

## Rubber Reinforcement by Starch Poly(ethylenimino Thiourethane)

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### Synopsis

Starch xanthates with degrees of substitution (D.S.) ranging from 0.08 to 0.58 were reacted with high or low molecular weight polyethylenimine (PEI, two of six times the stoichiometric amount) to form starch poly(ethylenimino thiourethanes). Aqueous thiourethane solutions were mixed with commercial styrene-butadiene and acrylonitrile-butadiene latices, and the solids were coprecipitated by adding 1M ZnSO<sub>4</sub> and 1N H<sub>2</sub>SO<sub>4</sub>. The master batches (filtered, dried at 70°C), having 15 to 50 parts of starch (equivalent) per 100 parts of rubber (phr), were masticated and compounded in a sulfur-accelerator recipe and press cured to yield vulcanizates of improved physical characteristics compared to control vulcanizates. About 0.22 D.S. produced best results. With this D.S. xanthate and a 3.5 ratio of 100,000 MW PEI, a 25 phr starch loading gave maximum tensile strength (2720 psi) in a styrene-butadiene vulcanizate. Hardness generally increased with increasing D.S. and starch contents. The thiourethane decreased compression set and increased abrasion resistance. The former was lowest and the latter highest at ca. 0.20 D.S. and 25 phr starch. Both set and abrasion were lowest with thiourethane prepared from xanthate made in a "Roto-feed" process rather than a "Ko-Kneader" operation. Rebound was not appreciably changed, and increase of volume swelling in water was small upon thiourethane incorporation.

### INTRODUCTION

Starch xanthate reacts with polyethylenimine (PEI) to yield a thiourethane containing 1.75 to 2.5 ethylenimine units per original xanthate group.<sup>1</sup> In an effort to discover potential applications for the product, the utility of starch poly(ethylenimino thiourethane) as a reinforcing agent in styrene-butadiene and butadiene-acrylonitrile rubbers was investigated.

In work previously reported, starch xanthate and elastomer were quantitatively coprecipitated by the addition of dilute zinc sulfate and sulfuric acid, simultaneously coagulating latex and forming zinc starch xanthate.<sup>2,3</sup> Since it was known that starch poly(ethyleniminothiourethane) could be precipitated from its alkaline aqueous media by the addition of dilute acid to pH 6.5 to 4.5,<sup>1</sup> the latex masterbatching technique appeared to be a feasible way of introducing the product into rubber stocks.

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in the equation of Figure 1. If the amount of PEI made  $x$  equal to 0, then there was 1 mole of ethylenimine to react with 1 mole of xanthate group, and the relationship was considered stoichiometric, or 1s. Excess PEI is expressed as a multiple of  $s$ . The reaction mixture was manually stirred and allowed to stand covered at room temperature. After a pre-determined reaction time dependent upon D.S. of the xanthate and the molecular weight of PEI,<sup>1</sup> the mixture was diluted with distilled water to yield an approximately 3% aqueous solution of starch poly(ethylenimino thiourethane).

### Coprecipitation

Each latex was added to a thiourethane solution while stirring with an air-driven stirrer. After an additional  $\frac{1}{2}$  hr of mixing, molar zinc sulfate and sufficient normal sulfuric acid were added dropwise, with continual agitation until the final serum had a pH of 6.0. The precipitate, containing 15, 25, 35, or 50 parts of starch (equivalent) per 100 parts rubber (phr) was easily filtered on a Buchner funnel and dried to approximately 2% moisture in a forced-draft oven at 70°C. Dried product crumbs were analyzed for moisture, ash, and zinc.<sup>8</sup>

In two separate experiments, SBR 2105 latex was added to an aqueous solution of gelatinized corn starch (25 phr starch) and to a quantity of aqueous HMW PEI corresponding to the amount used in a 3.5s ratio reaction of 0.24 D.S. xanthate. Coprecipitation was attempted as described above. In both experiments, filtration occurred only with difficulty.

### Processing of Coprecipitate

The dried crumb was passed through a roll mill as described by ASTM D15-66T at 0.010- to 0.025-in. clearance without banding to consolidate into sheets.<sup>7a</sup> The sheets were combined and banded on the mill, with the opening adjusted to give a small rolling bank. Milling was continued for a short time, and the master batch was then rolled, wrapped in aluminum foil, and stored until compounded.

