluted with pentane to a solids content of 6.5–10.5%. For a given solids content, the higher-bulk viscosity GR in the swollen rubber produced at Sacaton would yield a more viscous cement than the material produced as part of this study.

An effective phenolic antioxidant (AgeRite Superlite) was added during cement preparation to assure polymer stability. Under production conditions, antioxidant is added at the upstream end of a solvent-extraction process. Native GR latex, which must be stabilized either with water-soluble (and therefore rubber-insoluble) antidegradants or with emulsions of organic-soluble (and therefore phase-separated) antidegradants. The semisynthetic latices described here have antioxidant in their polymer phases from the outset. Since such antidegradants are soluble in the polymer phase only, they are not lost in the course of processing.

An alternative feedstock to solvent-extracted bulk polymer is native GR latex or any other natural rubber latex. A cement can be produced by mixing latex with a hydrocarbon solvent such as pentane. Water-soluble components in the latex, including proteins, fail to dissolve and are easily removed by centrifugation. Making latex from latex might seem to be an inappropriate multiplication of processing steps, but there is one significant advantage at least as applied to non-guayule latices. In the case of a native latex such as that from *Hevea* where the rubber has a high bulk viscosity, where the latex can be harvested by tapping, and where the resin content is low, extraction of the polymer into a hydrocarbon solvent would be an effective way of separating rubber from proteins without having to fractionate the polymer. Latices containing other bioactive serum components, such as Madagascar rubbervine latex [*Cryptostegia grandiflora* (Roxb.)

Table 3
Mooney viscosities [ML1+4 (100°C)] and resin contents of *cis*-1,4-polyisoprenes

Origin	ML1+4 (100°C)	Resin (%)
NR latex ^a	100.4–109.0	1.9–2.3
GR latex (native) ^a	49.9–69.2	8.2–9.9
GR bulk (fractionated)	92 ± 12^b	1.5 ± 0.6^c

^a Schloman et al. (1996).

^b Mean of 123 lots, Sacaton processing facility (Cole et al., 1991).

^c Mean of 62 lots, Sacaton processing facility, includes 0.5% antioxidant (Cole et al., 1991).

Table 4
Surfactant performance

Class	Surfactant ^a	Oil-in-water emulsion ^b	Latex yield (% GR recovery)
Anionic	Potassium oleate	+	75
	Dresinate 731	—	
	Sodium lauryl sulfate (SDS)	+	73
	Triton X-301 ^c	+, +	44, 73
	Darvan No 7	—	
	Darvan SMO	±	
Amphoteric	Lecithin ^d	—, —	
	Rewoteric AM DML-35	±	
Nonionic	Igepal CO-710	—	
Mixed	SDS+Igepal CO-730 (1:1)	—	
	K oleate+lecithin (0.08:1) ^e	+	80

^a Sources of proprietary surfactants: Hercules (Dresinate 731); Union Carbide (Triton X-301); R.T. Vanderbilt (Darvan No 7, Darvan SMO); Witco (Rewoteric AM DML-35); Rhône-Poulenc (Igepal CO-710, Igepal CO-730).

^b +, stable oil-in-water emulsion formed; ±, oil-in-water emulsion formed initially with subsequent inversion to water-in-oil emulsion; —, stable oil-in-water emulsion not formed.

^c Rotary evaporation followed by mechanical stirrer (run A), rotary evaporation only (run B).

^d Cement added to aqueous phase containing lecithin (run A) or cement containing lecithin added to water (run B).

^e K oleate in aqueous phase, lecithin in cement.

R. Br.] which contains cardiac glycosides (Doskotch et al., 1972), would provide an interesting test of this approach to latex detoxification.

