

Characteristics of Experimental *cis*-1,4 Polyisoprene Latices

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INTRODUCTION

Many of the characteristics of natural rubber latex that vary considerably because of its origin in biological processes should be subject to closer control in a synthetic product because of the possibility of uniformity in production processes. The present paper deals with the properties and utilization of experimental *cis*-1,4 polyisoprene latices prepared on a laboratory scale. In the course of this work with a new polymer latex, a need for a knowledge of the effective chain density at various stages of use became apparent. The importance of crosslink density determinations as a measure of the extent of cure in latex during maturation and cure and in the final products is demonstrated.

LATEX PROPERTIES

Because of the marked structural similarity of the synthetic latex polymer to the natural rubber, *Hevea brasiliensis*, many of their properties are comparable.¹ In the synthetic latex polymer the predominant isomer is *cis*-1,4 polyisoprene (92-97%) as indicated by infrared spectroscopy,² the balance of the polymer being the *trans* and 3,4 isomers. The intrinsic viscosity of the *cis*-polyisoprene in the experimental latices described here was about 8 dl./g., corresponding to a viscosity average molecular weight of about 2,100,000. Weight average molecular weight of the synthetic polymer was about 2,500,000. The similarity of these molecular weights indicates a relatively narrow molecular weight distribution. Important differences from the natural latex polymer are that the synthetic latex polymer is essentially linear in structure, does not contain branched structures, and is free of gel. The nonrubber content of the latex solids consisted of only phenolic antioxidant and emulsifier.

The experimental latices described in this investigation contained anionic surfactants as stabilizers in amounts near their critical micelle concentrations. Because of the absence of proteins, carbohydrates, phospholipids, etc. normally present in natural latex, ammonia was not required for preservation or stabilization of the synthetic latex. Some physical characteristics of a representative experimental *cis*-polyisoprene

TABLE I
Properties of an Experimental *cis*-polyisoprene Latex

Total solids, %w	63
pH	9-10
Surface tension, dynes/cm.	37
Viscosity at 60% solids, cps. (Brookfield, No. 2 spindle, 30 r.p.m.)	50
Particle size range, μ	0.1-4
Weight median particle diameter, μ	0.9

latex are given in Table I. The weight median particle diameter of the latices was about 0.9 μ , close to that of many natural rubber latices but considerably larger than styrene-butadiene latices which have weight median particle diameter values of about 0.1 μ . The particle size distribution in the synthetic polyisoprene latices was close to log normal and covered the range of about 0.1-4 μ (upper and lower deciles). The larger particle size of these latices relative to styrene-butadiene latices allows stabilization by a much lower emulsifier content than normally encountered in synthetic latices. This fact also makes for more flexibility in formulating, especially in foam applications. In addition, good mechanical stability is obtained at a relatively low emulsifier level in the synthetic polyisoprene latex.

STRESS-STRAIN PROPERTIES OF UNVULCANIZED LATEX FILMS

Structural differences in the raw natural rubber and synthetic *cis*-polyisoprene polymers deposited from latices are reflected in their stress-strain properties as shown in Table II where the lower modulus and higher elongation of the raw *cis*-polyisoprene latex films may be seen. The

TABLE II
Stress-strain Properties of Raw Polymer Films from Latex^a

	300% Modulus, p.s.i.	500% Modulus, p.s.i.	% Elongation at break	Stress at break, p.s.i.
Hevea	80	150	1450	1900
<i>cis</i> -polyisoprene	15	25	2000	100

^a Microdumbbells tested at 20 in./min., 74.5°F.

introduction of a small number of crosslinks into the latex has been found to provide a means of polymer modification whereby reduced flow and higher film strengths are achieved. Table III shows the effects on polymer properties produced by introducing small, but important, amounts of crosslinking into the latex by heating for various lengths of time at 50°C. with 0.5 phr. sulfur and 0.75 phr. of the ultra-accelerator zinc diethyldithiocarbamate. The level of crosslinking achieved and the rate of the reaction

TABLE III
Properties of Slightly Crosslinked *cis*-polyisoprene-Latex Films^a

Crosslink density moles/cc.	Tensile strength psi	% Elongation at break	Modulus, p.s.i.	
			300 %	500 %
0	100	2000	15	25
0.02×10^{-4}	200	1000	40	70
0.04×10^{-4}	320	1220	50	80
0.06×10^{-4}	460	1150	60	90

^a Microdumbbells tested at 20 in./min., 74.5°F.

can be controlled by modification of crosslinking agent, accelerator, and their respective levels as well as by modifying the time and temperatures.