The master batches were compounded according to a sulfur-accelerator recipe by incorporating 5.0 phr zinc oxide, 1.5 phr stearic acid, 2.0 phr sulfur, 1.5 phr benzothiazole-2-thiol, and 1.0 phr octylated diphenylamine antioxidant by mill mixing. Samples for determining tensile properties were press cured for 3, 5, or 10 min at 150°C in a slab mold.<sup>7a</sup> Specimens for impact resilience, durometer hardness ( $1.129 \times 0.5$  in.), compression set, and abrasion resistance testing were press cured 15 min in molds specified by their ASTM procedures.

### Physical Testing

An Instron (Model TT-C) was used for tensile testing by ASTM procedure D412-66.<sup>7b</sup> Tensile properties and cure times reported are those associated with the highest total energy needed to rupture. Volume swelling after 70

hr immersion in water at 23°C was measured by the ASTM D471-66 method<sup>7c</sup>; durometer hardness, by ASTM D2240-64T<sup>7d</sup>; and compression set, by ASTM D395-67, method B.<sup>7e</sup> Abrasion resistance of the vulcanizates was tested according to ASTM D394-59 (1965).<sup>7f</sup> It was expressed as a percentage of the abrasion resistance of vulcanizates from a commercial SBR-type 1606 master batch. Impact resilience (rebound) was determined according to the ASTM D2632-67 method.<sup>7g</sup>

Mooney curing characteristics were investigated with the large rotor at 125°C. Sufficient masterbatch was milled with SBR 1500 rubber to yield a specimen containing 1 part thiourethane functional group,  $-\text{C}(\text{S})\text{NCH}_2\text{-CH}_2(\text{-CH}_2\text{CH}_2\text{NH})_{0.75}$ , per 100 parts SBR stock. The thin sheet was compounded in the same recipe as were the master batches. Curing was performed according to the ASTM D1646-67 procedure.<sup>7h</sup>

## RESULTS AND DISCUSSION

### Product Preparation

Variables examined in the reaction of starch xanthate with PEI included: (1) D.S. of the starting xanthate, ranging from 0.08 to 0.58; (2) molecular weight of PEI; (3) ratios of HMW PEI (2, 3.5, and 6 times the stoichiometric amount based on the moles of xanthate group); and (4) preparation of xanthate by two continuous methods, Ko-Kneader or Roto-feed. Xanthate made by the Roto-feed process had greater viscosity than that prepared with the Ko-Kneader. By processing the Roto-feed material through a Cowles disperser, the viscosity decreased slightly. The reaction times (in hours) and viscosity (in centipoises) of the reaction solutions were dependent to the greatest degree on the first three variables.

The starch poly(ethylenimino thiourethane) solutions mixed well with SBR 2000, SBR 2105, or NBR 236 latices and coprecipitated nicely with latex on addition of  $\text{ZnSO}_4$  and  $\text{H}_2\text{SO}_4$ . The amount of sulfuric acid needed to reach a final serum pH of 6.0 increased with increasing D.S. of starch xanthate and increasing starch load, a reflection of the change in the amount of alkaline materials present. Most coprecipitates were easily filtered, and the yields of dry products indicated nearly quantitative coprecipitation over the entire range of variables given in Table I.

Mooney curing data revealed that the thiourethanes increased the vulcanization rate of SBR rubber stocks. Cure time was decreased from 58.5 min recorded for the blank (SBR 1500, scorch time = 33 min) to an average of about 10 min when the thiourethane was present. The lower D.S. materials produced the shortest cure time and shortest scorch time. Conversely, when the loading of derivative was made at a constant starch level (25 phr, which provides increased loading on the thiourethane functional group basis), a variance of cure time with D.S. did not show as the D.S. was increased. Resort to the technique of diluting SBR 2105 master batches with

TABLE I  
Preparation of Starch Poly(ethylenimino Thiourethane)  
and Coprecipitation with Rubber Latices

Latex	Xanthate <sup>a</sup>		Reaction		Masterbatch preparation				
			Ratio <sup>b</sup>	Time, hr	Starch <sup>c</sup>	Precipitant, ml <sup>d</sup>		Dry yield, g <sup>d</sup>	Run no.
	Prep.	D.S.				1M ZnSO <sub>4</sub>	1N H <sub>2</sub> SO <sub>4</sub>		
SBR 2105	K-K	0.08	3.5	18	25	30	50	128.7	1
	R-F	0.13	3.5	18	25	30	57	132	2
	K-K	0.14	3.5	18	25	10	87	126.5	3
	R-F	0.18	3.5	16	25	33	33	135.1	4
	K-K	0.22	3.5	12	15	17.5	55	123	5
	K-K	0.22	3.5	12	25	24.5	82	102	6
	K-K	0.22	3.5	12	35	28	112	140	7
	K-K	0.23	3.5	16	50	63	100	180	8
	K-K	0.24	2	16	25	27	40	124	9
	K-K	0.24	3.5 <sup>e</sup>	72	25	30	88	144	10
	K-K	0.24	6	16	25	30	100	142	11
	K-K	0.58	3.5	0.5	15	25	80	131	12
	K-K	0.53	3.5	0.5	25	25	125	147	13
	K-K	0.58	3.5 <sup>e</sup>	22	25	32	117	148	14
SBR 2000	K-K	0.24	3.5	16	25	30	200	169	15
	K-K	0.58	3.5	0.5	25	33	80	137	16
NBR 236	K-K	0.24	3.5	12	25	33	142	146	17
	K-K	0.24	3.5	12	25	25	68	133	18
	K-K	0.48	3.5	0.5	25	28	100	150	19

