

Filler Crosslinking by Diisocyanate in a Starch Xanthide-Reinforced Elastomer

R. J. DENNENBERG and E. B. BAGLEY, *Northern Regional Research
Laboratory, U.S. Department of Agriculture, Peoria, Illinois 61604*

Synopsis

Starch xanthide is an effective reinforcing agent for vulcanized elastomers. On prolonged exposure to water, however, the effectiveness of the starch xanthide as a reinforcing agent is greatly reduced. The xanthide crosslink density is too low to prevent plasticization of the filler by water. The introduction of additional crosslinks into the filler by treatment with diisocyanates increases the modulus of the filler, significantly improving the physical properties both of the dry vulcanizate and of the vulcanizate after a 70-hr water immersion test. Studies, which included the use of model systems, showed that the diisocyanates crosslinked the starch filler and did not introduce starch-rubber or rubber-rubber crosslinks. Several diisocyanates worked satisfactorily in the final vulcanizate.

INTRODUCTION

The coprecipitation of starch xanthide with a variety of elastomers, e.g., nitrile, styrene-butadiene (SBR), and natural rubber, has been reported by Buchanan et al.^{1,2} and by Stephens et al.³ The elastomer latex is initially dispersed in a starch xanthate solution at pH 11 or above. Acidification under oxidizing conditions brings about the simultaneous precipitation of elastomer and starch xanthide, the product being in the form of a powder composed of elastomer encased in starch xanthide.⁴

Powdered rubber is currently of great interest to the rubber industry for reasons outlined in the Delphi Report.⁵ These reasons include energy and labor savings in processing and convenience in handling. The coprecipitation method described here is particularly important since the powdered rubbers can readily be formed at low (~ 5 parts per hundred rubber by weight, phr) starch xanthide loadings.⁶

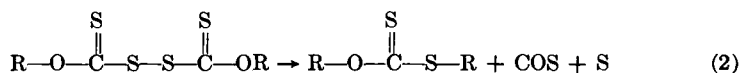
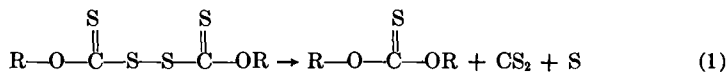
The vulcanizate prepared from this powdered rubber is composed of a rubber phase and a rigid starch xanthide phase. The starch xanthide can be in the form of rigid particles,⁴ or it can be distributed throughout the rubber (as seen from transmission electron micrographs) as a structured network.⁷ In either event, the rigid starch xanthide acts as an effective reinforcing agent so that, for example, an SBR vulcanizate reinforced with 40 phr starch xanthide will routinely exhibit ultimate tensile strengths of 2400 psi.

In the presence of water, the reinforcing efficiency of starch xanthide diminishes. Because the hydrophilic starch xanthide absorbs water and

becomes plasticized, the rigidity or modulus of the filler decreases. This decrease in filler modulus is reflected in a decrease in the vulcanizate modulus, as would be expected from the Kerner⁸ equation which relates the modulus of a filled system to the elastic constants of the matrix and filler. Tensile strength of the filled vulcanizate also decreases as the filler modulus declines during plasticization with water. There are several treatments, however, by which the starch xanthide reinforcement can be rendered water insensitive.

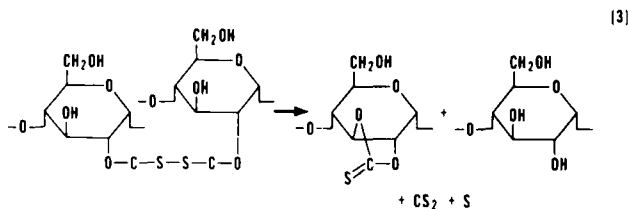
Water sensitivity of the reinforcing starch xanthide can be reduced if it has a high degree of substitution (D.S.). (A D.S. of 3 corresponds to complete substitution of the three hydroxyl groups on the starch anhydroglucose unit, AGU). Xanthides produced from high D.S. xanthates (>1.0) are less sensitive to water for two reasons: first, the number of hydroxyl groups in the AGU is reduced; and second, the degree of crosslinking of the starch through xanthide linkages is increased. Both effects would decrease water sensitivity.

