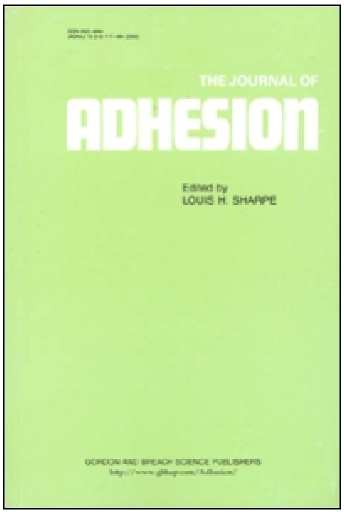

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Silane-Modified Polybutadienes†

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This work had as an objective the development of polymeric coupling agents by introduction of silane groups into liquid polybutadienes of high vinyl content. A fraction of the pendant vinyl groups were converted to organic silane moieties by addition of monomeric silane to the double bond. Platinic chloride was found to catalyze the reaction, and the amount of silanation could be controlled by varying the proportion of reagents. The trichlorosilane pendant groups were further reacted with methyl and ethyl orthoformates yielding triethoxy and trimethoxy derivatives. The silanation could be performed up to the point of complete disappearance of infrared unsaturated bands, thus yielding silane-substituted polymers.

Monomeric analogs also have been prepared. The polymers were used to treat glass for coupling with liquid polybutadiene matrix.

INTRODUCTION

Skeist Laboratories, Inc. has undertaken, under sponsorship of HYSTL Corporation, a research project aimed at the synthesis of polymeric organosilane compounds which could be used as coupling agents on glass. These silanated polybutadiene compounds were designed for maximum compatibility with hydrocarbon resins.

Their general structure is that of high vinyl content, low-molecular-weight polybutadiene resin, containing pending trichloro- or trialkoxysilane groups,

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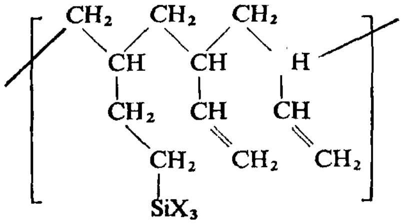
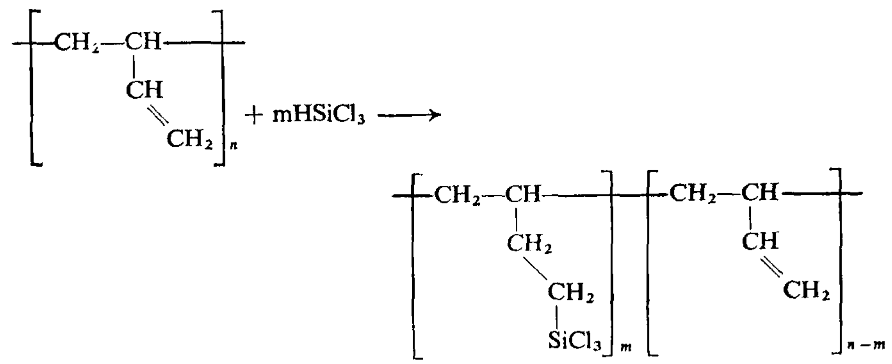
as shown below:



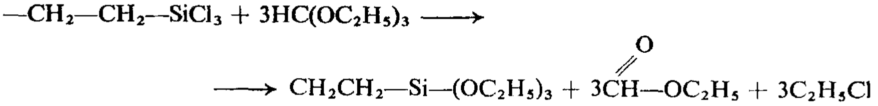
where X = Cl, OCH_3, OC_2H_5.

It has been understood that with the increased popularity of high vinyl content polybutadiene resins[1] used as matrices for glass-reinforced composites, the coupling agents should be synthesized with a structure resembling that of a matrix resin. The advantage of this approach can be envisioned as formation of a uniform polymeric layer on glass having maximum affinity to the matrix, thus ensuring proper wetting on the matrix-coupling agent interface.