<sup>a</sup> K-K = Ko-Kneader, R-F = Roto-feed process, D.S. = degree of substitution.

<sup>b</sup> In moles of ethylenimino units per mole xanthate group.

<sup>c</sup> In grams of equivalent starch in the starch poly(ethylenimino thiourethane) per 100 g rubber solids.

<sup>d</sup> Based on 100 g total latex solids.

<sup>e</sup> Low molecular weight (3000) polyethylenimine was used; in all other runs, high molecular weight (100,000) polyethylenimine was used.

the SBR 1500 solid stock was made in the Mooney cure test because at constant thiourethane group loading (1 phr) in the straight SBR 2105 master batches, high cure rates, ca. 30 min, were found with other starch xanthate derivatives, and variation with D.S. was not discernible. The minimum viscosity dropped with increasing xanthate D.S. at all starch loading levels.

Cured rubbers were opaque (because of the zinc oxide added) and light tan in color. Without zinc oxide, the products were rather translucent. Preliminary experiments indicated that commonly used industrial dyes mixed well with the vulcanizates to yield evenly colored specimens.

### Product Tensile Strengths

The addition of starch poly(ethylenimino thiourethane) through latex masterbatching resulted in vulcanizates with improved physical proper-

TABLE II  
Properties of Starch Poly(ethyleneimine Thiourethane)-Reinforced Rubbers

Latex run no.	Master batch composition D.S. <sup>a</sup> Starch <sup>b</sup>	Mooney <sup>c</sup>				Tensile properties					Compression set, %	Abrasion resistance	Rebound	Volume change on water immersion, %
		Minimum viscosity, units	Scorch time, min	Cure time, min	Press cure time, min <sup>d</sup>	300% Modulus, psi	Ultimate elongation, %	Tensile strength, psi	Shore A hardness	Compression set, %				
SBR 2105	—	48	16.5	30	10	115	920	405	40	43.6	5	58	3.82	
1	0.08	62	5.6	8.3	3	1,560	365	1,940	70	23.2	19	55	—	
2	0.13	25	5.2	8.5	5	1,560	340	1,920	—	—	—	—	—	
3	0.14	25	—	—	3	1,440	430	2,320	66	21.0	162	56	3.91	
4	0.18	25	6.3	9.6	3	1,270	350	1,600	59	24.4	61	59	2.45	
5	0.22	15	5.9	10	10	2,160	360	2,720	68	29.9	70	58	4.14	
6	0.22	25	—	—	5	—	290	2,640	72	32.3	53	55	5.89	
7	0.22	35	6	10	5	—	260	2,400	88	21.5	13	49	8.93	
8	0.23	50	9.4	16.8	5	—	395	1,790	66	28.8	78	56	4.52	
9	0.24	25	6.8	10.6	3	1,270	300	2,130	72	22.1	116	57	2.20	
10	0.24	25	5.4	9	5	2,130	300	2,030	69	25.6	52	52	4.04	
11	0.24	25	8	14.2	5	—	235	2,000	70	25.8	64	58	4.38	
12	0.58	15	5.8	10.4	3	1,720	330	2,400	—	—	—	—	—	
13	0.53	25	6.5	10.5	3	1,600	410	2,400	78	26.0	169	53	4.43	
14	0.58	25	12	26.8	5	—	260	2,320	82	30.3	25	47	6.06	
15	0.58	35	13.3	27	5	—	240	2,370	82	30.3	25	47	6.06	
SBR 2000	—	—	—	—	—	300	630	925	—	—	—	—	—	
16	0.24	25	7.4	13.4	5	1,340	410	1,700	72	36.8	18	7.5	4.28	
17	0.58	25	7.2	11.2	5	1,140	420	1,580	74	43.7	16	11	7.98	
NBR 236	—	—	—	—	—	180	815	1,160	52	56.8	—	—	—	
18	0.24	25	15.4	34.8	15	2,240	300	2,240	84	60.8	93	10.4	10.88	
19	0.48	25	12.8	31	6	—	285	2,250	88	66.5	52	10.8	9.48	

<sup>a</sup> D.S. of the starch xanthate. See Table I for type of polyethyleneimine and amount used (s ratio).