Under pyrolytic conditions, that is, vulcanization temperatures, the xanthide yields either the thionocarbonate, CS₂ and elemental sulfur, or the xanthate ester, carbonyl sulfide and elemental sulfur, as shown in the following equations:



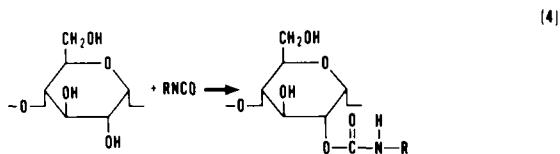
Recent kinetic studies by Trimnell et al.⁹ indicate that 70% of the xanthide is decomposed by these mechanisms within 10 min at 150°C and that 100% is decomposed within 10 min at 175°C. As a consequence, the liberated elemental sulfur is the source of the self-curing characteristics of high D.S. xanthide reinforcement as reported by Bagley and Dennenberg.¹⁰

When the starch filler is crosslinked, either through xanthide, xanthate ester, or thionocarbonate linkages, the water uptake of the filler is greatly restricted. Consequently, the properties of the reinforced vulcanizate become insensitive to water exposure to an extent dependent on the degree of crosslinking as described by Bagley and Dennenberg.¹⁰ The difficulty with this approach is that the xanthide crosslink has a tendency to form or rearrange to a cyclic thionocarbonate product as proposed by Stout et al.¹¹ Such a cyclic rearrangement eliminates a crosslink:



To avoid the problems inherent in this rearrangement to cyclic thionocarbonates, low-D.S. xanthates were used and crosslinking of the starch

xanthide by isocyanates was investigated. Isocyanates are known to react with starch to form a urethane linkage which should be stable at temperatures well above those of vulcanization.¹² Any of the hydroxyl groups can react as follows:



A comparative study of mono- and diisocyanates, therefore, could separate the effects of hydroxyl substitution and crosslinking in reducing the deterioration of physical properties of starch xanthide-reinforced vulcanizates on exposure to water. Treatment with diisocyanates results not only in reinforced elastomers of excellent dry strength (>3000 psi) but in materials little affected by water immersion. Similar wet and dry strength properties can be achieved by treatment with resorcinol-formaldehyde.¹³ Our work with isocyanates indicates clearly, however, that it is the crosslinking of the filler rather than mere substitution of hydroxyl groups that reduces water sensitivity.

EXPERIMENTAL PROCEDURES

Masterbatch Preparation

An unmodified corn starch (Globe pearl corn starch) was dispersed in distilled water at about a 10 wt-% level and gelatinized by the addition of 0.5 mole NaOH per mole of starch AGU. After this mixture was stirred to a homogeneous consistency, 0.1 mole CS₂ per mole starch AGU was added to give xanthate D.S. 0.05–0.07 by analysis. This mixture was stirred vigorously for 3 hr and stored at 5°C for a minimum of 24 hr before use. Final xanthate D.S. was determined by the acid titration method of Swanson.¹⁴ Rubber latex and sodium nitrite were added to the starch xanthate solution, 0.1 mole NaNO₂ normally being added to 1 mole starch AGU. Coprecipitation was brought about by the subsequent addition of 3.6*N* sulfuric acid which destabilized the latex and formed HNO₂ which, in turn, oxidatively crosslinked the starch xanthate to starch xanthide. The masterbatch was drained, washed with water, and dehydrated with ethanol. The ethanol was removed in a vacuum oven maintained at 70°C for 24 hr.

Isocyanate Reaction

To take full advantage of the powdered rubber form in which the starch xanthide-elastomer is coprecipitated, the isocyanate could have been added directly to the powder. The powder could have been directly injection molded and cured. Instead, the dry powder was mixed with isocyanate and catalyst and then converted to a continuous phase by milling. Pyridine (0.33 ml per 100 g masterbatch) served as catalyst for the reaction of isocyanate with the starch hydroxyl groups. The milled sample was

TABLE I
Recipe Used for Masterbatch Vulcanization

Ingredients	Parts by weight
SBR ^a	100
Starch (present as xanthide)	40
Stearic acid	1.5
Zinc oxide	5.0
Benzothiazyl disulfide	3.0
N-Phenyl-2-naphthylamine	1.25
Sulfur	2.0 ^b
Vulcanization temperature, 150°C	

^a SBR = styrene-butadiene rubber.

