

Comparative Study of the Elasticity and Permeability of Vulcanized Films Made with Skim and Cream Natural Rubber Latex

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ABSTRACT: The purpose of this study was to gain a clearer picture of the structure and properties of vulcanized films made with skim and cream latex from *Hevea brasiliensis*. The two properties targeted for this study were the elasticity of the films and their permeability to acetone. Surface characterization by atomic force microscopy revealed that vulcanization substantially modified the structure of the films compared to unvulcanized films. Unlike unvulcanized films, particle identity was retained in the vulcanized films made with cream latex, even after 4 weeks of aging. In addition, skim latex gave vulcanized films with greater elasticity

than those obtained with cream latex. On the basis of the structural characterization carried out on the latex and films and information from the literature, the greater elasticity of the skim films arose from more entanglements between polyisoprene chains and associations between proteins. Despite differences in the structure, the acetone permeability was very similar for skim and cream vulcanized films. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 960–968, 2008

Key words: atomic force microscopy (AFM); films; particle size distribution; rubber

INTRODUCTION

In these times of sustainable development, *Hevea* is becoming an increasingly strategic crop for the production of natural rubber (NR), the only industrially used elastomer of biological origin. In 2005, almost 8.7 million tons were produced, of which around 10% was in latex concentrate form [dry rubber content (DRC) = 60%]. Latex concentrate, also known as cream latex, results from the centrifugation of field latex harvested after rubber tree tapping, which has, in its original form, a DRC of 25–45%. The main use of latex concentrate is for film items (gloves). The centrifugation process also generates a liquid byproduct known as skim (DRC ≈ 5%).¹ The particles making up cream and skim differ notably in their average size (Table I) and density (Fig. 1). Solid NR of mediocre quality, which fetches a low price, is produced by the treatment of skim with large amounts of sulfuric acid, which leads to environmental problems with effluent treatment. Rubber

tree latex is made of particles containing poly(*cis*-1,4-isoprene) or rubber particles, lutoids (intracellular organelles of *Hevea laticifers*²), and an aqueous phase containing a large number of biochemical compounds.² Even today, the structure of rubber particles^{3,4} and their biosynthesis^{5,6} still give rise to debate. Results obtained by Singh et al.⁴ suggest that a single-layer membrane surrounds cream particles.

The mechanisms by which synthetic latex films are formed have been widely described in the literature,^{7–9} whereas few studies have been undertaken on NR film formation.^{10,11} Ho and Khew¹⁰ used atomic force microscopy (AFM) to study the aging at room temperature of films made from a commercial latex concentrate (cream). They showed that particles retained their identity for a short aging time at room temperature (<2 h). During aging, the particles tended to lose their identity, and the films appeared to be quite smooth after 4 weeks. In contrast with synthetic films, the particles of films made with cream latex from *Hevea*, studied by Ho and Khew, had no very clear spherical morphology. Infrared studies showed that proteins accumulating between particles were involved in the phenomenon. Rippel et al.¹¹ used AFM and transmission electron microscopy

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TABLE I
Size of the Rubber Particles in the *H. brasiliensis* Latex

Technique	Mean size (nm)	Distribution	Reference
DLS	Cream: 467 Skim: 297	—	11
DLS	960 Cream: 900 Skim: 220	Bimodal	33
DLS	550	Bimodal Peak 1: 200–300 nm Peak 2: 700–1500 nm	34
DLS	Cream: 1030 Skim: 130	100–3000 nm 50–300 nm	13
SEM		Trimodal 80–750 nm	4
DLS	Cream: 800 Skim: 200	bimodal	This study
TEM	Cream: 800 Skim: 200	bimodal	This study

SEM = scanning electron microscopy.

(TEM) to study unvulcanized films prepared with the two fractions, cream and skim latex, from *Hevea brasiliensis*. They highlighted differences in the poly(*cis*-1,4-isoprene) particles of the two fractions, notably in terms of their membrane. The coalescence of cream particles remained incomplete, whereas the skim particles merged totally. Unvulcanized films made from skim displayed a very smooth surface compared to films prepared from cream. In the work by Rippel et al., no details were provided on the aging time at room temperature before imaging.

Several authors have taken an interest in the properties of dry rubber obtained after skim coagulation,^{12,13} but there have been no studies on the properties of latex films made from skim. In addition, the industrial process to make films from NR latex (gloves and condoms) involves vulcanization. Earlier studies^{10,11} on the structural characterization of films were performed on unvulcanized films, and no properties were studied in parallel. Consequently, our study focused on two properties of vulcanized films prepared from the skim fraction. The elastic properties of vulcanized films and their permeability to a small molecule (acetone) were examined. These properties were compared to those of films prepared from the cream fraction. Structural characterizations of the latexes [TEM analysis of particles and dynamic light scattering (DLS)] and the films (AFM, macromolecular structure, and nitrogen content) were carried out to link the differences observed in the properties with differences in the structure.