The basic reaction employed to synthesize silane-modified polybutadienes was the catalyzed addition of trichlorosilane to the double bond of the pendant vinyl group.[2,3]



Methoxy and ethoxy groups were introduced by reacting the trichlorosilyl moiety with methyl or ethyl orthoformate.[4]



$$-CH_2-CH_2-SiCl_3 + 3HC(OC_2H_5)_3 \longrightarrow$$

$$\longrightarrow CH_2CH_2-Si-(OC_2H_5)_3 + 3\overset{O}{\overset{\|}{C}}H-OC_2H_5 + 3C_2H_5Cl$$

MATERIALS

A-19 Trichlorosilane: Union Carbide Corp. HYSTL B-1000 polybutadiene resin: HYSTL Corp. Platinic chloride: Fischer Scientific Co. Triethyl- and trimethyl orthoformate: Kay-Fries Chemicals. Aluminum chloride: City Chemical Corp. BF_3-monoethylamine complex: Allied Chemical Corp. Benzoyl Peroxide: Cadet Chemical Corp.

EXPERIMENTAL

HYSTL B-1000 liquid polybutadiene resin was vacuumed and mixed with the catalyst. Subsequently, trichlorosilane was added. The solution was placed in a glass tube and sealed. The reaction product was vacuumed to remove volatile byproducts. Infrared spectroscopy and silicon content determination were employed to characterize the product.

A stoichiometric amount of trialkyl orthoformate was added to the reaction product and allowed to react at room temperature in order to obtain ethoxy and methoxy derivatives. Volatile byproducts were then removed by heating and vacuuming. Platinic chloride, BF_3-amine complex, aluminum chloride and benzoyl peroxide were used as catalysts. Temperature, time and reagent proportions were varied. However, only platinic chloride catalysis resulted in the reaction between resin and trichlorosilane. (Table 1).

Subsequently, a series of reactions were carried out with platinic chloride catalysts at room temperatures, varying reactant ratios and the time of the reaction. The final product was hydrolyzed in water, and the degree of silanation was determined by volumetric and gravimetric means. An 80-minute reaction was satisfactory to yield close to 100% of theoretical silicon content. (Table 2).

The volumetric analysis was performed by placing the liquid silanated resin in water, and titrating the HCl formed on hydrolysis. The gravimetric determination was performed by ignition of the hydrolyzed product to yield silica.

The infrared spectral analysis showed the disappearance of the polybutadiene unsaturation peak at 6.1 μ as a function of trichlorosilane-to-resin ratio. The polymer chain of HYSTL B-1000 averaged 18 butadiene residues; of this, approximately 2 units had a 1,4 structure and the remainder in the form of 1,2 vinyl unsaturation. (See Fig. 1).

Typical spectra of chlorosilanated polybutadiene is shown as compared to non-modified HYSTL B-1000 resin. (See Fig. 2 and Fig. 3).

The typical new features of IR spectrum were decrease in intensity of peaks on 6.1, 5.5 and 11 μ, all of these representing unsaturation, and appearance of peaks on 12.9 μ (775 cm^{-1}). The peak on the band at 10.3 is a measure of unsaturation present in the chain. It was found that this band is not reduced significantly even when the 6.1 band disappears. It will indicate

TABLE I

Experiment #	H-2	H-8	H-3	H-5	H-10	H-17	H-29	H-38
Catalyst	—	—	BF_3, 0.5%	$AlCl_3$, 0.5%	BF_3, 1%	$AlCl_3$, 1%	Benzoyl peroxide 0.5%	Platinic chloride 0.5% dissolved in acetone
Moles trichlorosilane per mole polybutadiene B-1000	7	36	12	3	9	9	10	9
Solvent	—	—	—	—	—	—	Toluene, 25% solution of mixture	—
Time, temperature	3 hrs. at 150°C.	20 hrs. at 120°C.	4 hrs. at 130°C.	20 hrs. at 120°C.	18 hrs. at 70°C.	18 hrs. at 150°C.	25 min. at 70°C. and 2½ hrs. at 190°C.	80 min. at room temp.
Results	none	none	none	Crosslinked product	none	Crosslinked product	none	Reaction (see Fig. 1)