The crosslink density or effective chain density in the latex is determined

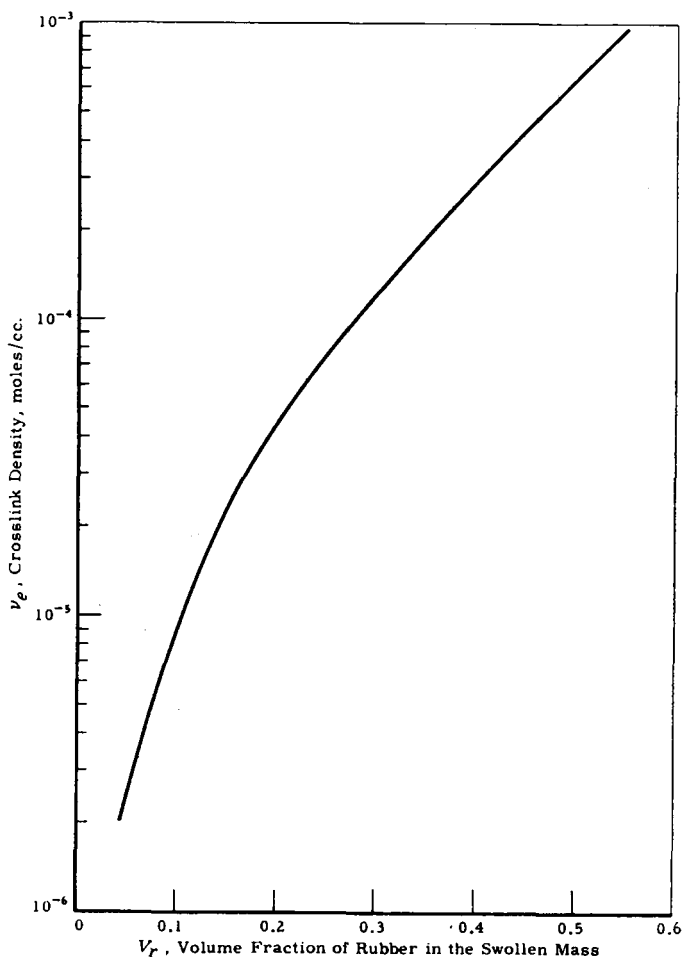


Fig. 1. Relationship between V_r and ν_e for *n*-heptane and *cis*-polyisoprene at 25°C.

by measuring the swelling in *n*-heptane of a circular disc of latex film about one inch in diameter. The thin films of the latex (cast on glass plates) which are used in these measurements generally swell to equilibrium within an hour or less. From the initial and swollen diameters the volume fraction of rubber in the swollen mass V_r is determined ($V_r = (\text{initial diameter}/\text{swollen diameter})^3$) and the crosslink density is calculated from the well known Flory-Rehner equation.³ In applying this equation, the functionality of the crosslinks has been assumed to be 4 and the Huggins solubility parameter μ for the solvent-polymer pair (*n*-heptane-*cis*-polyisoprene) at 25°C. has been taken as $\mu = 0.46 + 0.20 V_r$. The nonrubber constituents of latex products which are not part of the crosslinked network are generally present in sufficiently small amounts to be ignored in the crosslink density calculations. The solution to the Flory-Rehner equation for the volume fraction of polymer in the swollen mass V_r and the effective chain density or crosslink density ν_e for *cis*-polyisoprene is given in Figure 1. The application of this concept of effective chain density or crosslink density to latex has been found to be a useful guide in latex conditioning and in controlled curing of latices.

FORMULATION AND PROPERTIES OF VULCANIZED FILMS

In studying the vulcanization of films cast from the latex, the formulations given in Table IV were used. Slightly higher levels of sulfur and ultra-accelerators were used with the synthetic *cis*-polyisoprene to provide for the structural differences between the two polymers as well as for compositional differences between the synthetic latex and the naturally occurring latex. Figure 2 shows values of tensile strength for *cis*-polyisoprene latex films only slightly lower than values obtained for natural rubber latex films made with similar formulations. The elongation at break is in the range 900–1000% in each case. The 300% and 500% modulus values are also equivalent but at higher elongations the modulus values for the synthetic latex are generally lower than those of the natural latex. The modulus values at break are essentially identical because of the similar tensile and elongation values at break.