EXPERIMENTAL

Samples

Latex suspensions

The samples used came from clone RRIM 600 and were taken at Prince of Songkla University (Surat

Thani, Thailand). Before they were sent to France, ammonia (0.6% w/w of latex) was added to the freshly harvested latex to prevent coagulation. Four samples were examined (Fig. 1): unwashed field latex with 60% DRC (UWFL), cream or fraction 1 centrifuged once (F1_1C), cream or fraction 1 centrifuged twice (F1_2C), and skim or fraction 2 centrifuged twice (F2_2C). To more effectively control the uniform thickness of films obtained with the different samples, all the latexes (UWFL, F1_1C, F1_2C, and F2_2C) were prepared with a DRC of 60%.

UWFL

This sample was raw field latex and contained the largest amount of non-isoprene compounds, notably proteins. The simplest procedure would have been to centrifuge the raw field latex directly at 30,000g with a Beckman Avanti J-E apparatus (Villepinte, France). That was not possible because the latex and particularly the cream coagulated during centrifugation at 30,000g. It was therefore necessary to centrifuge it first at 5000g to recover the uncoagulated cream (fraction 1) and then at 30,000g to concentrate the skim (fraction 2), both of which were then dispersed again in the serum to obtain a latex at 60% DRC. This was achieved by the placement of the field latex at 25% DRC (30 g) in a centrifuge tube (50-mL capacity) and centrifugation at 5000g (19°C, 1 h) to separate the large latex particles (fraction 1) from the other fractions. After centrifugation, the suspension was in three phases (cream or fraction 1,

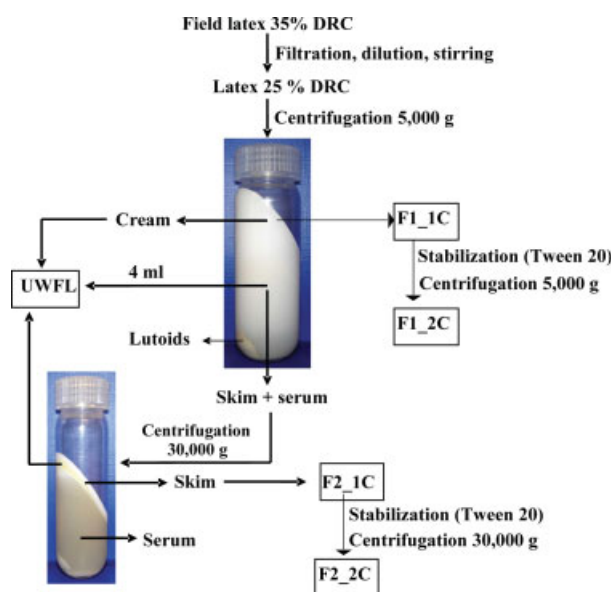


Figure 1 General latex preparation diagram used to prepare the different latexes studied. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

skim and serum, and lutoids; Fig. 1). Four milliliters of the phase containing the skim and serum was drawn off in a syringe and placed in a flask. The cream (or fraction 1) was recovered on a spatula, added to the same flask, and stirred (vortex for 3 min). The rest of the skim and serum mixture was centrifuged again at 30,000g, thereby giving two phases: skim and serum (Fig. 1). The skim, minus the serum, was recovered with a spatula and added to a flask containing the 4 mL of skim and serum recovered beforehand, along with the cream, or fraction 1. UWFL was thus obtained.

F1_1C

After centrifugation at 5000g (see the previous paragraph), the cream was recovered on a spatula and added to a 20-mL flask containing 4 mL of an aqueous solution of Tween 20 (0.75% w/w), rather than serum, to eliminate some of the non-isoprene compounds in the serum (proteins, sugars, etc.). The suspension was stirred (vortex for 3 min).

F1_2C

By centrifugation twice, more proteins were eliminated.^{1,14} Some of the F1_1C latex was diluted to 25% DRC and centrifuged again at 5000g (19°C, 1 h). After centrifugation, the aqueous phase was drawn off in a syringe, and the cream was recovered and suspended once again in a 20-mL flask containing 4 mL of an aqueous solution of Tween 20 at 0.75% (w/w).

F2_2C

This fraction was prepared by the centrifugation at 30,000g (19°C, 1 h) of the fraction containing the skim and serum (Fig. 1), which was obtained after centrifugation at 5000g. Two phases were obtained (Fig. 1, tube 2), the serum was drawn off in a syringe, and the skim was recovered on a spatula and added to a 10-mL flask containing 2 mL of an aqueous solution of Tween 20 at 0.08% (w/w). The latex obtained in that way was centrifuged once again at 30,000g (19°C, 1 h). The aqueous phase was drawn off again with a syringe, and the skim was recovered and resuspended in a 10-mL flask containing 3 mL of an aqueous solution of Tween 20 at 0.4% (w/w).

The four latexes prepared in that way were filtered through a stainless steel sieve (average mesh of 180 μm) before the films were made.

