Table V. Performance of Chemigum SL in Tread Stocks

Rubber Stock	Dynamic Properties Dynamic modulus, kg./sq. cm.	Internal friction, kilopoises	Dynamic resilience, %	Relative heat generation
Chemigum SL	84.4	15.9	63.3	65
Chemigum SL plus 30 parts MPC black	196.0	49.1	54.5	128
Natural rubber tread	91.8	35.1	39.6	109
Oil-extended GR-S tread	116.0	59.3	29.0	141

APPLICATIONS

A great deal of work has been done in developing uses for elastomeric polyester-urethanes. Potential uses include wear resistant veneers on pneumatic tires as shown in Figure 9. Solid tires (Figure 10) have given outstanding performance in the plant on Goodyear electric lift trucks. A high degree of cut resistance is exhibited. Soles, heels, belt surfaces, and floorings may be protected by localized application of wear resistant Chemigum SL.

Table VI. Oxygen Absorption

Time, Hours	O_2 Absorbed, Ml./Gram of Polymer at 100° C. Natural rubber tread stock[a]	GR-S tread stock[a]	Chemigum SL
0	0	0	0
40	10	4	0.01
80	27	10	0.02
120	58	14	0.04
160	92	18	0.08
240	..	27	0.11
320	..	36	0.13
450	..	..	0.16
910	..	..	0.25

[a] Natural rubber and GR-S tread stocks contain 45 parts of carbon black per 100 parts of rubber and 1.25 parts of *N*-phenyl-β-naphthylamine as antioxidant.

Since the raw gum stocks are readily soluble in standard solvents, they lend themselves to cement compounding and find use as protective coating on rubber, plastics, and fabrics. A solution of Chemigum SL sprayed on the surface of rubber or plastic gives an adherent, flexible, and scuff-resistant coating that is at the same time resistant to sunlight, ozone, and general weathering.

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Substituted Silyl Derivatives of Starch

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THE production of a large number of organosilicon compounds in recent years with substituent groups that readily react with aliphatic hydroxyls (*3*) makes possible the production of a new and interesting class of starch derivatives. These polymers may be soluble in water, soluble in organic solvents, or under certain conditions, may be, or may become insoluble in all neutral solvents.

The substituted silanes may have from one to four reactive groups per silicon atom. Those found to be more reactive with starch hydroxyls so as to form a silicon-oxygen-carbon (Si-O-C) linkage with the carbohydrate contain groups such as chloro, amino, and the lower alkoxyls, particularly methoxyl, ethoxyl, *n*-propoxyl, and *n*-butoxyl. Of these, the chloro group appears to be the most reactive and the *n*-butoxyl group the least. Of much less reactivity are *tert*-butoxyl and the higher alkoxyl groups. In each of these cases where reaction does occur, it is an exchange reaction wherein the hydrogen of the carbohydrate hydroxyl combines with a substituent group on the silicon, forming hydrochloric acid, ammonia, or alcohol, as the case may be, and creating an S-O-C linkage. Alkyl or aryl groups attached directly to silicon are exceptionally unreactive.

Starch molecules have, on the average, three free hydroxyls per glucopyranose unit. Accordingly, when the carbohydrate is treated with a reactive substituted silane, as many as three substituent groups may be introduced per glucopyranose unit. When the substituted silane is monofunctional, those starch derivatives which have one or more substituted silyl groups per glucopyranose unit [D.S. (degree of substitution), or higher] are, in general, soluble in organic solvents such as the hydrocarbons or halohydrocarbons, while products having very low degrees of substitution are either water-soluble or dispersible in water by heating. However, when the silane derivative is bi- or polyfunctional, such as, for example, diphenyldichlorosilane, then the starch molecules may become cross-linked, probably by the formation of a substituted silylene bridge, C—O—Si—O—C, between adjacent carbohydrate chains, or possibly by a siloxane or polysiloxane cross linkage, $C—(OSi—O—Si)_n—O—C$. These cross-linked derivatives, even at relatively low degrees of substitution, are insoluble in all neutral solvents. When the substituted silane is essentially monofunctional, such as diphenyl-*n*-butoxychlorosilane, but contains a potentially functional group—such as the *n*-butoxyl which may be induced to react after the chloro group has reacted—then a solvent-soluble derivative usually forms in the primary reaction and with heating and time develops into a cross-linked insoluble resin.