Controlling the efficiency of emulsification requires aggressive agitation to maximize interphase contact. While many agitators, including propeller-type agitators (Kostin et al., 1970), have been recommended for emulsification, a variable-speed tissue homogenizer with a high-shear impeller was selected as being most suitable for semimicro-scale preparations. While a few latex applications, such as adhesives, use lower-viscosity polymers, the stress-strain specifications for gloves and condoms necessitate the use of high-viscosity, high-molecular weight rubber in dipped film formulations. To evaluate the effect of emulsification on high-viscosity GR, a cement was prepared from a bale produced at the Sacaton processing facility. This material had a Mooney viscosity of 96.0. Processing into latex lowered the viscosity to 43.4, a 55% reduction directly ascribable to shear degradation during emulsification. The procedure employed here for the preparation of GR latices from solvent-swollen polymer was a batch process. As a result, a portion of the poly-

mer spent considerable time in contact with the homogenizer impeller. The cement was added by pouring as rapidly as effective dispersion could be maintained. Typical addition times were about 3–5 min. This meant that most of the polymer underwent high-shear mixing for more than 2 min. Making latices with high-viscosity polymer will require a continuous process that minimizes emulsification time. The actual extent to which shear degradation must be controlled will depend ultimately on product performance. Sakaki et al. (1996) report that, while enzymatic deproteinization of *Hevea* latices leads to a 29–40% reduction in bulk viscosity and reduced green strength, the stress-strain and dynamic properties were comparable to untreated material.

Controlling emulsification also requires a surfactant to reduce interphase surface tension. Various classes of surfactants, usually nonionic and anionic surfactants, have been used for the emulsification of synthetic polymers such as ethylene–polypropylene copolymer (Cull, 1965) and butyl rubber (Ernst and Betts, 1957). A range of nonionic, amphoteric, and anionic surfactants were evaluated (Table 4), including several described as

useful for the emulsification of synthetic polyisoprene. Only certain anionic surfactants (alkali metal carboxylates and sulfates) proved acceptable when used alone. A modified rosin soap (Dresinate 731) and a poly(methacrylic acid) salt (Darvan No 7) produced only water-in-oil emulsions. A sulfated alkyloleate (Darvan SMO) underwent phase inversion as the concentration of GR cement increased, although there was a good initial oil-in-water emulsion. An important benefit of anionic surfactants is that the pH of the final latex can be sufficiently high that adjustment with KOH or ammonia would be unnecessary. Lecithin, an amphoteric surfactant, was included as much for its potential to enhance polyisoprene cure rates (Goncharova et al., 1995) as for its ability to form micelles. An added attraction is its solubility in hydrocarbon solvents. Nevertheless, whether dispersed in the emulsification aqueous phase or added to the GR cement, lecithin by itself yielded only water-in-oil emulsions. Used in combination with an anionic surfactant, lecithin did yield a stable latex with a low (26%) initial rubber content.

As the penultimate step, emulsions were stripped of solvent to yield dilute latices. Desolventization was ultimately effected using a rotary evaporator. Direct distillation of organic solvents from emulsions led to rapid coagulation of polymer, even with gentle mechanical agitation. Distillation of solvent at 30–32°C from a partially-stripped latex resulted in a substantial reduction in yield due to coagulation (Triton X-301 run A, Table 4). Solvent removal was slow, often requiring overnight runs in order to control foaming. Once stripping was complete, the crude latices had dry rubber contents of about 8–17%. In certain runs using potassium oleate and SDS, the crude latices creamed on standing to yield final products with rubber contents of about 35–40%. More commonly, ammonium alginate was used (final concentration in the latex of about 0.05%) to adjust latex solids to 26–46%. This range is similar to that reported for native GR latex (Schloman et al., 1996). Centrifugation would be a more suitable concentration method under production conditions.

In-situ formation of surfactants was evaluated as an alternative emulsification method. Oleic acid was incorporated into the GR cement and the GR-fatty acid mixture emulsified in the presence of dilute KOH. A fatty acid soap was formed as the organic phase was dispersed. The hydrophobic tails of pre-formed potassium oleate must migrate into the surface region of the cement droplets in order for stable micelles to form. It was felt that dispersion could be more efficient and could require less surfactant with fatty acid in the organic phase from the outset. The film-forming properties of a latex prepared in this way were indistinguishable from those of latices prepared by addition to pre-formed surfactants. It should be pointed out that, in light of the reduction observed in polymer phase bulk viscosity, no attempt was made to evaluate or compare particle size distributions in the finished latices or to compare cure rate and stress-strain properties after compounding.

The rubber in a typical semisynthetic GR latex had a resin content of 3.0% (including antioxidant). Such low resin contents are expected, since the extraction and fractionation process used to prepare swollen GR assures resin contents below about 2% under pilot-scale operating conditions. While shear degradation was sufficient to reduce bulk viscosity, the level of chain cleavage was low enough that very short, and therefore acetone-soluble, chain fragments were not produced.

