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Film from Mixtures of Natural and Synthetic Rubber Latex

PHYSICAL PROPERTIES

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THE principal tonnage uses of GR-S-type latices, aside from tire cord adhesives, are in products in which natural rubber latex is the principal or an important component. The amount and type of synthetic latex used in blends of commercial importance have been influenced by economic factors and by the processing and physical properties of the product, but more often the synthetics have been looked upon chiefly as "extenders" for the natural latex.

However, with the introduction of the so-called cold rubber latices, there has been much evidence that the use of synthetic rubber latices may now be extended into these applications as 100% synthetic, and the products will have useful physical properties somewhat comparable to those made using natural-synthetic rubber blends.

No comprehensive evaluation of the effect of the several polymerization variables on the vulcanized film properties of natural rubber-GR-S blends has been reported, although studies on some aspects of this problem have been described (3, 11). A preliminary study of the variables of butadiene-styrene ratio, polymerization temperature, percentage conversion, and Mooney viscosity, on the properties of blends varying from 0 to 100% synthetic content, has been undertaken. In this initial phase of the study attention has been confined to those variables affecting only the polymer properties, and the so-called latex properties—amount and type of surface active agents, catalysts, particle surface unsaturation, pH, etc.—have been varied, of necessity, over fairly wide limits in order to make possible the preparation of latices of the desired range of polymer characteristics. Further, the study was confined to a more or less uniform evaluation procedure, rather than an attempt to develop casting, drying, and curing conditions which are optimum for each latex. The evaluation technique used adheres closely to procedures which have been widely practiced in the latex industry for years (4).

The restriction of the scope of the evaluation procedure and the

Because the use of cold rubber latices may be extended into the field of latex applications as 100% synthetic, rather than as an extender for natural rubber latex, a study was undertaken to evaluate the effect of several polymerization variables on the properties of blends containing 0 to 100% synthetic rubber. It was found that blends containing 70% or more natural rubber latex had little effect of the stress-strain properties of the mixture; that cold rubber latices gave higher stress-strain values of natural rubber blends than did hot rubber latices; and that low conversion synthetic polymers produced higher stress-strain properties than the high conversion polymers in the blends. The physical properties of a natural rubber stock are superior to those of any of the synthetic rubber latices so far tested.

comparative lack of uniformity in the colloidal and other nonpolymer properties of the latices will, it is realized, fail to bring out the maximum potential properties of many of the polymers. Such compromises were necessary in a preliminary program of this nature in order to keep the variables within a practical number. It was felt, moreover, that the evaluation should roughly approximate the conditions of use, and that methods that were completely unattainable

in commercial practice should not be employed. This eliminated from consideration certain techniques which had been observed to give improvements in sheet properties, such as casting the sheet in special atmospheres, drying in vacuum desiccators, curing at low temperatures, and the like.

An important property which has a considerable influence on the technical usefulness of a latex, but which is not easily controlled or susceptible of precise measurement, is its ability to form well-knit, strong sheets during drying or when treated with gelling agents—i.e., prior to cure. This property is commonly known as wet gel strength, and reflects the effects of a large number of variables of the polymer, latex colloidal properties, pretreatment, viscosity, drying environment, and so on. Natural rubber latex is outstanding in exhibiting high wet gel strength under an extremely wide variety of conditions of use, whereas GR-S synthetics have been very erratic in this respect. Several techniques have been developed which help to overcome this deficiency of the GR-S synthetic latices in the manufacture of frothed sponge (2, 8, 13). The attainment of high vulcanizate strength in cast latex sheets is usually tied in with the attainment of high wet gel strength under the conditions of use. Thus, high vulcanizate strengths on cast latex films of cold GR-S rubbers have been obtained in some cases (3, 10), but they have often been found difficult to reproduce from one laboratory to the next. Also, widely variable results have been obtained by the same investigators on supposedly similar latices, as has been the experi-