The formula adopted for film vulcanization was very similar to that proposed for surgical gloves by Pendle and Gorton¹⁵ (Table II). The zinc oxide (ZnO) content was increased to 1%, rather than 0.5%, to enhance its effect.

TABLE II
Details of the Vulcanization Formula
(Adapted from Pendle and Gorton¹⁵)

Products	Quantity (g)
60% NR latex	167
10% KOH solution	3
20% potassium laurate solution	1
50% sulfur dispersion	1
50% zinc diethyldithiocarbamate dispersion	1.5
50% zinc oxide dispersion	1

Film preparation

Latex suspensions were cast onto a glass plate with an automatic coater (K Control coater, Erichsen, Rueil-Malmaison, France) in a glovebox at 25°C and dried on a drying bench (40 \pm 0.5°C) under a laminar air flow for 2 h to a constant weight. The initial film thickness was around 160 μm . After drying, the films were vulcanized in the oven at 120°C for 20 min and stored in a desiccator covered with aluminum foil to protect them from UV light and limit water transfer before use.

Protein content

The total nitrogen content was determined by the method derived from the Dumas combustion technique. A test piece was calcined (850°C) in an oxygen stream where the combustion gases were trapped to remove dust, halogens, water vapor, and carbon oxides. The nitrogen oxides went to a copper column at 730°C in a helium stream, which reduced them to N₂ gas. The nitrogen content was determined by a thermoelectric cell. The nitrogen content was multiplied by a specific factor of 6.25 to give the protein content.

Macromolecular structure by size exclusion chromatography (SEC)

The SEC system consisted of an Erma ERC-3112 solvent degasser (Erma Optical Works, Ltd., Japan), a Waters 510 pump (Water Corp., Milford, MA), a Waters 717 Plus automatic injector, and a Waters 486 UV detector (220 nm). The two Styragel columns (mixed, 30 cm \times 7.8 mm, porosity of 20 μm ; Water Corp.) were thermostated at 65°C, and the cyclohexane [high-performance liquid chromatography (HPLC) grade] flow rate was 0.8 mL/min. Three rubber solutions from each sample were prepared (see Bonfils and Char¹⁶) and injected (100 μL) after filtration (25-mm disposable filters, porosity of 1 μm).

DLS analysis

The average particle size and particle size distribution (PSD) were determined with an Autosizer 4800

(Malvern Instrument Co., Orsay, France) on the basis of the DLS theory. The advantage of this apparatus came from the angle of detection, which could be varied from 30 to 140° in 1° steps. The CONTIN algorithm, which is widely used for solving DLS problems and has a wide following in the academic world, and the non-negative least squares (NNLS) algorithm, which has the best resolution currently available and provides good results for broad or multimodal distributions, were used and compared for this study. Most studies have used this algorithm to analyze multimodal samples.^{17,18} Each sample was diluted with deionized water (2.5×10^{-4} % w/w). Before the measurement, samples were filtered on a membrane with a pore size of 10 μm to eliminate any dust that might disrupt measurements.

TEM analysis

The samples for TEM were prepared by the deposition of latex dispersions (dilution of 0.2% w/w with deionized water) on 400-mesh copper grids and drying at room temperature. TEM observations were carried out under a JEOL 1200 EXII transmission electron microscope (Croissy-sur-Seine, France) at a voltage of 100 kV. The micrographs obtained were analyzed with image processing freeware (Image Tool, San Antonio, TX). Around 200 particles were measured per sample to determine the particle size and PSD.

AFM analysis

The equipment used was a Nanoscope III A Dimension 3100 (Digital Instruments, Dourdan, France; large sample) with scanned tips. The tips used were in silicon nitride (Si_3N_4), were pyramid-shaped with a square base (4 μm) and 3 μm in height, and were fitted to the end of a triangular cantilever in Si_3N_4 with a normal stiffness coefficient of k_N of 0.12 N/m. The images observed were displayed in 512 points per row. Height or phase variations were indicated by colors, where the light areas represented the highest levels. In the event that topography variations were undetectable, friction images were used to distinguish the different physicochemical variations in the surface.

Elastic properties

The tensile properties of the vulcanized films were measured according to ASTM Standard D 412 with an Instron type 5544 universal tester (Elancourt, France). The tensile strength and elongation at the break point were determined. To study the elasticity of the films obtained with the different latexes, Young's modulus [E ; Hooke's law, eq. (1)] and parameters C_1 and C_2 of the Mooney–Rivlin phenome-

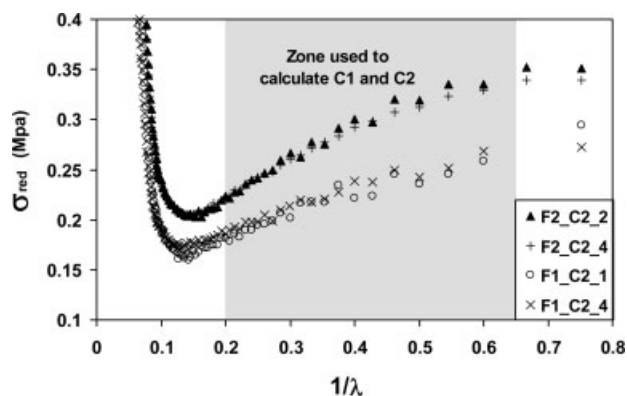


Figure 2 σ_{red} as a function of $1/\lambda$ for the films made from skim latex (F2_2C) and cream latex (F1_1C). Two replicates are shown for each latex.