Each type of starch derivative containing silicon is of potential industrial importance. The water-dispersible type shows altered colloidal properties compared to untreated starch, which may enhance its use in the many industrial applications for which this water dispersible colloid is used. The higher D.S., solvent-soluble derivatives are unique in that they are dispersible in hydrocarbons such as hexane and xylene. Common derivatives of starch such as esters and ethers—e.g., starch triacetate and trimethyl starch—are not soluble in hydrocarbon solvents and accordingly the production of substituted silyl derivatives of starch may extend the use of starch to applications that employ these solvents. When the substituent groups in an organosilane reagent are relatively small, such as in trimethylchlorosilane, the resulting starch derivative (2 D.S.) is originally soluble in xylene but develops insolubility in this solvent on exposure to water or methanol; the starch molecules are freed, become water-soluble, and stain blue with iodine. This deposition of starch from solution in an organic solvent may find industrial application. Phenyl-, or even *tert*-butoxyl, radicals in the silyl group greatly improve the stability of the derivative. The insoluble starch derivatives of the second group belong to the industrially important class of thermoplastic resins when the D.S. is in higher ranges; those that are originally soluble in organic solvents but become insoluble in all neutral solvents with heat and time, through formation of cross linkages, belong to an equally important class of thermosetting resins.

Examples are given in the following experimental section of reactions for the production of several of the starch derivatives studied in this work; the properties of these products are also described.

The soluble derivatives made from native starch, in general, dissolve slowly and with difficulty to form very viscous solutions. Viscosity of these may be reduced and the rheological properties of the resinous products may be altered by the use of starch which has been treated with acid to reduce its molecular weight. This procedure is also outlined in the experimental section.

REACTION OF STARCH WITH SUBSTITUTED SILANES

Silanes Having Only One Functional Group. TRIMETHYLCHLOROSILANE. Nine grams of starch were dispersed in 200 ml. of formamide by heating the mixture to 110° C. Then about 175 ml. of formamide were removed by distillation under reduced pressure and the resultant anhydrous gel was diluted with 40 ml. of anhydrous pyridine. After cooling to 20° C., a solution of 0.20 mole of trimethylchlorosilane (Dow-Corning) in 100 ml. of hexane was added slowly under anhydrous conditions maintaining the reaction temperature at 20° C. After 2 hours, methanol was added in excess and precipitated the starch derivative. The product formed a clear viscous solution in xylene, and analysis for silicon indicated approximately two trimethylsilyl groups per glucopyranose unit. It was insoluble in water but rapidly decomposed in water to give a positive iodine test for starch. It was observed, furthermore, that clear solutions of the derivative in xylene deposited a blue, iodine staining starch when methanol or aqueous methanol was present.

Silanes Having One Highly Reactive Group and One Group of Less Reactivity. DIPHENYL-*n*-BUTOXYCHLOROSILANE. The reagent was prepared by adding slowly with agitation an anhydrous solution containing 29.6 grams of *n*-butyl alcohol in 100 ml. of xylene to a solution of 101 grams of redistilled, commercial diphenyldichlorosilane in 100 ml. of xylene at 2° C. The reaction mixture was distilled at a reduced pressure of 1 mm. of mercury, and the fraction collected at 110° to 160° C. was fractionally redistilled through a 36-inch column packed with glass helices. A fraction weighing 40 grams was collected at 128° C. and 0.5 mm. of mercury.

Calculated for diphenyl-*n*-butoxychlorosilane: Chlorine, 12.2%; silicon, 9.63%. Found: Chlorine, 12.4%; silicon 9.75%.

Corn starch was hydrolyzed with hydrochloric acid until a neutralized and purified sample showed an intrinsic viscosity of 0.2 in *N* potassium hydroxide at 35° C. (*1*). An anhydrous dispersion of 4.1 grams of this starch was prepared in 20 ml. of formamide by adding the dried starch to an excess of formamide and distilling at reduced pressure to eliminate the water. To this anhydrous dispersion, a solution of 14.5 grams of the above silane derivative in 50 ml. of xylene was added at 2° C. After a reaction time of 2 hours, with the temperature slowly rising to 30° C., the product was precipitated by the addition of 500 ml. of methanol. Purification was accomplished by several extractions with fresh methanol. The air-dried product weighed 14.1 grams and was completely soluble in xylene, ether, chloroform, and dibutyl phthalate. The silicon content of 8.12% is equivalent to a starch derivative containing approximately 1.8 diphenyl-*n*-butoxysilyl groups per glucose unit (D.S. = 1.8).