Table I. Principal Polymerization Variables and Properties of Latices Used

Latex Identification	Type of Recipe ^a	Reactor Size ^b	Polymerization Temp., ° F. ^c	Monomer Charge, B-S	Combined Styrene, %	Conversion, %	Mooney Viscosity, MS 1 1/2	Solubility in Benzene, %	Swelling Volume of Gel	Figures in Which Data Used
P3375-V93	Type V	Small	122	100-0		95	86	13	21	6, 7, 8, 13, 14
P3375-V79C	Type V	Small	122	100-0		60	48	51	31	3, 4, 6, 7, 8
P4381 ^d	Type V	Large	122	100-0		60	108	30	34	5
P3375-V79B	Type V	Small	122	100-0		40	42	48	95	6, 7, 8
P3375-V76A	Type V	Small	122	100-0		25	52	29	76	6, 7, 8
Type VII ^e		Commercial	122	80-20		90-95	24	41	26	11, 12, 13, 14
P1986-34	Type V	Small	122	80-20	18.5	95	72	24	22	11, 12
Type V ^e	Type V	Commercial	122	70-80	29.5	95	65	10	19	1, 2, 8, 13, 14
Type V ^e , low conversion	Type V	Commercial	122	70-80	27.4	60	61	38	62	1, 2, 5, 8, 9, 10
Type V ^e , low conversion	Type V	Commercial	122	70-80		60	100	26	24	9, 10
P3490-18/	Type II	Small	122	70-30		53	52	63	123	9, 10
RXL-3902	Type V	Small	122	70-30		50	14	72	75	9, 10
RXL-3868	Type V	Small	122	70-30	24.6	34	74	28	67	8
RXL-3938	Type V	Small	122	50-50	49.0	60	60	35	63	5, 8
Chemigum 101A ^g	Type V	Commercial	122	45-55	54.0	95	60	26	18	8, 13, 14
P4487-8	Polyamine hydroperoxide	Small	50	100-0		60	40	100		3, 4
RXL-3928	Type V	Small	50	70-30	32.0	87	75	35	42	1, 2
J4437D ^h	Polyamine hydroperoxide		50	87-13		80	44	64	82	15, 16
J4248B ^h	Polyamine hydroperoxide		50	70-30		80	65	53	58	15, 16
X-547 ^h	Iron-hydroperoxide	Commercial	50	70-30	26.4	60	50	82	113	1, 2, 5, 15, 16
J4248D ^h	Polyamine hydroperoxide		50	70-30		60	57	69	120	15, 16
J3630D ^h	Iron-hydroperoxide		50	70-30		60	39	84		15, 16
P4427-1	Polyamine hydroperoxide	Large	50	70-30		60	78	65	80	15, 16
RXL-3935	Polyamine hydroperoxide	Small	50	50-50	46.7	65	74	56	119	5

^a Recipes: 1. Type V described in text.

2. Type II, standard hot GR-S, 100 monomer, 180 water, 5.0 soap, 0.3 K₂S₂O₈, *n*-dodecyl mercaptan modifier.

3. Iron hydroperoxide, X-547 type, 100 monomer, 65 water, 3.0 potassium soap, 1.5 potassium salt of sulfonated naphthalene-formaldehyde condensation product, *tert*-dodecyl mercaptan modifier; amounts of alkaryl hydroperoxide, iron sulfate, K₄P₂O₇, and Na₂S₂O₄ adjusted to give desired reaction rates.

4. Polyamine hydroperoxide, X-635 type, 100 monomer, 70 to 80 water, 3.0 potassium soap, 1.5 alkali salt of sulfonated naphthalene-formaldehyde condensation product, *tert*-dodecyl mercaptan modifier; amounts of alkaryl hydroperoxide and alkylene polyamine adjusted to give desired reaction rates.

^b Small, 5 or 20 gallons; large, 1200 gallons; and commercial, 1600 or 2500 gallons.

^c Many of the latices listed as being polymerized at 122° F. were initiated at 115° or 120° F. and carried to 135° to 140° F. when necessary to reach high conversions. The average temperature was in the range 120° to 125° F.

^d Produced in RRC plants as X-621.

^e Office of Rubber Reserve, RFC, production latices.

^f Agglomerated and creamed.

^g Goodyear Tire and Rubber Co., Chemical Division.

^h U. S. Rubber, Naugatuck, acting as agent of Rubber Reserve.

ence in this laboratory. The evaluation technique used has failed to obtain any of the tensile strengths of 2000 to 3000 pounds per square inch which have occasionally been obtained by others on cold rubber latices.