The formulation of Table IV has been modified along several lines in order to obtain an impression of the effects of various ingredients normally required in other applications, particularly in foam type formulations. Adjustments of the basic formulation of Table IV were made by the addition of more potassium oleate (normally required as a frothing aid) plus methyl cellulose and Trimene Base (an adduct of ethyl chloride, ammonia, and formaldehyde, Naugatuk Chemical Company). These ingredients produced a reduction in the tensile strength and a drop in modulus of the *cis*-polyisoprene product with a slight increase in elongation. Addition of zinc oxide raised the modulus and decreased the elongation of both the natural and the synthetic latex products but caused the tensile strength to drop in the synthetic latex product without influencing the the natural latex films. The addition of sodium silicofluoride raised the

TABLE IV
Formulation and Properties of Vulcanized Latex Films

Ingredient	Amount used, phr., dry basis					
	<i>cis</i> -Polyisoprene rubber latex			Natural rubber latex		
Potassium oleate	1.5			1.5		
Sulfur	2.5			2.0		
Zinc diethyldithiocarbamate	1.5			1.0		
Zinc salt of 2-mercapto-benzothiazole	1.5			1.0		
Antioxidant	1.0			1.0		
Cure time at 100°C., min.	20	30	45	10	20	30
Tensile, p.s.i.	5930	5990	5850	5959	6070	6100
% Elongation	900	900	950	1000	1000	1000
300% Modulus, p.s.i.	180	220	200	220	245	240
500% Modulus, p.s.i.	420	410	400	420	415	410

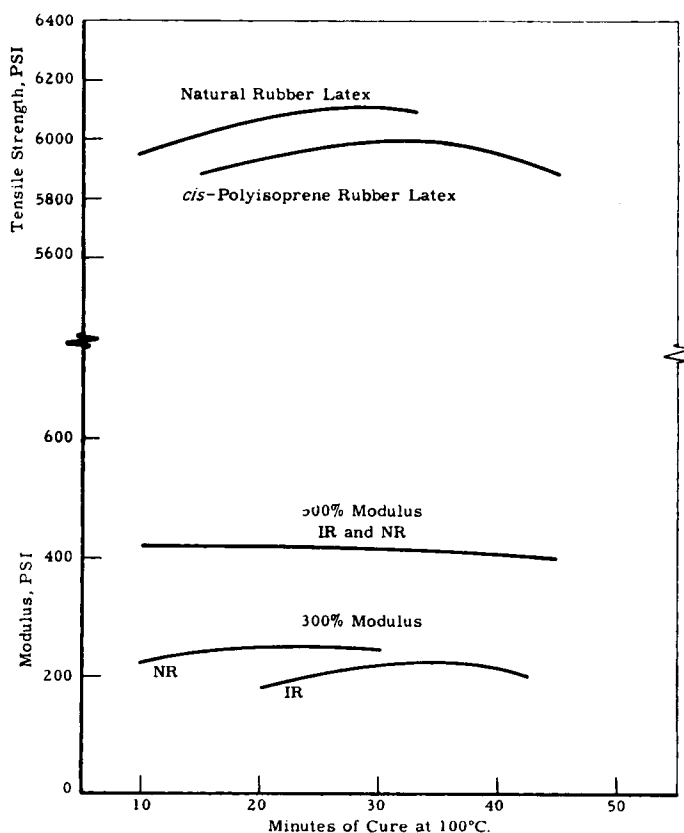


Fig. 2. Properties of vulcanized latex films.

modulus considerably and the tensile strength moderately in both elastomers.

STATE OF CURE FOR *cis*-POLYISOPRENE LATEX

Progressive compounding studies have been carried out with a range of sulfur content and cure times at 100°C. ranging from 10–60 minutes at