^b Sulfur levels were adjusted in some cures to increase elongation and reduce modulus

allowed to stand at room temperature for 24 hr before materials were added to make up the standard vulcanization recipe described below.

Compounding and Curing

Starch xanthide-reinforced rubber samples were compounded according to the recipe given in Table I. Mixing was done on a laboratory differential roll mill. Curing characteristics were determined with an oscillating disk rheometer operating with a rotor frequency of 100 cpm at an amplitude of $\pm 3^\circ$. Samples were cured to t_c' (90%) at a temperature of 150°C. Tensile specimens were cut according to ASTM D412, die C specifications.

Infrared Spectral Measurements

Infrared frequency and absorbance data were measured on a Perkin-Elmer 621 grating spectrophotometer equipped with a linear absorbance potentiometer.

RESULTS AND DISCUSSION

The vulcanizate properties of SBR 1500 reinforced with 40 phr starch xanthide (from xanthate D.S. 0.07) at varying levels of tolylene diisocyanate (TDI) addition are given in Table II. TDI level is tabulated as equivalents of isocyanate per equivalent of starch hydroxyl. The vulcanizate moduli, elongation, tensile strength, and set are given for dry specimens and for specimens from the same sample after a 70-hr water immersion test at room temperature.

Both the 100% and 300% modulus increase markedly with TDI addition, and tensile strength rises from 2400 to 3100 psi as the TDI level goes from zero to 0.1725 isocyanate equivalents/equivalent of starch hydroxyl group. The effect of increasing the diisocyanate concentration is quite spectacular. While the untreated control has a tensile which drops from 2400 psi (dry) to 450 psi (wet), the wet tensile at 0.1232 isocyanate:hydroxyl ratio is 2000 psi.

TABLE II
Physical Properties of SBR 1500, 40 phr Starch Xanthide with Added Isocyanate

Isocyanate equivs./starch hydroxyl equivs.	After 70-hr water immersion									
	Modulus, psi		Elongation at break, %	Tensile strength, psi	Set, %	Modulus, psi		Elongation at break, %	Tensile strength, psi	Set, %
	100%	300%				100%	300%			
0.0000	590	1670	425	2410	42	165	450	300	460	0
0.0316	680	2245	340	2530	40	310	—	285	945	10
0.0809	850	2670	300	2740	32	535	1710	315	1815	30
0.1232	965	2900	320	2980	35	660	2000	300	2000	35
0.1725	1,075	3100	300	3100	35	790	—	275	2110	38
				Tolylene diisocyanate						
0.0158	575	1610	430	2470	43	160	440	325	510	3
0.0405	525	1495	—	2715	50	170	425	365	615	2
0.0616	525	1470	450	2360	40	175	435	335	525	3
0.0863	530	1510	480	2625	48	180	445	345	565	5
				Phenyl isocyanate						

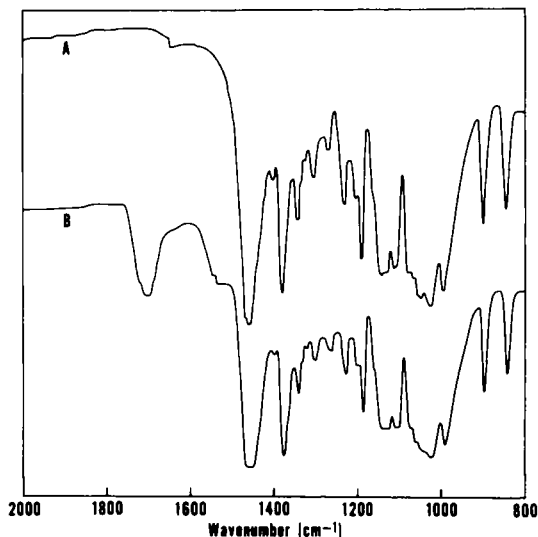


Fig. 1. Infrared spectra of methyl- α -D-glucopyranoside (A, Nujol); methyl- α -D-glucopyranoside reacted with hexamethylene diisocyanate (B, Nujol).