PROCEDURES

Latex Preparation. Most of the high temperature latices were prepared in a base recipe and with a procedure similar to that used for preparing Type V latex (1). One hundred parts of monomer were charged into a reactor equipped with a high displacement agitator containing 50 to 60 parts of water, 0.5 to 1.0 part of carboxylic acid soap, 0.3 part of potassium persulfate, and an amount of normal or tertiary dodecyl mercaptan adjusted to give the desired Mooney viscosity. Increment addition of soap solution after 15% conversion was used to maintain latex stability, a total of 3 to 4 parts of soap generally being present in the final latex. The soaps were mixtures of sodium or potassium salts of oleic and rosin acids. Particle diameters of latices so produced are of the order of 2000 to 3500 Å., as determined by soap titration (1, 7), and are classified as large particle size latices in comparison with the much smaller sizes, 600 to 900 Å. diameter, obtained in the polymerization recipes used for making latex to be processed into dry rubber.

A few high temperature latices were prepared in a recipe giving a small initial particle size—viz., a recipe similar to that used for making Type II latex—and were agglomerated with acetic acid and ammonia (12) to particle sizes comparable to those obtained with the large particle size procedure outlined above. These latices were creamed from 15 to 20% solids to 45 to 55% solids with 0.1 to 0.2% ammonium alginate (on the water phase) prior to use.

Low temperature latices were prepared in a polyamine-hydroperoxide high solids type of recipe, which the U. S. Rubber workers pioneered and which is being currently produced as X-635 (9).

Shortstopped latices were vacuum stripped to remove residual styrene prior to use.

The natural rubber latex was an ammonia-preserved Hevea

latex from the Goodyear plantation in Sumatra, concentrated by centrifuging. It was similar in properties to the regular concentrated natural rubber latices of commercial use.

Tests on Latex and Raw Polymer. Latices were examined for mechanical stability, pH, and approximate particle size before acceptance for use. The particle size estimate was based on a turbidity measurement (1), and served simply to eliminate latices of too small a particle size. A few particle sizes by soap titration were run to confirm the particle sizes obtained by turbidity measurements. Mooney viscosities (small rotor, 1 1/2 minutes) were determined on very lightly milled salt-acid coagulated samples to which antioxidant had been added. Solubility in benzene and swelling volume of the gel were measured by leaching unmilled crumbs in benzene, 1 gram per 100 ml., at room temperature for 20 to 40 hours without agitation, and filtering the soluble portion through 80-mesh screen. The solubility was determined from a dried down aliquot of the filtrate and the swelling volume of the gel was estimated from the volume of swollen material—the difference between the initial and filtrate volumes—and the known weight of gel. These parameters provide useful information concerning macrostructure which is not furnished by the Mooney viscosity or other rheological tests.

The latices used and their principal properties are enumerated in Table I.

Preparation of Cast Latex Sheets. For convenience and simplicity the evaporated sheet method was used for comparing the

Table II. Compounding Recipe for Evaporated Sheet Samples

Material	Parts by Weight
Rubber, latex solids	100.00
Potassium oleate	0.00 to 1.20
Potassium hydroxide	0.50
Agerite White	1.00
Sulfur	1.00
Zinc oxide (XX-50)	1.00
Zinc diethyldithiocarbamate	1.00
Ammonium alginate	0.00 to 0.10

physical properties of the latex rubbers. This method consisted of stabilizing the latices with a soap and potassium hydroxide so that, when mixed together, they remained fluid. The compounding ingredients, consisting of sulfur, zinc oxide, accelerator, and antioxidant, were added as a mixture of dispersions in water and thoroughly stirred into the blended latices (Table II).

oxide, and stearic acid (Table III). The fully compounded slabs of rubber were then allowed to set for 24 hours, after which they were cut into test pieces to fit the mold cavity of $4\frac{1}{2} \times 6\frac{1}{2} \times \frac{3}{32}$ inches. The vulcanization was done in the conventional laboratory press at 275° F. for 10, 20, and 30 minutes, after which the sheets were allowed to condition at 77° F. for 24 hours before