3.2. Latex allergenicity

The potential for a substance to elicit an allergic response is determined by both the amount and types of protein present. Native guayule latex, in part because of the isolation and concentration process, had a total protein content (2.3 mg/g dry rubber) less than 20% of NR latex (Table 5). The semisynthetic latices described here have total protein contents (0.9–1.1 mg/g dry rubber) that are less than 50% of native GR latex. This is due to the extremely low (2.3 µg/g) level of protein in the swollen GR used to make the latices. While proteins are easily transported in aqueous media, they have limited solubility in organic solvents such as those which may be used to extract and

fractionate bulk GR. This means that solvent extraction effectively strips the native protein complement from GR in the course of processing. The semisynthetic latices described here do have higher protein contents than the swollen GR from which they were prepared. This most likely results from proteins entrained in the ammonium alginate creaming agent, a commercial-grade marine algae derivative.

The allergenicity of semisynthetic latices and various control latices was determined by enzyme-linked immunosorbent assays (ELISA) using both antibodies raised against *Hevea* latex proteins and antibodies raised against guayule latex proteins. Proteins purified from NR latex reacted strongly to anti-*Hevea* antibodies, whereas none of the guayule latices gave any reaction (Fig. 1). Subjects with a hypersensitivity to NR latex would not respond to either native GR latex or any of the semisynthetic GR latices.

Latex isolated from guayule contains a smaller complement of proteins than does latex isolated from *Hevea* (Table 5). Nevertheless, the very presence of these proteins means that there exists a potential for sensitization in susceptible individuals (Siler et al., 1996). It is especially noteworthy that, while native GR latex proteins reacted strongly to these anti-guayule antibodies (Fig. 2), none of the semisynthetic guayule latices gave rise to any reaction. Semisynthetic GR latices, therefore, would not elicit an allergic response in subjects with a hypersensitivity to either *Hevea* latex or native GR latex.

Table 5
Latex protein concentrations

Latex	Protein level (mg/g dry rubber) ^a
NR	11.8 ^b
Native GR	2.3 ^b
GR (SDS surfactant)	0.91
GR (K oleate surfactant)	1.1
GR (in-situ K oleate surfactant)	1.0

^a Protein level for swollen GR: 2.3 $\mu\text{g/g}$ dry rubber

^b Schloman et al., 1996.

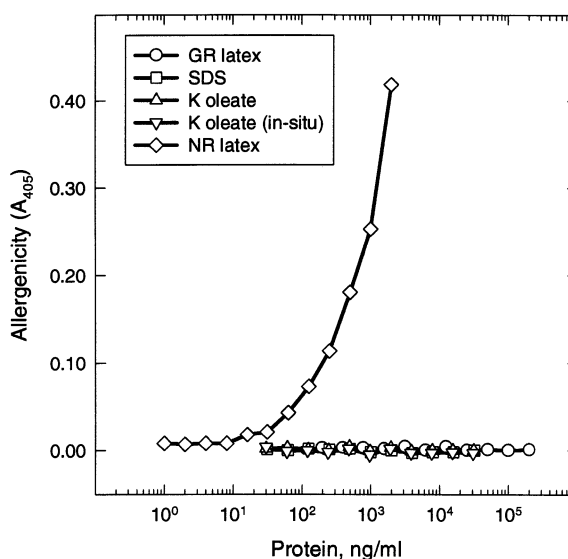


Fig. 1. ELISA of *Hevea*, native guayule, and semisynthetic guayule latices (by surfactant): antibodies raised against *Hevea* latex proteins.