Elongation at break decreases somewhat in the dry vulcanizate with increasing TDI concentration, but for the wet vulcanizate, elongation at break is approximately constant.

The monoisocyanate-treated sample of Table II behaves quite differently. To a good approximation, the physical properties of the dry vulcanizate are independent of the amount of phenyl isocyanate added. Physical properties of the vulcanizate after the 70-hr water immersion test are essentially constant and approximately the same as the control (i.e., with zero isocyanate added, and after 70-hr water immersion test). At the same isocyanate/hydroxyl equivalent ratio (about 0.08), the difference between the wet vulcanizate properties of the mono- and diisocyanate-treated examples are well illustrated by their respective tensiles, 565 and 1800 psi. Superior vulcanizate properties result from urethane crosslinks (via diisocyanates) but not from simple urethane capping of the starch hydroxyl groups (via monisocyanates).

To confirm that increases in vulcanizate modulus were brought about by crosslinking the starch xanthide rather than by the formation of a starch-rubber linkage or rubber-rubber linkage, several model reactions were studied. Methyl- α -D-glucopyranoside, a model for starch, and hexamethylene diisocyanate (HMDI) were refluxed in toluene for 2 hr. The infrared spectrum of the reaction products (Fig. 1, B) shows absorption at 1705 cm^{-1} (carbonyl stretch) and 1540 cm^{-1} (N-H bending) consistent with formation of the methyl- α -D-glucopyranoside carbamate. In addition, the band at 2280 cm^{-1} , characteristic of isocyanate, was no longer present.

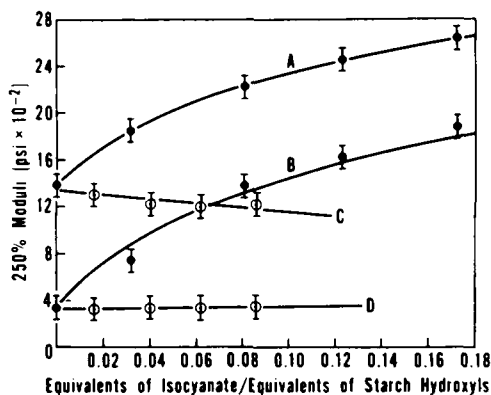


Fig. 2. Vulcanizate moduli vs. isocyanate addition for a sample of styrene-butadiene rubber (SBR) 1500, 40 phr starch xanthide. Curves A and B represent the addition of tolylene diisocyanate (TDI); curve B is after 70-hr H₂O immersion; curves C and D represent the addition of PhNCO; curve D is after 70-hr H₂O immersion.

A mixture of SBR 1502 and HMDI in refluxing toluene was followed by observing the NCO infrared absorption band at 2280 cm⁻¹. Because the intensity of the band remained constant, no isocyanate reaction occurred with the rubber.

Table III gives the physical properties of a carbon black-filled sample compounded with (1) pyridine and (2) pyridine-TDI. Evidently, addition of TDI does not increase the modulus of the vulcanizate. In fact, the modulus is lowered slightly by addition of TDI, an effect which indicates that plasticization of the rubber by TDI is occurring rather than a crosslinking reaction between the diisocyanate and the rubber contrary to the proposal by Mills.¹⁵

These model reactions show that under our experimental conditions, the starch xanthide filler is crosslinked by reaction with diisocyanate and that consequent changes in vulcanizate properties with diisocyanate are due to changes in the starch xanthide chemical structure.

Returning to the samples treated with TDI (Table II), we can now infer that the starch is unable to swell under the influence of water because of the crosslinks induced by the reaction of TDI and starch. The monoisocyanates induce no such restrictions, and the uncrosslinked starch is able to swell; its modulus drops, and, in turn, the vulcanizate modulus falls. Figure 2 gives the 250% moduli of a 40 phr starch xanthide sample as a function of isocyanate added. Curves A and B show the addition of TDI, dry and after 70-hr water immersion, respectively. Curves C and D show the addition of PhNCO, dry and after 70-hr water immersion, respectively. TDI gives substantial improvement to both dry moduli and 70-hr water immersion moduli.