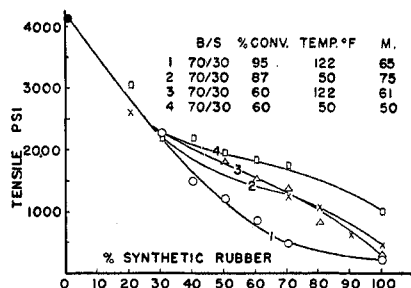


Figure 1. Effect of Reaction Temperature

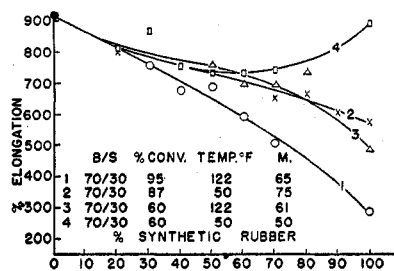


Figure 2. Effect of Reaction Temperature

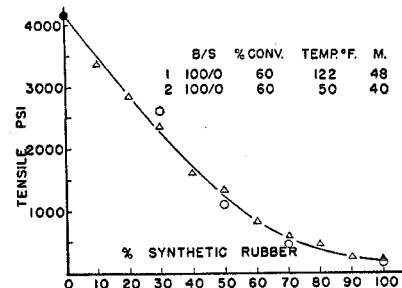


Figure 3. Effect of Reaction Temperature

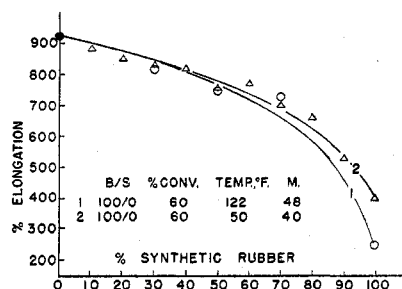


Figure 4. Effect of Reaction Temperature

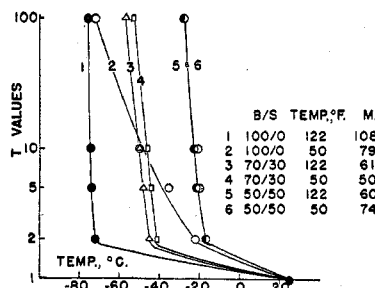


Figure 5. Effect of Reaction Temperature
60% conversion

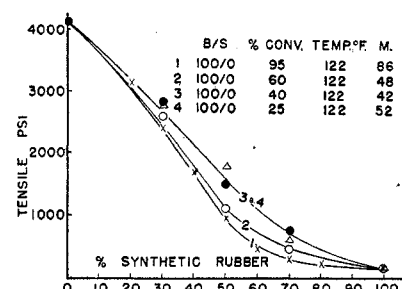


Figure 6. Effect of Conversion

The latex mix of 50 to 58% total solids was matured 16 hours at room temperature without agitation. The viscosity of the mix was then increased by the addition of a thickening agent such as ammonium alginate, and a sufficient quantity was poured onto a glass plate framed by glass strips to make dried sheets of $9.25 \times 6.50 \times 0.060$ inches. The drying of the latex was controlled at a temperature of 75° to 80° F. for 16 hours in a confined space to maintain high humidity, after which the almost dry sheets were stripped from the glass and allowed to dry for 7 days at the same temperature.

The dried rubber sheets were cured in an air oven at 212° F. for 5, 10, 15, 20, 30, and 40 minutes.

The sheets were then conditioned for at least 24 hours in a room at 50% relative humidity and 77° F. before determining their physical characteristics.

Preparation of Milled Sheets. The milled rubber test sheets were made by mixing the antioxidant dispersion into either the latex or latex blend and then pouring the latex on glass plates, 36×36 inches, framed by glass strips. The latex was dried at 75° to 85° F. for approximately 24 hours, after which the rubber sheets were stripped from the glass and hung up for additional drying at the same temperature for 3 days. The sheets were approximately 0.04 inch thick.

These sheets were further compounded on the conventional two-roll rubber mill by the addition of sulfur, accelerators, zinc

they were cut into the same size dumbbell strips as used for the evaporated latex sheets. The test strips were conditioned 24 hours at 50% relative humidity and 77° F. before stress-strain determinations were obtained.

TESTING

The stress-strain data were obtained using a dumbbell-type test strip having a center section of 2.50×0.394 inches. This differs slightly from that specified by ASTM, as it was designed especially for the Albertoni autographic machine. The horizontal-type autographic machine with a speed of jaw separation of 30 inches per minute was used and the stress-strain curve was plotted automatically. The advantage of this type of machine was that modulus determinations could be easily obtained at all elongations.