nological model [eq. (2)] were determined. E was calculated from the initial linear part of the stress (σ)–deformation curve [ε (%); eq. (3)]. The C_1 and C_2 parameters were obtained from the reduced stress (σ_{red}) curves as a function of the inverse of the extension ratio [λ eq. (4)] modeled at low deformations ($1.5 < \lambda < 5$; Fig. 2):

$$\sigma = E\varepsilon \quad (1)$$

$$\sigma_{\text{red}} = \frac{\sigma}{(\lambda - \lambda^{-2})} = \left[2C_1 + \frac{2C_2}{\lambda} \right] \quad (2)$$

$$\varepsilon = \frac{\Delta L}{L_0} \quad (3)$$

$$\lambda = \frac{L}{L_0} = \varepsilon + 1 \quad (4)$$

where L_0 is the initial length and L is the length after the application of force.

Permeability measurements

During the acetone permeation measurements (Fig. 3), the active area of film in the cell was 13.85 cm^2 . Two peristaltic pumps (Masterflex) were used to circulate the solutions upstream and downstream, which were thermostatically controlled at 25°C. Acetone concentrations were determined over time by automatic injections (Autosampler 360, Kontron Instruments) in an HPLC system (Kontron Instruments) fitted with a UV detector (HPLC detector 742, Kontron Instruments) at a wavelength of 230 nm. The initial acetone concentration in the upstream tank was 440 g/L. Each assay was replicated three times with a new film each time. At the end of the process, the film was removed and dried for 30 min, and its thickness was measured at 20 points with a micrometer (Mitutoyo, Roissy, France) to determine its average thickness.

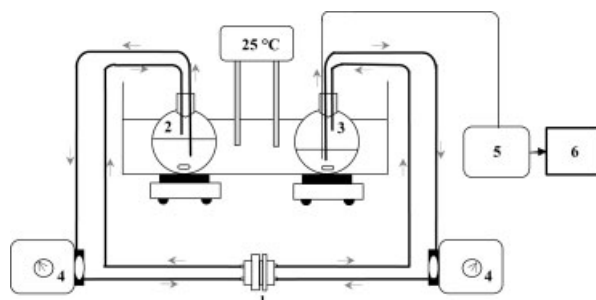


Figure 3 General diagram of the permeability unit used: (1) permeation cell, (2) feed vessel, (3) permeate collector, (4) peristaltic pump, (5) HPLC and UV detector, and (6) data recorder.

The experimental results for acetone transfer through the NR films were used in accordance with the solubilization–diffusion model.¹⁹

The acetone flow [$J_{C_3H_6O}$ ($\text{kg m}^{-2} \text{s}^{-1}$)] through the film was written as follows:

$$J_{C_3H_6O} = \frac{P_{C_3H_6O}}{\delta} (C_0 - C_1) \quad (5)$$

where $P_{C_3H_6O}$ is the coefficient of acetone permeability (m^2/s), δ is the average film thickness (m), C_0 is the acetone concentration in the upstream tank (kg/m^3), and C_1 is the acetone concentration in the downstream tank (kg/m^3).

$P_{C_3H_6O}$ through a dense film was therefore obtained with the following equation:

$$P_{C_3H_6O} = \frac{\delta J_{C_3H_6O}}{\Delta C} \quad (6)$$

where $\Delta C = C_0 - C_1$ is the motive force of acetone transfer through the film. Because of the high ace-

tone concentration used in these experiments ($C_0 = 440 \text{ kg}/\text{m}^3$) and the low permeability of the films studied (C_1 reached a maximum of $5 \text{ kg}/\text{m}^3$ at the end of the experiment, i.e., barely over 1% of C_0), it was concluded that ΔC was constant throughout the experiments to determine $P_{C_3H_6O}$ with eq. (6). $P_{C_3H_6O}$ was independent of the difference in the concentrations used on either side of the film. That property was checked with three different concentrations. A standardized flow ($J_{C_3H_6O} \cdot \delta$) was calculated [eq. (7)] to compare the acetone permeation properties of the different films studied, which were of similar but not identical thickness:²⁰

$$J_{C_3H_6O} \cdot \delta (\text{kg } \mu\text{m s}^{-1} \text{m}^{-2}) = \frac{(\text{amount of permeant})(\text{film thickness})}{(\text{membrane area})(\text{time})} \quad (7)$$