TABLE II

Experiment #	H-31	H-38	H-39
Catalyst	Platinic chloride, 0.5%, dissolved in acetone	Platinic chloride, 0.5%, dissolved in acetone	Platinic chloride, 0.5%, dissolved in acetone
Moles trichlorosilane per mole polybutadiene B-10000	9	9	12.4
Time, temperature	18 hrs. at room temp.	80 min. at room temp.	80 min. at room temp.
Yield (% theoretical):			
Volumetric determination	90	—	100
Gravimetric determination	—	100	—

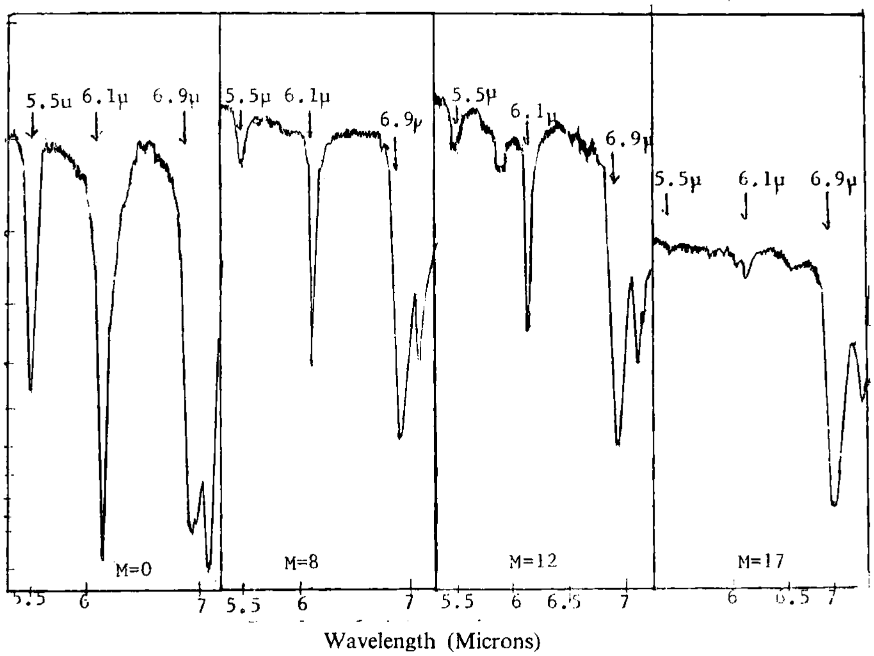


FIGURE 1 I.R. spectra of chlorosilanated polybutadiene B-1000 M-trichlorosilane/B-1000 ratio, mole/mole