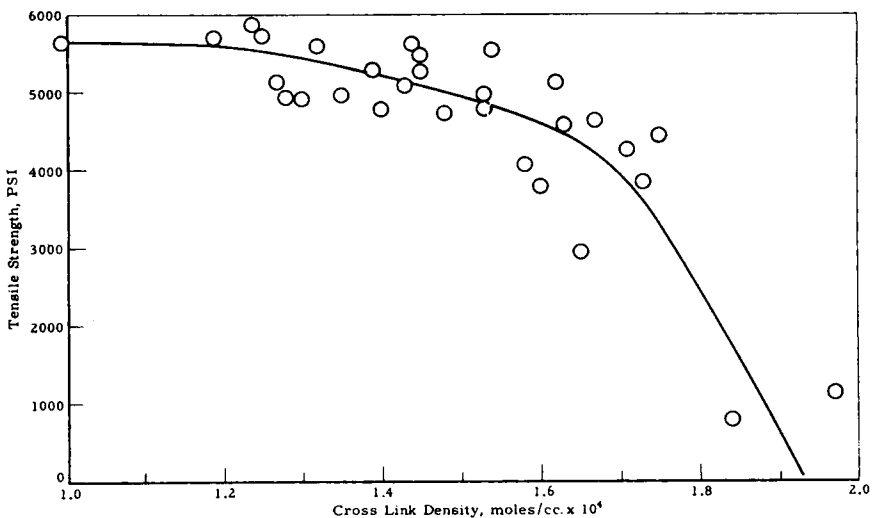


Fig. 3. Tensile strength vs. crosslink density-polyisoprene films from latex.

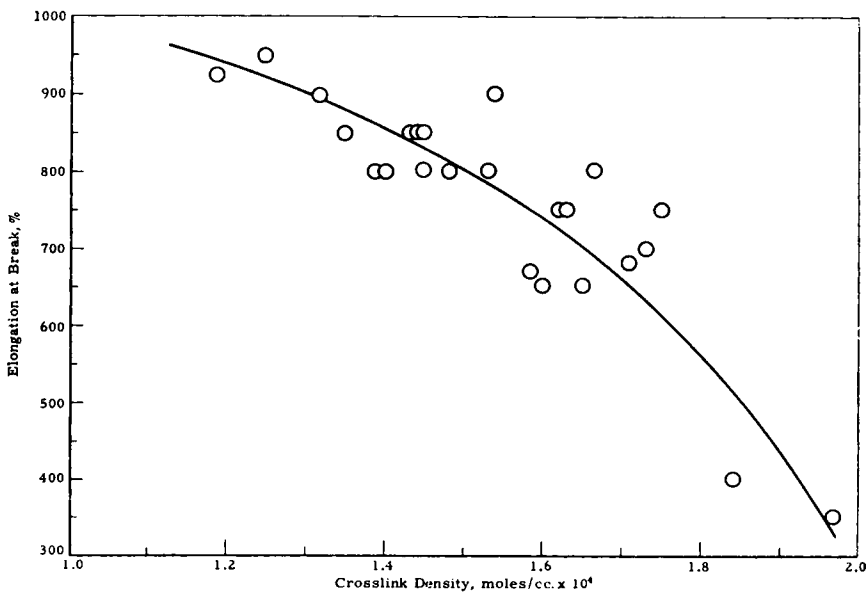


Fig. 4. Crosslink density vs. elongation-polyisoprene films from latex.

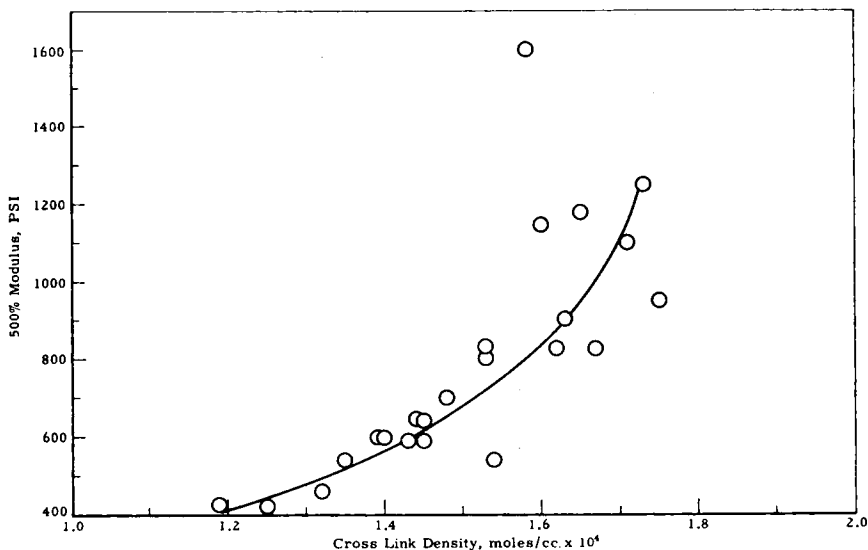


Fig. 5. 500% Modulus vs. crosslink density-polyisoprene films from latex.