Films were cast from solutions of the starch derivative in xylene that contained 10 to 20% dibutyl phthalate—based on starch product. These were heated at 150° C. After 1 hour the films were found to be insoluble in xylene, as well as in water, and alcohol. Development of insolubility in xylene on heating indicates that the *n*-butoxyl group attached to the substituted silyl radical had been induced to react, probably with other carbohydrate hydroxyls, thereby forming an insoluble cross-linked polymer. However, in the case of this and other cross-linked starch derivatives to follow, the possibility exists that the cross linkage is a siloxane linkage formed by the action of a hydrolyzed (or diphenyl hydroxysilyl) group on one starch molecule with a substituted silyl group or with a hydrolyzed group on another starch molecule.

DI-*tert*-BUTOXYMETHOXYCHLOROSILANE. The reagent was prepared by reacting one equivalent of methanol with one equivalent of di-*tert*-butoxydichlorosilane. The starch used was acid hydrolyzed to a level corresponding to an intrinsic viscosity of 0.2 in *N* potassium hydroxide at 35° C. An anhydrous dispersion of 8.1 grams of the starch in 25 ml. of formamide was prepared to which was added 27 grams of the substituted silane in 25 ml. of xylene at 5° C. After 2 hours the reaction mixture was concentrated under reduced pressure to 50 ml. and the starch product was precipitated by adding methanol. The gummy mass was purified by washing in methanol, 50% aqueous methanol, and finally water. The dried product weighed 8.3 grams and contained 9.65% silicon (D.S. = 1.82). It was completely soluble in xylene, hexane, chloroform, and *n*-butyl alcohol but insoluble in water and methanol.

The reaction was repeated using an anhydrous dispersion of otherwise untreated corn starch. This product contained 10.4% silicon but dissolved very slowly in xylene to form a thick gellike mass.

DI-*tert*-BUTOXY-*n*-BUTOXYCHLOROSILANE. This reagent was prepared by slowly adding 0.05 mole of *n*-butyl alcohol, 10 grams of pyridine, and 15 ml. of xylene to an agitated solution of 0.05 mole of di-*tert*-butoxydichlorosilane in 25 ml. of xylene at 2° C. After warming to room temperature the above mixture was slowly added to an agitated, anhydrous dispersion of 4.1 grams starch (intrinsic viscosity 0.2) in 20 ml. of formamide. After 3 hours a volume of methanol equal to that of the reaction mixture was added, whereupon a sirup separated. This sirup was diluted with xylene and the resultant solution repeatedly extracted with water. Concentration of the xylene layer to approximately 25 grams total weight gave a solution of the starch derivative containing 10 grams of dry substance which contained 8.47% silicon.

After the addition of 18% tricresyl phosphate (as plasticizer) to the starch product, films were cast from the xylene solution. These films were heated for 1 hour at 150° C., whereupon insolubility in all neutral solvents developed.

Silanes Having at Least Two Highly Reactive Groups. DIPHENYLDICHLOROSILANE. A practical grade of this reagent (Dow-Corning) was purified by fractional distillation. Boiling point, 114° to 116° at 2 mm. of mercury pressure. Chlorine: calculated, 28.0%; found, 27.9%.

Starch was pretreated with hydrochloric acid to reduce its intrinsic viscosity to 0.2 in N potassium hydroxide at 35° C., and an anhydrous dispersion of 4.10 grams of the starch was prepared in 20 ml. of formamide and 8 ml. of pyridine. This was stirred into 50 ml. of xylene to which was slowly added 0.0375 mole of the substituted silane. After 2.5 hours' additional stirring at 30° C., an insoluble product was isolated by filtration, followed by washing in xylene, hexane, and methanol.

The dried product contained 9.4% silicon, equivalent to approximately 1.5 diphenylsilyl groups per glucopyranose residue, but no chlorine. The product was insoluble in water and alcohol but swelled slightly in xylene and was apparently, therefore, a cross-linked, thermoplastic, diphenylsilyl starch polymer. When shaken in 20% acetic acid at room temperature a positive starch-iodine test developed after about 24 hours.

DI-*tert*-BUTOXYDIAMINOSILANE. One mole (170 grams) of silicon tetrachloride in 500 ml. of hexane was added slowly to an agitated solution of 160 grams of anhydrous pyridine in 300 ml. of hexane. At 5° C. a solution of 2 moles (150 grams) of anhydrous *tert*-butyl alcohol in 200 ml. of hexane was added slowly, after which the reaction mixture was saturated with anhydrous ammonia. The reaction mixture was protected throughout from atmospheric moisture.

The liquor was filtered to remove ammonium chloride and distilled at a pressure of 10 mm. of mercury. Fractional distillation at this pressure gave 50 grams of product boiling at 70° C. that contained 12.8% nitrogen and 13.4% silicon. Calculated, nitrogen, 13.6%; silicon, 13.6%.