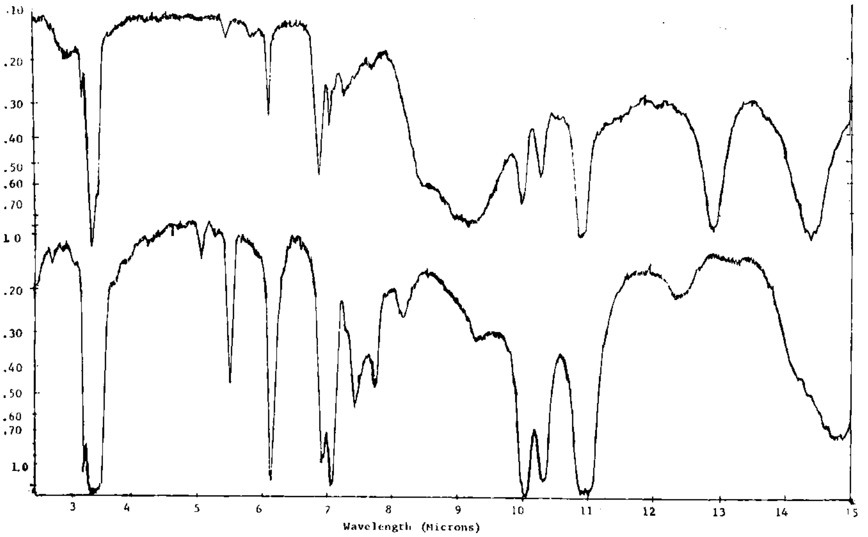


FIGURE 2 Chlorosilanated polybutadiene B-1000
FIGURE 3 Polybutadiene HYSTL B-1000

that the silanation occurs exclusively on the pendant vinyl and that no significant amount of silane has been introduced in the backbone of the polymer.

When the trichlorosilyl derivative of HYSTL was reacted with alkyl orthoformate to yield trialkoxysilyl moieties, the main change in IR spectrum was observed in the 13–14 μ range. (See Fig. 4 and 5). Also, one observed an increase in the intensity of the 10.3 μ band because of the superposition of $Si\text{-}OC_2H_5$ absorption on the original 1.4 unsaturation. In the methoxy derivative, $SiOCH_3$ bands at 8.4 μ, 9.1 μ and 12.0 to 12.5 μ range were clearly visible.

Silanated polybutadienes are viscous liquids which hydrolyze in water easily, yielding a crosslinked, brittle, solid product. They are easily soluble in most organic solvents, especially hydrocarbons. The molecular weight of the resin depends on the molecular weight of the liquid polybutadiene precursor and upon the degree of silanation, and therefore, may vary from 1000 to over 5000.

The critical surface tension of glass treated with silanated polybutadiene was determined by the extrapolation from the Zisman plot and was found to be 30 dyn/cm. The surface tension of liquid polybutadiene resin HYSTL G-2000, was also measured and found to be 30 dyn/cm. This perfect match of the silane treated surface with that of the matrix should, we hope, result in better adhesion between glass and the polymer.

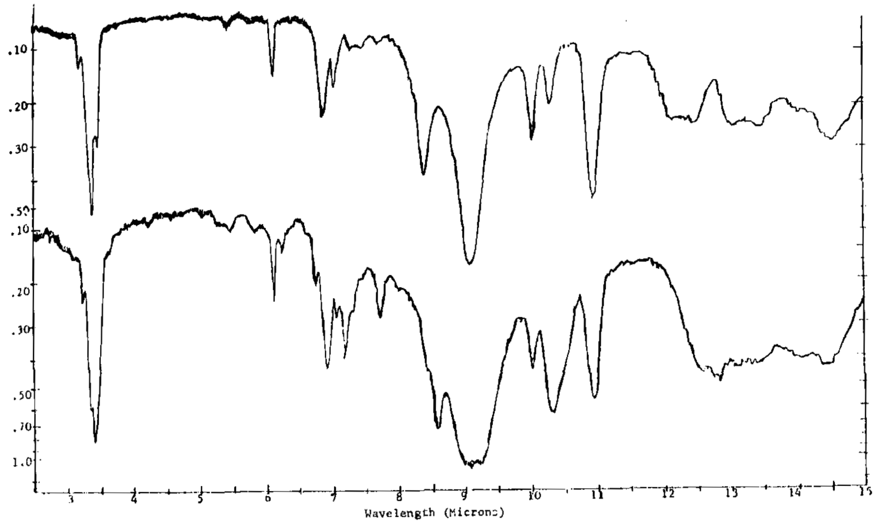


FIGURE 4 Methoxysilanated polybutadiene B-1000
FIGURE 5 Ethoxysilanated polybutadiene HYSTL B-1000

The preliminary measurements of the peel strength of the polypropylene to glass bonded thermally show the silanated glass results at up to 7–8 lbs./in. while no bond was formed when untreated glass was used.

We expect silanated polymer products to be useful as coupling agents and adhesives.

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