each of the sulfur levels. The crosslink densities of the films indicate the state of cure for *cis*-polyisoprene rubber latex as shown in Figure 3. The tensile strength develops rapidly with the formulation used and is at its highest level at crosslink densities in the range $1.0\text{--}1.2 \times 10^{-4}$ moles/cc. The tensile strength declines gradually in the range $1.2\text{--}1.6 \times 10^{-4}$ but decreases sharply at crosslink densities above 1.7×10^{-4} moles/cc. While the tensile strength and elongation at break (Fig. 4) are relatively insensitive to changes of crosslink density in the range $1\text{--}1.6 \times 10^{-4}$, it can be seen from Figure 5 that high or low values of 500% modulus (400–800 psi.) can be obtained from *cis*-polyisoprene latex by controlling the crosslink density achieved in the vulcanization. The information obtained on the crosslink density and physical properties of films is found to be applicable not only to dipped and cast products but to foam rubber as well.

FOAM RUBBER

Preparation of foam rubber from the experimental *cis*-polyisoprene latices was carried out in the following basic steps: Maturation of the partially compounded latex, production of a froth by mechanical beating of the fully compounded latex, gelation of the froth in a mold with sodium silicofluoride, steam curing and washing, and drying of the article. The foam formulations and procedures used with *cis*-polyisoprene rubber latex and natural rubber latex are shown in Table V. When a gelation system based on addition of sodium silicofluoride during the frothing operation is employed, gelation occurs at room temperature in 2–10 min. and can be regulated by adjustment of the sodium silicofluoride content.

TABLE V
Typical Foam Rubber Formulations

	<i>cis</i> -polyisoprene rubber latex	Natural rubber latex
Rubber	100	100
Potassium oleate	1.0	1.0
Sulfur	0.5	0.5
Zinc diethyldithiocarbamate	0.75	0.75
Zinc salt of 2-mercaptobenzothiazole	—	—
Antioxidant	1.0	1.0
Maturation temperature, °C.	50	40
Maturation time, hr.	16	16

After maturation, foams were prepared by mechanical beating with the addition of the following materials:

Sulfur	2.0	1.5
Zinc diethyldithiocarbamate	0.75	0.75
Zinc salt of 2-mercaptobenzothiazole	1.5	1.0
Methyl cellulose	0.4	—
Trimene base	1.0	0.2
Shellwax 100	3.0	3.0
Zinc oxide	3.0	3.0
Sodium silicofluoride	1.0	1.0
Gel time, 25°C., min.	7	8

Maturation in the presence of at least part of the sulfur and accelerators which are added as aqueous dispersions can have three functions: (1) to produce an intimate mixture of the latex particles and vulcanizing ingredients; (2) to provide an opportunity for sulfur (and probably accelerators as well) to dissolve molecularly in the rubber particles; and (3) to permit the production of a controlled amount of crosslinking in the rubber. When the chief functions of the maturation are (1) and (2) as described above, room temperature may be used. Since very little chemical action takes place at this temperature, all of the sulfur and accelerators may be added in the maturation step and its duration may be short because of the relatively rapid diffusion of sulfur into rubber.⁴ In order to accomplish function (3) above, elevated temperatures may be employed, the desired extent of crosslinking being achieved by adjusting the time, sulfur, and accelerator concentrations or temperature.

The prevulcanization occurring under various conditions of maturation was followed quantitatively by periodic determination of the crosslink density on films as described earlier. For the particular sample of Hevea latex, the raw polymer before maturation had a crosslink density of 0.01×10^{-4} moles/cc.; this is a reflection of the presence of microgel and macrogel which normally occurs in varying amounts in Hevea Latex. Since the synthetic polymer is free of gel, the initial crosslinking in unmaturred latex is always zero. Using recommended maturation conditions⁵ (Table V), the Hevea latex increased in crosslink density to a value of 0.03

$\times 10^{-4}$ moles/cc. In the case of *cis*-polyisoprene latex, a crosslink density of 0.03×10^{-4} moles/cc. was obtained for the same time of maturation at a slightly higher temperature (Table VI) using the formulation of Table V.

The effects of various degrees of latex maturation on the physical properties of *cis*-polyisoprene rubber foams are shown in Table VI. The formulation of Table V was used in each case with uniform curing conditions of 30 min. at 100°C.; only the maturation times and temperatures were varied.