The tensile and elongation data used in the figures were picked from the best cure of the range mentioned above. Thus, in Table IV, the 15-minute cure for the natural rubber, the 5-minute cures for the Type V and X-547 latices, and the 5- and 15-minute cures for the 50-50 natural rubber-synthetic blends of Type V and X-547, respectively, would be chosen.

The Gehman torsional flexibility apparatus was used in obtaining the low temperature properties of the rubbers (5, 6).

RESULTS

Before discussing the data it is appropriate to point out the difficulty of predicting the modifier requirement accurately enough to obtain a desired Mooney viscosity within closely set limits when other variables are also being manipulated. Consequently, all polymers having Mooney viscosities within certain ranges were considered to be equivalent, these ranges being

Table III. Compounding Recipe for Milled Rubber Samples

Material	Parts by Weight
Rubber, latex solids	100.000
Stearic acid	1.000
Agerite White	1.000
Zinc oxide	1.000
Sulfur	1.600
Captax	0.675
Diphenylguanidine	0.825

roughly divided as follows: high, 70 MS and higher; medium, 40 to 70 MS; and low, below 40 MS. The authors have been reluctant to adopt the Mooney viscosity as the sole measure of molecular size and toughness, since it fails to distinguish between linear and netted species. However, since no simple parameter

effect, and the properties were at a generally lower level than for the styrene-containing polymers.

The solubility and swell volume properties of the butadiene-styrene cold rubber latices differed substantially from their hot rubber counterparts (see Table I).

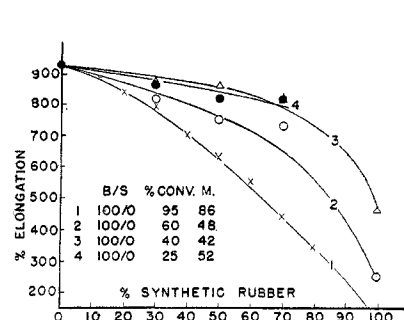


Figure 7. Effect of Conversion

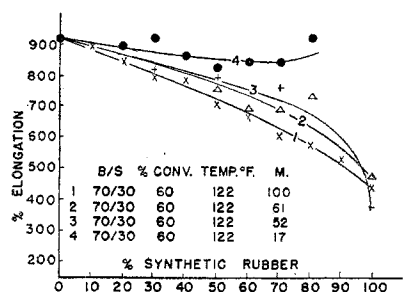


Figure 10. Effect of Mooney Viscosity

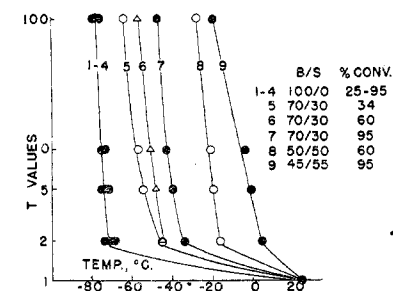


Figure 8. Effect of Conversion
122° F.

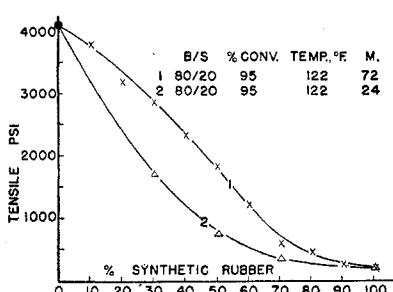


Figure 11. Effect of Mooney Viscosity

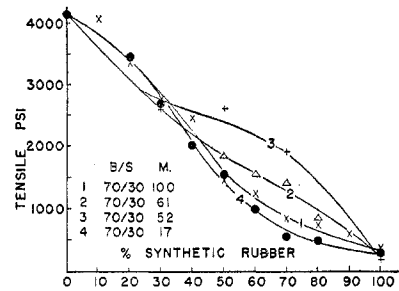


Figure 9. Effect of Mooney Viscosity

60% conversion, 122° F.

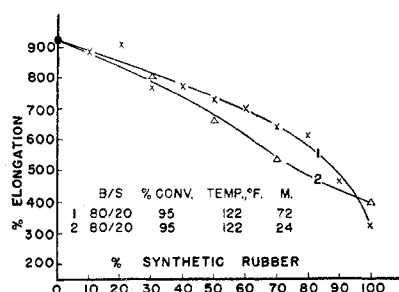


Figure 12. Effect of Mooney Viscosity

reflects accurately the gross changes in macrostructure which diene polymers are capable of undergoing, they have been compelled to describe such changes in terms of Mooney viscosity, and are reporting benzene solubility and swell volume of the gel (Table I) for what added information they give.