In Figure 3, the ratio of wet/dry moduli at 250% elongation is plotted as a function of added isocyanate. The optimum addition of diisocyanate for

TABLE III
Physical Properties of SBR 1500, 48 phr SRF Black

100 g Masterbatch additives	Modulus, psi		Elongation at break, %	Tensile strength, psi	Set, %	After 70-hr water immersion				
	100%	300%				Modulus, psi	Elongation at break, %	Tensile strength, psi	Set, %	
					100%	300%				
Control	305	1450	520	2740	10	300	1455	440	2280	4
0.33 ml Pyridine	350	1780	405	2500						
0.50 ml Pyridine	430	2030	350	2430	5	410	2000	350	2335	
0.33 ml Pyridine + TDI ^a	365	1600	425	2115						
0.50 ml Pyridine + TDI ^a	390	1745	400	2205	6	400	1805	445	2425	11

^a Quantity of TDI used corresponded to 0.1232 equivalent of isocyanate/equivalent of starch hydroxyls, if SRF Black were replaced by starch.

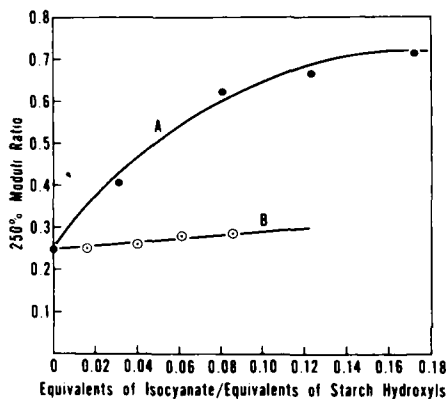


Fig. 3. Ratio of vulcanizate moduli after 70-hr H₂O immersion and dry vs. isocyanate addition for a sample of SBR 1500, 40 phr starch xanthide. Curve A represents the addition of TDI; curve B represents the addition of PhNCO.

the reduction of water sensitivity and cost would be enough to crosslink about 8% of the starch hydroxyls.

A number of theories have been developed to describe the reinforcing action of spherical filler particles, the Kerner⁸ equation being the most elaborate and versatile of these¹⁶:

$$G = G_1 \left[\frac{\frac{\phi_2 G_2}{(7 - 5 \nu_1) G_1 + (8 - 10 \nu_1) G_2} + \frac{\phi_1}{15(1 - \nu_1)}}{\frac{\phi_2 G_1}{(7 - 5 \nu_1) G_1 + (8 - 10 \nu_1) G_2} + \frac{\phi_1}{15(1 - \nu_1)}} \right] \quad (5)$$

where G is the shear modulus of the two-phase system while G_1 and G_2 are the respective shear moduli of the continuous phase and the dispersed phase; the volume fraction of the continuous phase is ϕ_1 , whereas that of the filler is ϕ_2 ; Poisson's ratio of the material in the continuous phase is ν_1 .

To our system, eq. (5) is applicable only qualitatively. However, it permits an estimate of the modulus of the xanthide filler to be made. When the Kerner equation is applied to our data, little difference between the modulus of the starch xanthide and the isocyanate-treated starch xanthide was apparent at low strain values. This result was surprising, but is supported by Figure 4, where the apparent modulus from stress relaxation studies is plotted versus strain (λ) for two loading levels, with and without TDI treatment. The strain is given by $\lambda = (l/l_0)$ where l_0 is the original length and l is the deformed length.

Clearly the apparent moduli are the same for both the untreated and TDI-treated starch xanthide systems as λ^{-1} approaches 1. Thus TDI treatment affects the filler modulus little at low strain values.

As strain increases, the difference between TDI-treated and untreated starch xanthide becomes evident, and the difference increases substantially as the breaking strain is approached. This unexpected result suggests

TABLE IV
Physical Properties of SBR 1500, 40 phr Starch Xanthide with Several Diisocyanates^a

Isocyanate equivs./starch hydroxyl equivs.	Modulus, psi		Elongation at break, %	Tensile strength, psi	Modulus, psi		Elongation at break, %	Tensile strength, psi
	After 70-hr water immersion							
	100%	300%			100%	300%		
Control	605	1725	345	2015	150	—	240	370
Control + pyridine	550	1650	375	2140	150	—	260	360
0.1232 TDI	910	—	245	2345	1320	—	220	1480
0.1232 TDI ^b	740	2140	395	2700	500	1380	300	1380
0.1232 HMDI ^b	680	2170	340	2440	445	—	260	1270
0.1232 BPDI ^b	840	2340	345	2660	740	1880	345	2110

^a All isocyanate reactions were catalyzed with 0.33 ml pyridine/100 g masterbatch.