RESULTS AND DISCUSSION

Characterization of the latex suspension

Figure 4 shows images taken by TEM for three different samples: the initial field latex, cream (F1_1C), and skim (F2_2C; Fig. 1). Figure 4 shows images of particles in a dry state after they were deposited onto a grid to make them observable by TEM. In the field latex [Fig. 4(a)], some particles were visible that were linked to each other by a poorly defined continuum. That had already been found by Southorn¹⁴ using photomicroscopy results. He suggested that lutoids and Frey Wyssling particles could be attached to rubber particles and could form a thread-like reticulum. After initial centrifugation, which gave cream without skim and lutoids, the rubber

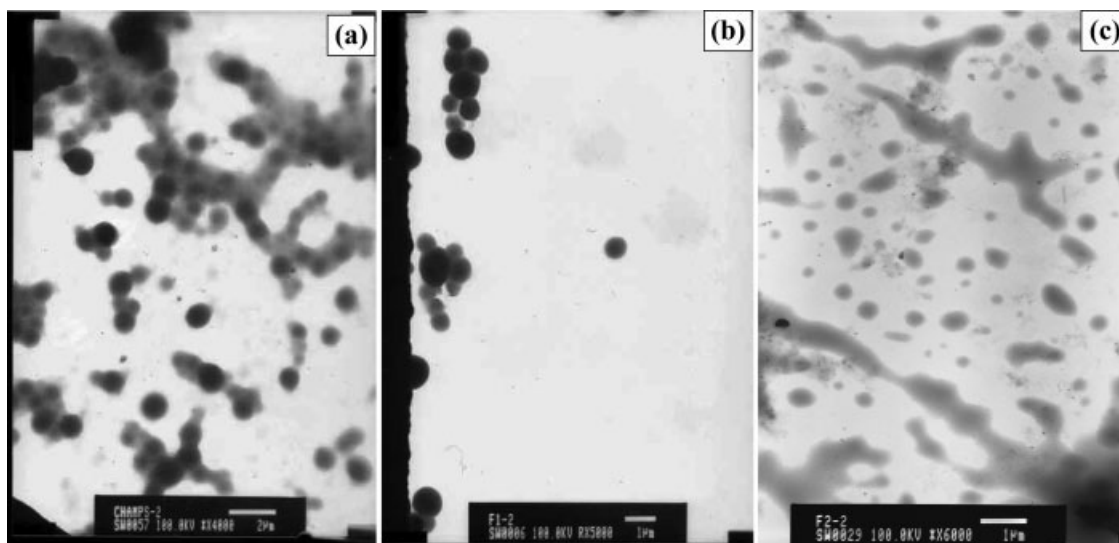


Figure 4 TEM micrographs of (a) field latex (UWFL), (b) cream (F1_1C), and (c) skim (F2_2C).

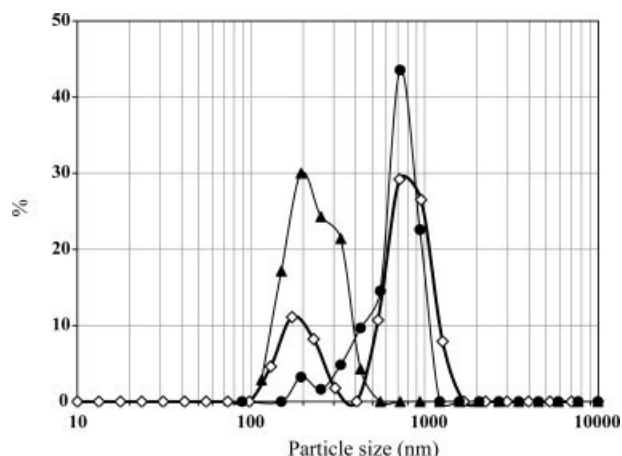


Figure 5 PSD of (\diamond) the field latex [DLS (Autosizer 4800, NNLS, 90°)], (\bullet) cream fraction (TEM), and (\blacktriangle) skim fraction (TEM).

particles could be observed by TEM [Fig. 4(b)]. The cream fraction mainly comprised the largest particles (ca. 80% of the total rubber particles). TEM analysis of the purified skim [Fig. 4(c)] showed that the particles did not have clearly defined shapes. Indeed, the type of continuum found with the field latex was also found for the skim. The continuum, which was attributed by Southorn to lutoids or Frey Wyssling particles, therefore appeared to come from the skim. Because the glass-transition temperature of NR is about -70°C , it would be understandable for the particles to flow after drying and to give a continuum, but that phenomenon was not seen for the cream [Fig. 4(b)].

The PSDs of the three samples (field latex, F1_2C or cream, and F2_2C or skim) were analyzed by DLS and TEM (Fig. 5). For DLS, different angles of detection (50° , 90° , and 140°) and two algorithms (CONTIN and NNLS) were studied with an Autosizer 4800. Because the two algorithms presented very similar results, only the results for the NNLS algorithm are presented in this article. In addition, the angle of detection was shown to have no significant influence on PSD, so only the results for a detection angle equal to 90° are presented. For field latex, Figure 5 shows that PSD tallied well with the TEM results, with two populations detected at approximately 200 and 800 nm (Table I). Also tallying with the TEM results, the larger particles (peaking ca. 800 nm) were detected in fraction 1 (cream), and the smaller particles were detected in fraction 2 (skim), with the modal peak around 200 nm.