Effect of Polymerization Temperature. Only the polymerization temperature ranges used in current commercial production, 41° to 50° F. and 115° to 140° F., have been studied in the present investigation. The tensile strength and elongation results are summarized in Figures 1 to 4. Figures 1 and 2 depict the effect on the properties when medium or high Mooney 70-30 butadiene-styrene polymers prepared at the two temperatures and two conversion ranges, 60% and 85 to 90%, are blended with natural rubber. In these, the incorporation of up to about 30% of all of the synthetics decreased the tensile strengths about equally, the differences between the various rubbers becoming pronounced only at the higher synthetic contents. The superiority of the 70-30 butadiene-styrene cold rubber latices in both tensile and elongation is evident. Actually, the superiority of the cold rubber polymers in blends is greater for technological purposes than would be deduced from the graphs, because of their higher wet gel strength. The differences would be rendered somewhat more striking if comparisons were made on some basis representing the total amount of energy to break the sample, which is roughly approximated by the product of tensile and elongation (tensile product). Tensile product is not too widely accepted by the rubber technologist as a measure of stress-strain characteristics and, accordingly, these results have not been depicted graphically.

Figures 3 and 4 show similar data obtained on the hot and cold medium Mooney 60% conversion polybutadienes. In this case, lowering of the polymerization temperature did not have much

The effect of polymerization temperature on the low temperature stiffening properties of polymers of several styrene contents, evaluated in 100% synthetic compositions, is seen in Figure 5. Except for the cold rubber polybutadiene, no significant effects of reaction temperature can be discerned. The apparently anomalous behavior of the cold polybutadiene (curve 2) has been observed in various stocks by many observers, and is attributable to the readiness with which the polymer crystallizes at low temperatures.

Effect of Conversion. The medium conversion polymers exhibited higher tensile strength than the high conversion polymers as shown in Figures 1 and 6. This trend became more pronounced with the 70-30 butadiene-styrene polymers than with the polybutadiene rubbers.

The medium and low conversion polymers exhibited higher ultimate elongations than the high conversion polymers (Figures 2 and 7).

The degree of conversion had no effect on the low temperature properties of polybutadiene. The behavior in low temperature stiffening of the copolymers at varying conversions was accounted for by the variations in their combined styrene content (Table I and Figure 8).

Effect of Mooney Viscosity. With blends of natural rubber latex and hot synthetic rubber latex, the tensile strength was optimum for the polymers of medium Mooney viscosity, as shown in Figures 9 and 11. The ultimate elongation increased with decrease in Mooney viscosity with 70-30 butadiene-styrene polymers (Figure 10), whereas the reverse was true with 80-20 butadiene-styrene polymers up to, but not including, the 100% synthetic polymers (Figure 12). The apparent anomaly obtained with the 80-20 polymers, which is contrary to general experience

Table IV. Stress-Strain Data for Several Polymers and Blends over Range of Cures

Vulcaniza- tion, Minutes at 212° F.	Natural Rubber			70-30 Butadiene- Styrene Hot (Type V)			70-30 Butadiene- Styrene Cold (X-547)			50-50 Natural-Type V			50-50 Natural-X-547		
	Ulti- mate elonga- tion, %	Tensile, lb./sq. in.		Ulti- mate elonga- tion, %	Tensile, lb./sq. in.		Ulti- mate elonga- tion, %	Tensile, lb./sq. in.		Ulti- mate elonga- tion, %	Tensile, lb./sq. in.		Ulti- mate elonga- tion, %	Tensile, lb./sq. in.	
		At break	At 600%		At break	At 600%		At break	At 600%		At break	At 600%		At break	At 600%
0	980	3350	375	310	200		Beyond limit	675	100	720	775	440	920	900	190
5	980	3800	500	290	250		900	1050	200	690	1225	650	900	1225	250
10	875	3825	620	260	225		720	425	250	825	1100	900	840	1475	250
15	920	4150	600							820	1100	975	735	1975	400
20	980	4125	675	290	200		700	475	300	630	1100	900	840	1725	335
25	850	3850	650							620	1050	925			
30	900	3825	600	230	200					630	975	775			
40	865	3825	375							610	950	900			