<sup>b</sup> In grams of equivalent starch in the starch poly(ethyleneimine thiourethane) per 100 g rubber solids.

<sup>c</sup> Data for latex are for pure latex; compounded. Data for runs are for latex master batch blended with SBR 1500 solid stock as a diluent; blend compounded. See experimental section of text.

<sup>d</sup> For tensile property tests only. Other test vulcanizates cured 15 min.

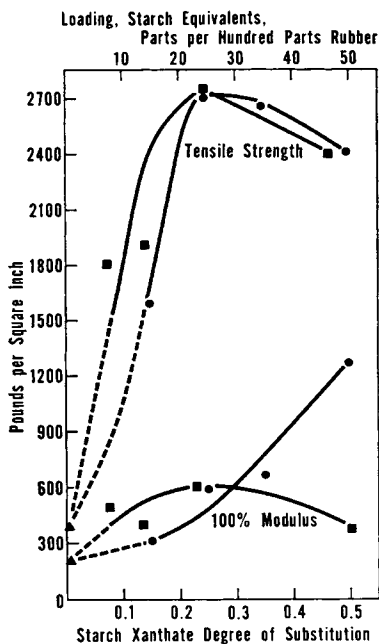


Fig. 2. Effect of starch xanthate D.S. and loading (as starch equivalent) on tensile properties of SBR 2105 vulcanizates containing starch poly(ethylenimino thiourethane): (●) loading of 0.22 D.S. derivative; (■) starch xanthate D.S. at 25-phr loading; (▲) control.

ties, compared to control vulcanizates containing all ingredients except thiourethane. Several factors affect the tensile strength. In equally loaded SBR 2105 vulcanizates, an intermediate D.S. of approximately 0.22 to 0.24 gave maximum reinforcement. When the thiourethane loading was varied at this D.S., a 25-phr loading appeared to be most effective (Fig. 2 and Table II).

The amount of PEI reacted with xanthate was also considered. A reactant ratio of 3.5 times the stoichiometric amount of PEI based on D.S. of the starting xanthate produced vulcanizates with highest tensile strengths. A lower ratio produced a thiourethane with poorer precipitation characteristics and yield, and ensuing vulcanizates showed lower tensile strength. A 6s ratio of PEI did not result in a vulcanizate possessing any greater tensile properties than one from a 3.5s ratio. The 3.5s level of polyimine represents nearly twice the amount present in the characterized, precipitated, crosslinked thiourethane.<sup>1</sup>

The use of LMW PEI yielded vulcanizates with slightly lower tensile strength than those prepared with the same ratio of HMW material. The former, however, possessed greatly enhanced abrasion resistance.

Specimens containing thiourethane synthesized from xanthate prepared by the Roto-feed continuous process appeared comparable in strength to vulcanizates containing thiourethane made from Ko-Kneader-prepared

material, even though the Roto-feed xanthate had a slightly lower D.S. No appreciable difference in tensile strength was noted between vulcanizates containing thiourethane prepared from Roto-feed xanthate which had or had not been processed through the Cowles disperser. The Roto-feed xanthate-thiourethane vulcanizates showed noticeably better abrasion resistance in comparison with Ko-Kneader xanthate-thiourethane vulcanizates.

To obtain preparations that would function as controls, the incorporation of gelatinized corn starch and PEI (separately) in SBR 2105 latex was attempted by masterbatching. No PEI appeared to be precipitated, though some adhered to the latex, and only minimal corn starch was incorporated. Both masterbatches yielded vulcanizates whose tensile strengths indicated that they would give no reinforcement in SBR 2105 rubber stocks.