The surfaces of the unvulcanized and vulcanized films were studied with AFM (Fig. 6). The films were characterized 1 month after preparation. The rubber particles in the unvulcanized films (Fig. 6) lost their identity. This phenomenon was consistent with the results shown by Ho and Khew.¹⁰ The sur-

face of the vulcanized films was rougher than that of the unvulcanized films, especially for films made from cream (F1_2C). For the cream fraction (F1_2C), the particles retained their identity (Fig. 6), even after being dried for 2 h in a reactor and then vulcanized (120°C , 20 min) and left for 1 month at room temperature before analysis. It would therefore seem that vulcanization fixed the system or considerably delayed coalescence on the surface of the vulcanized films and the interpenetration of polymer chains. When the behavior of the vulcanized films was compared, it appeared that films made from fraction 1 (cream) and those made from fraction 2 (skim) behaved differently during maturation. Fraction 1, which mainly contained larger rubber particles, had a rough surface with some rubber particles that were particularly visible in AFM. On the other hand, fraction 2, which mainly contained small particles, had a very different surface condition: the surface of those films was much smoother, with particles that had lost their identity on the surface (Fig. 6). The membrane of skim particles appeared to have been less rigid and likely to split more rapidly after drying. These results for unvulcanized cream- and skim-

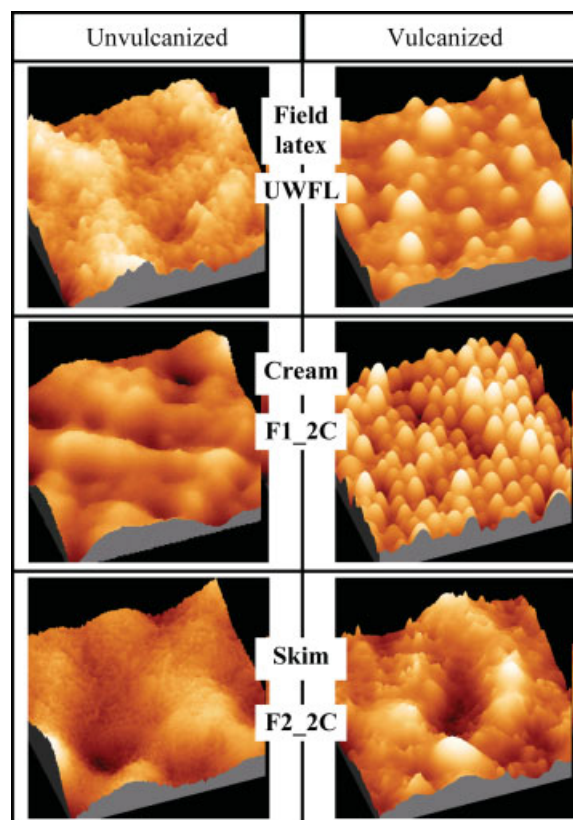


Figure 6 Surface of unvulcanized films characterized by AFM [$5 \times 5 \mu\text{m}^2$, except for F1_2C ($10 \times 10 \mu\text{m}^2$)]. The films were made 1 month before characterization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

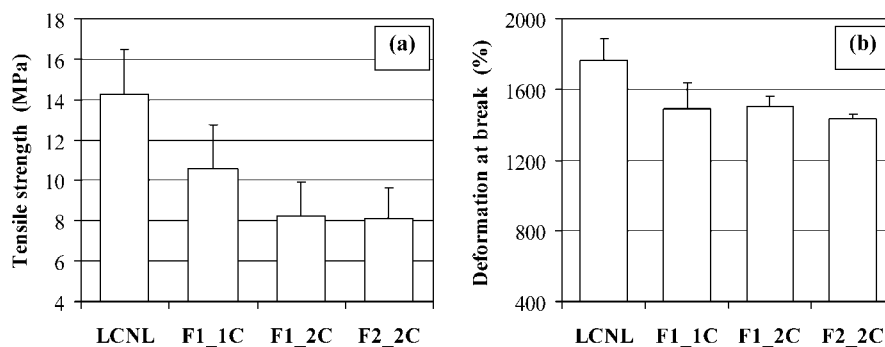


Figure 7 (a) Tensile strength and (b) deformation at the break point for the four latexes studied (mean of five replicates for each sample).

based films tallied with those obtained by Rippel et al.,¹¹ but vulcanization of the films appeared to seriously modify coalescence for cream latex particles. According to work by Cook et al.,²¹ the absence of cream particle coalescence might be due to vulcanization within particles during drying (2 h at 40°C). They showed that the morphology of films made with prevulcanized latex differed particularly from that of postvulcanized films. For prevulcanized films, vulcanization mainly occurred within particles, and they retained their shapes, whereas for postvulcanized films, the particles were less visible because they were nearly all embedded. However, prevulcanization of latex usually requires heating at 60°C for 5–6 h. Moreover, Cook et al., prevulcanized their latex for 6 h at 60°C and kept their films for another 3 h in water at 50°C. It is clear that further AFM studies of prevulcanized films are needed if that question is to be answered. However, in our study, the films made from skim underwent the same process as those made from cream, and the film surfaces revealed by AFM were very different, indicating different behavior and thus most likely a different structure.