An anhydrous dispersion of 8.1 grams of starch in 30 ml. of formamide was prepared to which was added at 35° C., 15 grams (0.075 mole) of the silane. A vigorous reaction occurred with liberation of ammonia. The reaction was continued for 180 minutes raising the temperature to 60° C. during which a total of 2.34 moles of ammonia was liberated per glucose residue. The insoluble product was filtered, washed in water and in methanol, and then dried. A yield of 16.4 grams of the insoluble starch polymer was obtained which contained 10.6% silicon but no nitrogen. This would correspond to a cross-linked starch polymer containing 1.3 di-*tert*-butoxysilyl cross linkages per glucopyranose residue.

The product gave a negative starch-iodine test in cold water and after boiling in water but gave a positive test after boiling in 2 N hydrochloric acid or sodium hydroxide and neutralizing.

To demonstrate further the formation of substituted silyl cross linkages between glucose units, 9.70 grams (0.05 mole) of methyl α-D-glucoside in 10 ml. of anhydrous pyridine was reacted with 20.6 grams (0.10 mole) of di-*tert*-butoxydiaminosilane for 2 hours raising the temperature to 40° C. During this time 0.197 mole of ammonia was liberated. A benzene solution of the reaction product was filtered and evaporated to dryness under reduced pressure. This product contained 11.7% silicon and had an average molecular weight of 3090.

These results are equivalent to those for a polymer in which there are approximately six methyl glucoside units and two di-*tert*-butoxysilyl cross linkages per glucose residue.

DI-*tert*-BUTOXYDICHLOROSILANE. This silane was prepared from silicon tetrachloride and *tert*-butyl alcohol according to the method of Miner, Bryan, Holysz, and Pedlow (*2*). In distilling the product a fraction was obtained on which was found, chlorine, 28.5%; silicon, 11.4%; calculated, chlorine, 29.0%; silicon, 11.4%. The boiling point of this fraction was 50° to 55° C. at 5 to 7 mm. of mercury pressure. The yield was 70%.

An anhydrous dispersion of 4.1 grams of starch was prepared in formamide. This was diluted with 8.0 grams of anhydrous pyridine and 50 ml. of xylene. Then 0.0375 mole of the substituted silane was slowly added. After 2.5 hours at 30° C., the insoluble product was filtered, washed with xylene, hexane, and methanol, and then dried. This product contained 7.9% silicon and only traces of chlorides. The results are equivalent to those for a starch polymer containing almost one di-*tert*-butoxysilyl cross linkage per glucose residue.

This product was insoluble in water, methanol, and xylene and gave a negative starch-iodine test after boiling in water. A positive iodine test for starch did develop after 12 hours in 20% acetic acid at room temperature.

DIMETHYLDICHLOROSILANE. When this silane (Dow-Corning Co.) was reacted with starch as in the manner given in the preceding experiment, an insoluble product was obtained that contained between 1 and 2 dimethylsilyl cross linkages per glucose residue but that proved to be very unstable because of the small methyl groups on the silicon. A positive starch-iodine test developed in about 5 minutes when shaken in 20% acetic acid.

SUMMARY

Methods for reacting starch and starch products with substituted silanes and the properties of these starch derivatives have been described. Three general types of products were obtained. Soluble polymers were obtained by reacting starch with monofunctional substituted silanes and with substituted silanes containing only one highly reactive substituent such as a chloro- or a small, *n*-alkoxy group. These starch derivatives at higher levels of derivatization were soluble in liquid hydrocarbons such as hexane or xylene. Thermosetting resins, which lost their solvent solubility with heating and time, were formed by reacting starch with bifunctional substituted silanes in which there was considerable difference in reactivity between the substituent groups attached to silicon. Insoluble cross-linked polymers resulted when starch was reacted with substituted silanes having at least two highly reactive groups. Stability of the siloxy linkage to starch appeared to increase with the size and to vary with the configuration of the other substituent groups attached to the silicon.

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Correction

In the Staff-Industry Collaborative Report, "Dextran," by Gordon H. Bixler, G. E. Hines, R. M. McGhee, and R. A. Shurter [IND. ENG. CHEM., **45**, 692 (1953)], on page 693, column 1, lines 25–26 should read:

Van Tieghem showed that *L. mesenteroides* acting on sucrose was responsible for dextran production. E. J. Hehre later showed that enzymes from *L. mesenteroides* were responsible for the production of dextran.