### Other Product Characteristics

In addition to tensile strength, several physical and chemical properties of the vulcanizates were examined. Durometer hardness increased with increasing starch load and increasing D.S. Impact resilience and rebound decreased with increasing amounts of starch (Fig. 3). Compression set of the vulcanizates varied from 21.5% to 32.3%, with a plateau maximum seen at 25–35 phr starch loading. When thiourethane was the reinforcing

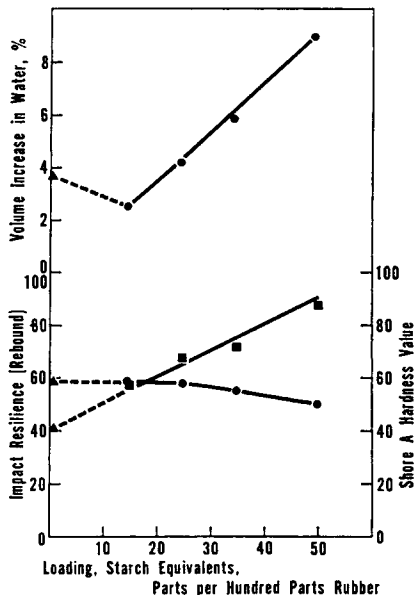


Fig. 3. Effect of starch poly(ethylenimino thiourethane) loading (as starch equivalent) on hardness, impact resilience (rebound), and volume swelling water of SBR 2105 vulcanizates: (●) read left ordinate; (■) read right ordinate; (▲) control; D.S. of parent xanthate = 0.22.



agent, abrasion resistance was always enhanced. The effect of thiourethane incorporation on the swelling of SBR 2105 rubbers in water is also shown in Figure 3. Swelling increased with increasing starch content, with a maximum of 9% change in volume appearing at  $\sim 50$  phr filler. In general, the properties exhibited by these vulcanizates are in an acceptable range for numerous rubber goods.

### Utility Potential Comparisons

The results obtained with 25-phr loading of starch (equivalent) were directly comparable to those reportedly obtained with a 25-phr loading of HAF carbon blacks.<sup>9</sup> At higher loadings (35–50 phr starch equivalent), tensile strengths compared with those given by equal loadings of SRF carbon black. When this thiourethane serves as a chemical reinforcing agent in styrene–butadiene rubber, vulcanizates formed have sufficient tensile strength to find commercial applications in tire components such as carcass, sidewalls, and inner liners; in footwear, belting, hose, heels, and soles; and in other mechanical rubber goods. However, on the basis of potential costs, starch thiourethanes would have to contribute unique properties in addition to their reinforcing effects to be competitive or practical.

With the SBR 2000 and NBR 236 latices, data were obtained only on master batches containing 25-phr starch equivalent. The thiourethane was prepared from HMW PEI and Ko-Kneader-prepared xanthate of 0.24 and 0.58 D.S. Tensile reinforcement in vulcanizates prepared from these coprecipitates was equivalent to that in vulcanizates with an equal loading of SRF black. Although the starch poly(ethylenimino thiourethane) did act as a reinforcing agent in these stocks on an absolute basis and on a percentage increase over control basis, it was not quite so effective in nitrile stocks at this loading as in the styrene type. These preliminary data perhaps indicate that the aliphatic hydrocarbon segments of the PEI are more compatible with a nonpolar styrene elastomer than with a more polar nitrile elastomer. Further experimentation with other polar rubber vulcanizates containing varying starch loadings and several D.S.'s in the thiourethane is needed before the scope of this reinforcing agent can be fully defined.

Since not all the nitrogen centers of the polyimine are involved in amide-type linkages in the thiourethane, there are free amine groups in the compounded rubbers to impart a cationic character. This character could be important in dye processes and could also contribute to possibilities for incorporating metallic elements in the rubbers. It is not necessary, in this regard, that zinc sulfate be used in precipitation as the sulfuric acid alone does it. The processes and products have been patented.<sup>10</sup>

Simpler diamines and LMW polyamines are also known to form thiourethanes from starch xanthate.<sup>11</sup> Although such derivatives were not precipitated from water by the pH drop method, they were so by ethanol addition. Those *ex situ*-precipitated, solid thiourethanes were incorporated (at comparable starch loadings) with precipitated latex solids in the mill-compounding step. The ensuing vulcanizates did not have significant en-

hanced physical properties; however, they did effect a cure time reduction to the 12- to 25-min range. Other starch xanthate (0.10–0.24 D.S.) derivatives in the Mooney viscosity test gave curing times as follows: (1) ex situ ethanol-precipitated starch xanthate, 25 min; (2) ex situ spray-dried starch xanthate, 27 min; (3) ex situ lyophilized starch poly(ethyleniminothiourethane), 30 min; (4) in situ zinc-precipitated starch xanthate, 33 min; (5) ex situ zinc-precipitated starch xanthate, 48 min; and (6) ex situ nitrite-precipitated starch xanthide, 57 min.

T. R. Naffziger, L. D. Miller, and W. L. Williams prepared the starch xanthates. Mabel Swanson performed analytical work. D. E. Smith (deceased) conducted Instron testing. R. A. Buchanan graciously provided technical advice and counsel throughout the investigation.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

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