Mechanical properties and elasticity

The gradual purification of the field latex (UWFL → F1_1C → F1_2C) reduced the tensile strength in the prepared films [Fig. 7(a)]. That was probably linked to a gradual elimination of natural vulcanization activators, notably nitrogen compounds (amino acids).²² However, granulometry did not have any effect on the tensile strength [F1_2C or cream versus F2_2C or skim; Fig. 7(a)]. For deformation at the break point [Fig. 7(b)], only the films made from field latex (UWFL) stood out from the others. Although there were no differences in the technological properties between films made from cream (F1_2C) or skim (F2_2C), both types of films stood out through their elasticity at low deformations (Fig. 2). The films made from skim had a much higher E value than those made from cream (0.63 ± 0.04 vs 0.47 ± 0.03 MPa; Table III). The σ_{red} curves as a function of the inverse of λ were also modeled with the Mooney–Rivlin phenomenological model [eq. (2)]. That model offered the advantage of being simple and of providing just two parameters, C_1 and C_2 , which could be linked to the structural characteristics of the material. Constant C_1 was proportional to

TABLE III
Results for Unvulcanized Films [Protein Content, Gel Content, and Weight-Average Molar Mass (M_w)] and Vulcanized Films (Elasticity Parameters) Prepared from the Four Latexes Studied

Sample	Protein content (%)	Gel content (%) ^c	M_w (kg/mol)	E (MPa) ^d	C_1 (MPa) ^e	C_2 (MPa) ^e
UWFL	1.85 (0.12)	42 (2.5)	741 (30)	0.54 (0.03)	0.073 (0.004)	0.125 (0.01)
F1_1C ^a	1.27 (0.08)	35 (1.5)	718 (9)	0.49 (0.03)	0.070 (0.004)	0.116 (0.013)
F1_2C ^a	0.97 (0.1)	27 (1.5)	680 (6)	0.47 (0.03)	0.065 (0.003)	0.119 (0.017)
F2_2C ^b	2.04 (0.12)	47 (7)	762 (6)	0.63 (0.04)	0.073 (0.002)	0.188 (0.009)

For all measurements, the mean of five replicates and the standard deviation are given, except for the gel content and M_w , for which three replicates were used. The protein content, gel content, and M_w were determined on unvulcanized films; E , C_1 , and C_2 were determined on vulcanized films.

^a Cream rubber.

^b Skim rubber.

^c Sum of the macrogel and microgel (see ref. 16).

^d See eq. (1).

^e Mooney–Rivlin parameters [see eq. (2)].

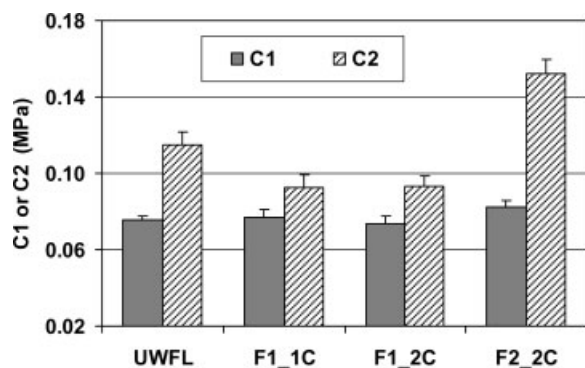


Figure 8 Mooney–Rivlin parameters C_1 and C_2 for the four latexes studied (mean of five replicates for each sample).

the crosslinking density^{23,24} of the network. C_2 varied very little or not at all with the crosslinking density.²⁴ C_2 was all the greater the more the behavior of the material deviated from the conventional, or statistical, theory of elasticity. That occurs when a large number of topological constraints, other than chemical crosslinking linked to vulcanization, disrupt the ideality of the network.²⁵ The nature of topological constraints always gives rise to debate, and the articles by Boyer and Miller²⁶ and more recently Sherbakov and Grishin²⁷ review this aspect. They involve either entanglement between macromolecules or physical crosslinks (van der Waals forces, etc.) or probably, depending on the nature of the polymer, both of them. In the case of NR, we shall go on to see that both types of topological constraints can be envisaged. Figure 8 shows that parameter C_1 did not display any significant difference, regardless of the latex tested. However, some very significant differences were found for constant C_2 between skim (F2_2C) and cream (F1_2C; Fig. 8). On the basis of the quantity of gels measured in the films studied (Table III) and the mechanisms proposed for gel formation in NR in the literature,^{28,29} the greater elasticity of the films made from skim may have been due to larger quantities of proteins existing in those films (Table III). Proteins act as