TABLE VI
Effect of Latex Maturation on Properties of Foam Rubber Prepared from
cis-polyisoprene Rubber Latex

Foam no.	1	2	3
Maturation conditions	16 hrs. at 25°C.	16 hrs. at 50°C.	24 hrs. at 50°C.
Crosslink density in latex, moles/cc. $\times 10^4$	0	0.03	0.06
Foam density, g./l.	100	100	100
Compression deflection, p.s.i. ^a			
25%	0.30	0.50	0.54
50%	0.66	1.20	1.22
Tensile strength, p.s.i.	14.0	12	10
Elongation, %	240	200	110
Compression set, %	23	12	10
Shrinkage, %	10	17.5	36
Cell structure ^b	Non-uniform	Uniform	Uniform

^a Load required to produce a compression of the stated percentage in a one-inch slab.

^b Uniformity of cell size and absence of gross flows.

The uniformity of cell structure originally present in the ungelled froth was retained to a greater extent in the cured foams from latices matured to 0.03 or 0.06×10^{-4} moles/cc. This probably accounts for the appreciable improvement in compressive properties (load required to produce a 25% or 50% compression foam) which is evident in foams 2 and 3 of Table VI. In foam 3, with the highest crosslink density in the latex stage, decreases in tensile strength and elongation and high shrinkage are noted. The drop in tensile strength and elongation of the foam which occurs when too high a level of crosslinks is introduced during maturation is believed to be a result of the influence of polymer properties on particle coalescence in the gelation process. Latex particles with too high a crosslink density and resistance to flow may not coalesce readily and completely, and the resulting decrease in the area of particle-particle contacts would be expected to lead to void spaces as sites of weakness leading to a reduction in overall tensile strength.

In vulcanization, a higher level of ultra-accelerators was used in *cis*-polyisoprene rubber latex than in natural latex foam formulations in order to compensate for the absence of naturally occurring accelerators present in Hevea. Cure is accomplished in open steam at 100°C. in 20–40 min. The kinetics of the vulcanization process under these conditions appear to be

similar to those of Hevea. The crosslink density of foams can be judged accurately by curing and drying a latex film cast on aluminum foil alongside the foam and subjecting the film to the previously mentioned swelling test. It was found that the crosslink density of foams is identical with films formulated and cured in the same manner. The range of crosslink density in vulcanized *cis*-polyisoprene films which gives best tensile properties applies also to the rubber in foams. In these studies, using formulations such as those of Table V it has been shown that *cis*-polyisoprene foams cured to crosslink densities of $1.5\text{--}1.75 \times 10^{-4}$ moles/cc. (within the range for optimum film tensile properties) have physical properties roughly equivalent to those of natural rubber foams as shown in Table VII. Rapid

TABLE VII
Comparison of Foam Properties

Latex	<i>cis</i> -1,4 polyisoprene rubber	Hevea
Gel time, min. at 25°C.	7	8
Density, g./l.	100	100
Compression deflection, p.s.i.		
25%	0.50	0.54
50%	1.20	1.22
Tensile strength, p.s.i.	12	14
Elongation, %	200	280
Compression set, %	12	16
Volume shrinkage, %	17.5	20
Crosslink density of matured latex, moles/cc. $\times 10^4$	0.03	0.03

recovery of the *cis*-polyisoprene foams from severe compression is insured by the inclusion of anti-blocking agents such as wax to control surface tack or by curing to higher crosslink densities.

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Synopsis

Experimental latices of synthetic *cis*-1,4-polyisoprene and films and cellular objects produced from them are described. The latices of the synthetic polymers with molecular weights of about 2,000,000 are stabilized by anionic surfactants and have weight median

particle diameters of about 0.9μ and log normal particle size distribution. Tensile properties and flow characteristics of unvulcanized latex films could be regulated by introduction of controlled, small, amounts of crosslinking into the latex. Procedures used for crosslink density determination on *cis*-polyisoprene latex at various stages of use are described. Vulcanized latex films having maximum tensile strengths (5500–6000 p.s.i. and 800–950% elongation) were obtained when the final crosslink density was in the range $1.0\text{--}1.6 \times 10^{-4}$ moles of effective chains/cc. Use of the synthetic *cis*-polyisoprene latex in production of foam is described. Gelation with sodium silicofluoride at room temperature occurs within 2–10 minutes. Production of a controlled level of crosslinking in the latex prior to frothing and gelling was found to improve the uniformity of cell structure of foams and to increase their resistance to compression. Excessive crosslinking in the latex during maturation was shown to cause a loss of tensile strength in cured products presumably because the coalescence of latex particles during gelation is adversely affected. The properties of synthetic *cis*-1,4-polyisoprene latices and the physical properties of films and foams derived from them are shown in general to be very similar to those of natural rubber latex and its products.