Table V. Evaporated Sheets Compared with Milled Sheets

Synthetic Rubber	Evaporated Sheets						Milled Sheets		
	Natural Rubber, %	Synthetic Rubber, %	Ultimate elongation, %	Tensile, lb./sq. in.		Ultimate elongation, %	Tensile, lb./sq. in.		
				At break	At 600%		At break	At 600%	
	100	0	920	4150	600	710	3450	1700	
Polybutadiene	70	30	790	2425	600	630	2250	1850	
95% Conversion	50	50	710	1250	550	570	1300		
Hot, MS = 109	30	70	520	300		450	800		
	0	100	150	150		200	450		
Polybutadiene	70	30	860	2800	525	600	2200	2200	
60% Conversion	50	50	800	1560	450	520	1550		
Hot, MS = 108	30	70	690	550	350	390	850		
	0	100	250	180		220	500		
Polybutadiene	70	30	830	2350	450	650	2400	1650	
60% Conversion	50	50	760	1325	280	640	1750	1300	
Cold, MS = 40	30	70	700	565	300	500	700		
	0	100	400	175		300	300		
70-30 Butadiene-styrene	70	30	760	2275	790	650	2650	2000	
95% Conversion	50	50	690	1225	650	570	1600		
Hot	30	70	510	450		470	700		
Type V, MS = 65	0	100	290	250		230	280		
70-30 Butadiene-styrene	70	30	810	2300	500	690	3000	1675	
60% Conversion	50	50	750	1450	500	600	2200	2200	
Hot, MS = 75	30	70	770	625	425	520	1275		
	0	100	470	250		400	750		
70-30 Butadiene-styrene	70	30	870	2200	390	730	2650	750	
60% Conversion	50	50	735	1975	600	650	2075	1500	
Cold	30	70	745	1775	500	650	1700	1400	
X-547, MS = 50	0	100	900	1050	200	420	275		

tration of gel for so low a Mooney plasticity.

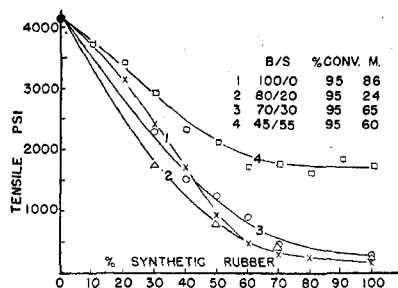
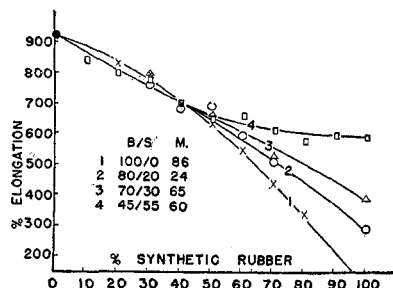
Effect of Monomer Ratio. When the butadiene-styrene ratio of the synthetic polymers (122° F. polymerization temperature and 95% conversion) was varied from 100-0 to 70-30 the tensile strength of natural rubber blends was approximately the same for each polymer. The 45-55 butadiene-styrene polymer, however, possessed much higher tensile strength—especially, as is shown in Figure 13, at the higher synthetic levels.

The ultimate elongation of blends of 50% or more synthetic content increased with increasing styrene content (Figure 14).

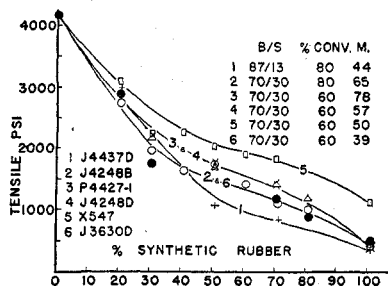
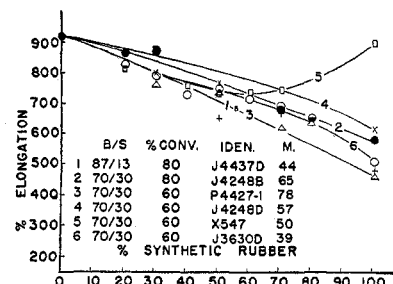
It is apparent that the tensile products of these polymers are more nearly an indication of their real value than either tensile strength or elongation considered separately.

The low temperature stiffening behavior of the 100% synthetic stocks followed the expected trend of increasing in stiffness with increasing styrene content (Figures 5 and 8).