crosslinking points in addition to bridges with sulfur. Some authors have suggested that proteins generate physical bridging,^{28,30} and others have suggested that they are both chemical and physical.^{31,32} Those additional bridges might also be due to lipids, other non-isoprene compounds involved in gel formation,²⁹ but rubber made from skim does not contain any ester groups.¹³ Proteins may therefore have been responsible for the greater elasticity of the films made from skim. It was found for unvulcanized films that the quantity of gel increased in line with the protein content (Table III). Yet, for an identical protein and gel rate, the films made from UWFL (whole latex: cream + skim) and F2_2C (skim) displayed very different elasticity. Those results show that these two parameters, gel and proteins, cannot be interpreted from a quantitative point of view only, and a qualitative study is needed. The entanglement rate may have played a not insubstantial role in the differences found between cream and skim. In fact, as mentioned earlier, analyzing them by TEM (Fig. 4) and by AFM (Fig. 6) revealed that the particle structure differed considerably between cream and skim. Although cream particles maintained a clearly defined identity after vulcanization, skim particles seemed to have flowed or even fused after moderate drying (room temperature; Fig. 6). The membrane of skim particles would seem to be very thin or nonexistent. That would enable polyisoprene end-chain entanglement and would also increase film elasticity. It should be noted that films made from UWFL, which contained around 5–7% skim, had a higher C_2 constant than films made from cream.

Permeability

Permeation assays were carried out on films made from UWFL, F1_2C (cream rubber), and F2_2C (skim rubber). Films made from commercial natural latex gloves were used as a reference. For each formulation, $J_{C_3H_6O}$, δ , $J_{C_3H_6O} \cdot \delta$, and $P_{C_3H_6O}$ were determined (Table IV). The statistical analysis, which was

TABLE IV
 $J_{C_3H_6O}$, δ , $J_{C_3H_6O} \cdot \delta$, and $P_{C_3H_6O}$ in Water

Sample	$J_{C_3H_6O}$ (10^{-5} kg m ⁻² s ⁻¹)	δ (μ m)	$J_{C_3H_6O} \cdot \delta$ (10^{-3} kg μ m s ⁻¹ m ⁻²)	$P_{C_3H_6O}$ (10^{-12} m ² /s)
Gloves ^a	1.7 (0.1)	139 (4)	2.4	5.42 (0.22)
UWFL	1.7 (0.2)	143 (13)	2.4	5.47 (0.2)
F1_2C ^b	1.6 (0.4)	135 (37)	2.2	4.72 (0.41)
F2_2C ^c	2.0 (0.1)	135 (9)	2.5	6.00 (0.06)

The mean of three replicates and the standard deviation are given for all the measurements except $J_{C_3H_6O} \cdot \delta$.

^a Safeskin (Thailand).

^b Cream rubber.

^c Skim rubber.

performed with Jump (SAS Institute) software, showed that only the permeability coefficient of F1_2C films differed (Table IV) from the other samples (gloves, UWFL, and F2_2C). Given the complex chemical composition of natural latex, it was difficult to establish how fractionation of the suspension affected physical interactions between acetone and the polymer matrix. The protein content of the films was probably an important factor in permeability, insofar as the existence of those polar compounds in the polymer matrix must have been conducive to acetone transfer. Indeed, films made from F2_2C (skim), which contained 2% proteins (Table III), were more permeable to acetone than those made from F1_2C (cream) containing around 1% proteins. UWFL films, with a protein content of 1.85%, displayed permeability closer to that of films made from F2_2C, which contained 2% proteins (Table III).

However, these results showed that thin films made from skim latex had, in terms of acetone permeability, properties similar to those of commercial films (gloves). Such a latex would therefore appear to be acceptable for glove manufacturing.

CONCLUSIONS

TEM and AFM analyses led to the same observation: the two fractions making up *H. brasiliensis* latex differ in the particle structure, theoretically in terms of their membrane. For unvulcanized, nonmatured films, the TEM study showed that skim particles lost their identity, and this gave rise to a continuum. After film vulcanization and maturation, AFM analyses indicated that skim particles, but not cream particles, also lost their identity, unlike in unvulcanized films.

Modeling of the tensile tests by the Mooney–Rivlin equation revealed that vulcanized films made from skim were more elastic than films made from cream. Given the complex composition and structure of NR, it is illusory to try to suggest an explanation for the difference in elasticity with any certainty (see the earlier discussion). However, the differences in particle coalescence revealed for skim and cream in AFM and TEM analyses suggested that the greater elasticity found in films made from skim latex was partly linked to greater chain entanglement and/or association between proteins than in films prepared from cream.

In terms of film permeability, although statistically significant differences were observed between films made with the skim fraction and cream fraction, they can be considered relatively slight and acceptable from a technological point of view because all

the measured permeability coefficients were of the same order of magnitude (ca. $5 \times 10^{-12} \text{ m}^2/\text{s}$).

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