Résumé

On décrit des réseaux expérimentaux de *cis*-1,4-polyisoprène synthétique, des films et objets cellulaires produits au moyen de ceux-ci. Les réseaux de polymères synthétiques de poids moléculaires d'environ 2.000.000 sont stabilisés par des agents superficiels anioniques; ils ont des diamètres de particule de poids moyen d'environ 0.9μ et un log de la distribution des dimensions de particules normale. Les propriétés à la traction et les caractéristiques d'écoulement des films de latex non vulcanisés peuvent être réglés par introduction dans le latex de quantités contrôlées, petites, d'agent de ramification. On décrit les procédés employés pour la détermination de la densité de pontage à différents degrés sur du latex de *cis*-polyisoprène. Des films de latex vulcanisé ayant des résistances à la traction maximum (5.500–6.000 psi et 800–950% d'élongation) sont obtenus quand la densité finale de ramification est du domaine de $1.0\text{--}1.6 \times 10^{-4}$ moles de chaînes effectives/cc. On décrit l'emploi de latex synthétique de *cis*-polyisoprène dans la production de mousse. La gélification avec du silicofluorure de sodium à température de chambre se produit endéans 2 à 10 min. On trouve que la production d'une teneur contrôlée de ramification dans le latex avant le développement de la mousse et la gélification améliore l'uniformité de la structure des cellules de mousse et augmente leur résistance à la compression. Une ramification excessive dans le latex durant la maturation cause une perte de résistance à la traction dans les produits vulcanisés, vraisemblablement par ce que la coalescence des particules de latex durant la gélification se trouve altérée de façons opposées. Les propriétés des réseaux de *cis*-1,4-polyisoprène synthétique et les propriétés physiques des films et des mousses dérivés de ceux-ci se montrent en général très semblables à celle du latex de caoutchouc naturel et à celles de ses dérivés.

Zusammenfassung

Versuchslatices aus synthetischem *cis*-1,4-Polyisopren sowie daraus hergestellte Folien und Porenkörper werden beschrieben. Die Latices des synthetischen Polymeren mit Molekulargewichten von etwa 2000000 werden mit anionischen Emulgatoren stabilisiert und besitzen Gewichtsmittelwerte des Partikeldurchmessers von etwa $0,9 \mu$ und eine lognormale Partikelgrößenverteilung. Zugeigenschaften und Fließcharakteristik von unvulkanisierten Latexfolien konnten durch Einführung eines kontrollierten, kleinen Ausmasses an Vernetzung in den Latex geregelt werden. Verfahren zur Bestimmung der Vernetzungsdichte an *cis*-Polyisoprenlatex in verschiedenen Verarbeitungstufen werden beschrieben. Vulkanisierte Latexfolien mit maximaler Zugfestigkeit (5500–6000 psi und 800–900% Dehnung) wurden bei einer Endvernetzungsdichte im Bereich von $1,0\text{--}1,6 \times 10^{-4}$ Mol effektiver Ketten pro cc erhalten. Die Verwendung des syn-

thetischen *cis*-Polyisoprenlatex zur Erzeugung von Schaumstoffen wird beschrieben. Mit Natriumsilikofluorid tritt bei Raumtemperatur innerhalb von 2 bis 10 Minuten Gelierung ein. Die Herstellung eines kontrollierten Vernetzungsausmasses im Latex vor der Schaumbildung und Gelierung verbesserte die Einheitlichkeit der Zellstruktur der Schaumstoffe und erhöhte ihren Kompressionswiderstand. Übermäßige Vernetzung im Latex während der Reifung führte, wahrscheinlich wegen einer ungünstigen Beeinflussung der Koaleszenz der Latexteilchen während der Gelierung, zu einem Verlust an Zugfestigkeit bei den vulkanisierten Produkten. Die Eigenschaften der synthetischen *cis*-1,4-Polyisoprenlatices und die physikalischen Eigenschaften der daraus hergestellten Folien und Schaumstoffe sind im allgemeinen denen des Naturkautschuklatex und der entsprechenden Produkte sehr ähnlich.

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