Comparison of Evaporated Sheets with Milled Sheets. A few of the latices used in this study were examined in a typical gum formula over a range of natural-synthetic ratios. The stress-strain properties were in good agreement at medium and high natural rubber contents, but at the low natural rubber contents the tensile strengths of the milled sheets were often higher. The elongation of the evaporated and milled sheets were approximately the same. One exception to this was X-547, which, except at high natural rubber contents, gave higher tensile strengths and elongations in evaporated sheets than in milled sheets (Table V).

Figure 13. Monomer Ratio Varied
122° F.Figure 14. Monomer Ratio Varied
95% conversion, 122° F.

in this laboratory, may be due in part to the fact that they were made under quite different polymerization conditions; the low Mooney sample (Type VII, see Table I) had an unusually tight and high concen-

Figure 15. Commercial and Pilot
Plant Latices
50° F.Figure 16. Commercial and Pilot
Plant Latices
50° F.

Commercial Low Temperature Latices. Figures 15 and 16 depict stress-strain properties of several 50° F. latices which have been produced commercially or have been made available as samples to the trade.

The values for tensile strength of several of the 70-30 butadiene-styrene polymers were widely divergent, even though the latices had been made under conditions intended to give equivalent properties (Figure 15).

The ultimate elongations of all the cold rubbers were markedly higher than for their hot rubber counterparts (Figures 2, 4, 10, and 14).

The tensile products of the cold commercial latices were sufficiently high to make them extremely interesting for industrial utilization.

CONCLUSIONS

When tested in a single standardized procedure for cast latex films, the type of synthetic rubber latex employed in latex blends containing 70% or more natural rubber latex had little effect on the stress-strain properties of the mixture.

Cold rubber latices imparted higher stress-strain values to blends with natural rubber than did the corresponding hot rubber latices. The improvement was particularly noted on comparison of tensile product values.

Low conversion synthetic polymers produced higher stress-strain properties than high conversion polymers in blends with natural rubber, even though their tensile strengths in 100% synthetic stocks were approximately equal.

Optimum physical properties were obtained by use of blends with synthetic polymers of medium Mooney viscosity. It is believed that the appearance of an optimum Mooney viscosity is tied in with the necessity of having quite high molecular weight on the one hand, and, on the other, the ability of the particles to knit well, the latter in turn requiring a comparative freedom from tight gel.

Tensile product values increased with increasing styrene content in the synthetic polymer, but, correspondingly, the low temperature stiffening increased.

The physical properties of a natural rubber stock are far su-

perior to those of any of the synthetic rubber latices tested to date. Cold rubber latices now in production are an improvement over high temperature latices, for example, in wet gel strength, but do not approach natural rubber latex in stress-strain properties.

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LATICES OF FLEXIBLE SYNTHETIC POLYMERS

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During the past ten years there has been rapid progress in manufacture and use of flexible synthetic polymers. There are now nearly two hundred synthetic rubber, plastic, or plasticizable polymer latices commercially available in the United States, which have been grouped into fifteen classes according to reported polymer composition. General properties of synthetic latices are discussed, including the effect of particle size on stability and viscosity; characteristics of typical emulsifiers and dispersing and thickening agents and their influence on stability, coagulatability, and application; and wet and dry film strength properties of typical synthetic polymers. The adoption of soap requirement titration for control of synthetic latex compounds is recommended. Each class of polymer is discussed with reference to inherent polymer properties and how these are related to principal applications. Certain deficiencies in existing materials are pointed out. New products entering the market in-

clude water-dispersible polymers (for hydrosols), water-soluble polymers (polyelectrolytes and hydrophilic compounds), and plastisols (resins dispersed in plasticizers). The first two types are classified by composition, and general properties of each class are summarized.

ONE of the earliest uses of a flexible high polymer latex was as an adhesive. The value of certain plant saps as flexible and shock-resistant glues and lacquers was recognized very early in the development of manufacturing technology. The art of making articles by dipping rubber latex is more recent, but as early as 1736 de la Condamine (43) reported such a practice by the natives of Peru.

The first report of an attempt to make an artificial water dispersion of natural rubber was in 1836 (171). The art of polymerization was discovered about the same time (158, 172), but emulsion polymerization to a synthetic latex was not described until 1912 (27). Many commercial synthetic rubbers and plastics