^b Cured with 0.33 g sulfur/100 g masterbatch; HMDI = hexamethylene diisocyanate; BPDI = 3,3'-dimethoxy-4,4'-biphenyl diisocyanate.

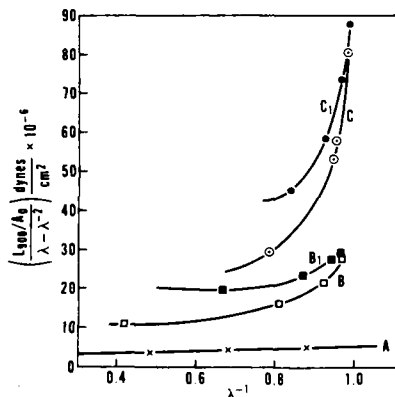


Fig. 4. Mooney-Rivlin plot of 900-sec apparent modulus at 0 phr (A), 30 phr (B), and 60 phr (C) starch xanthide SBR 1502. Included are plots with 11 phr TDI added to each starch xanthide level (B-1 and C-1).

that TDI crosslinking has little effect on filler modulus until the strain levels become large. At large strain levels, TDI crosslinking becomes significant because it gives higher tensile values and increased moduli (Table II).

Table IV shows the effects of various diisocyanates added to 40 phr starch xanthide-reinforced SBR 1500 on vulcanizate physical properties. TDI, HMDI, and 3,3'-dimethoxy-4,4'-biphenyl diisocyanate (BPDI) are compared with a control (zero diisocyanate added) and a control plus 0.33 ml pyridine/100 g masterbatch as catalyst. After 70-hr water immersion, the sample treated with BPDI possesses excellent strength. Increased crosslinking may be due either to greater reactivity of BPDI or to less loss of reactant through volatilization during processing with the higher molecular weight diisocyanate than with TDI or HMDI.

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.

References

1. R. A. Buchanan, O. E. Weislogel, C. R. Russell, and C. E. Rist, *Ind. Eng. Chem., Prod. Res. Develop.*, **7**, 155 (1968).
2. R. A. Buchanan, H. C. Katz, C. R. Russell, and C. E. Rist, *Rubber J.*, **153**, 28 (1971).
3. H. L. Stephens, R. J. Murphy, and T. F. Reed, *Rubber World*, **161**, 77 (1969).
4. T. P. Abbott, W. M. Doane, and C. R. Russell, *Rubber Age*, **105**, (8) 43 (1973).
5. E. I. du Pont de Nemours and Co., *Delphi Forecast of Future Rubber Processing*, 6 (1967).
6. T. P. Abbott, C. James, W. M. Doane, and C. R. Russell, *Rubber World*, **169**, No. 6, 40, 1974.
7. E. B. Bagley and R. E. Dixon, *Trans. Soc. Rheol.*, **18**:3, 371 (1974).
8. E. H. Kerner, *Proc. Phys. Soc. London*, **69B**, 808 (1956).

9. D. Trimnell, B. S. Shasha, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **17**, 1607 (1973).
10. E. B. Bagley and R. J. Dennenberg, *Rubber Age*, **105**, (6) 41 (1973).
11. E. I. Stout, W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *Carbohydr. Res.*, **3**, 354 (1967).
12. J. H. Saunders and K. C. Frisch, *Polyurethanes*, Part II, Wiley-Interscience, New York, 1964, p. 668.
13. R. A. Buchanan, W. M. Doane, C. R. Russell, and W. F. Kwolek, paper presented 105th Rubber Division ACS Meeting, Toronto, Canada, May 6-10, 1974.
14. C. L. Swanson, Northern Regional Research Laboratory, unpublished results, 1964.
15. G. S. Mills, U.S. Pat. 2,906,718 (1956).
16. L. E. Nielsen, *J. Compos. Mater.*, **1**, 100 (1967).

Received July 17, 1974

Revised August 13, 1974