3.3. Dipped film allergenicity

The ultimate test of a latex is its performance in a finished article, especially one prepared as a

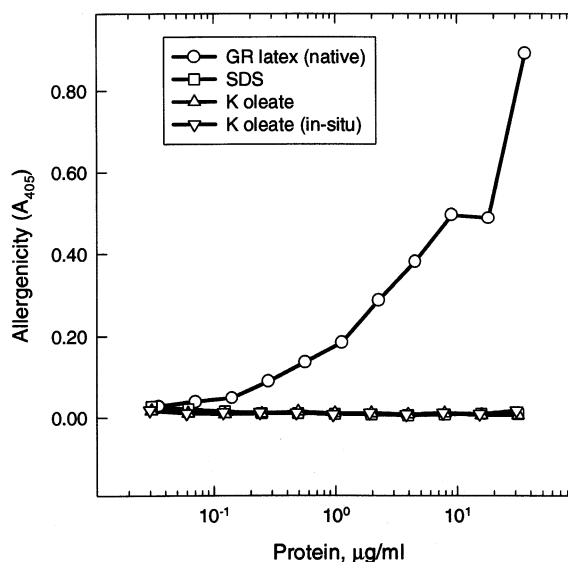


Fig. 2. ELISA of native guayule and semisynthetic guayule latices (by surfactant): antibodies raised against GR latex proteins.

Table 6
Leached film protein concentrations

Latex	Protein level ($\mu\text{g/g}$ dry solids)
Native GR	129
GR (SDS surfactant)	20
GR (K oleate surfactant)	12
GR (in-situ K oleate surfactant)	11

dipped film from a prevulcanized composition of latex and various cross-linking agents. It is the cured film rather than raw latex that comes into contact with a human subject. Compounding, vulcanization, and film formation affect both protein concentrations and extractable allergen yields. Schloman et al. (1996) reported extractable protein levels of $160 \mu\text{g/g}$ from a native GR film and $360 \mu\text{g/g}$ from a NR film. Cured, dipped films prepared from prevulcanized semisynthetic GR latices yielded $20 \mu\text{g}$ or less of extractable proteins per gram of dry latex solids, less than 16% of the protein from a native GR latex film (Table 6). In comparison, Hayashi et al. (1996) found $660 \mu\text{g/g}$ of extractable proteins in a dried NR latex film and $14 \mu\text{g/g}$ of extractable proteins in a dried enzymatically-deproteinized NR latex film. None of the proteins extracted from semisynthetic GR latex films was cross-reactive. As in the case of the semisynthetic latices themselves, the dipped film extracts prepared from semisynthetic latices did not react to anti-guayule antibodies (Fig. 3).

4. Conclusions and recommendations

We conclude that finished goods prepared with semisynthetic GR latex would have a significantly reduced likelihood of eliciting Type I allergic responses. Solvent extraction of rubber from guayule greatly reduces the protein content of the polymer product. Emulsification of cements prepared from solvent-extracted GR, followed by desolventization of the emulsions, provides a straightforward route to stable latices. These latices contain desirably low levels of resin

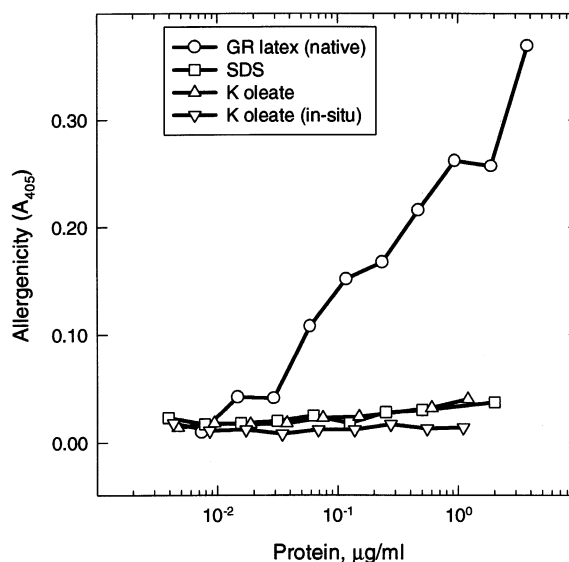


Fig. 3. ELISA of dipped film extracts prepared from native guayule and semisynthetic guayule latices (by surfactant): antibodies raised against guayule latex proteins.

(non-rubber extractables). Most importantly, semisynthetic GR latices and cured dipped films prepared from compounded latices contain none of the allergens associated with either NR latex or native GR latex. We recognize that a commercially-acceptable product with optimal cured film performance will require high-viscosity polymer. Batch processing of the type employed in this study reduces the bulk viscosity of the polymer phase. It would therefore be of considerable value to investigate continuous emulsification processes with mixing and agitation controlled so as to maximize rubber bulk viscosity.

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