

# Functional Silane-Modified Calcium Carbonate

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## Synopsis

In the course of graft polymerization of styrene on a calcium carbonate powder surface treated with a silane coupling agent such as  $\gamma$ -methacryloxypropyltrimethoxysilane, gelation of the reaction mixture was observed just as on silane-modified clay. Infrared spectroscopic and gel-permeation chromatographic studies have revealed that the extracts of styrene monomer from the powder surfaces contained polymeric silane coupling agent, having crosslinking ability, besides monomeric silane coupling agent. The catalytic effect on the condensation of the silane coupling agent on the powder surface was found to be increased in following order:  $\text{CaCO}_3 < \text{P-CaCO}_3 < \text{clay}$ , where  $\text{P-CaCO}_3$  is a calcium carbonate modified with phosphoric acid. The order was parallel to the gelation tendency and to the acidity order ( $H_0 \cong 6.8$ ) on the surfaces. Direct evidence for bonding between the silane coupling agent and the phosphate moiety on calcium carbonate was not available; however, the silane-modified  $\text{P-CaCO}_3$  filler exhibited more reinforcing effects in peroxide-cured ethylene-propylene-diene rubber (EPDM) and in sulfur-cured styrene-butadiene rubber (SBR) than the silane-modified calcium carbonate. These reinforcing effects are also discussed in relation to the molecular weight distribution of the silane coupling agent extracted.

## INTRODUCTION

Calcium carbonate powder has been extensively used as a white pigment or a filler in the manufacture of paint, paper, rubber, plastics, and so on. In these products, it is essential to improve the compatibility between the filler surface and organic matrices. Many kinds of modifications have been undertaken for the filler surface, as well as for the polymer matrices, e.g., preparation of precipitated calcium carbonate with surfactant organic compounds<sup>1</sup> or graft copolymerization of maleic anhydride with polypropylene or with polyethylene.<sup>2</sup>

Graft polymerizability of organic polymer onto filler surface<sup>3</sup> is thought to be one of the measures which indicates the reinforcing ability of the filler in the polymer matrix. Thus grafting polymer onto hydrophilic powder surface has been studied using surfactants or coupling agents. In particular, silane coupling agent<sup>4</sup> has been studied for practical and theoretical purposes.

A number of theories for the improved adhesion of silane coupling agent to hydrophilic surface have been proposed, including chemical bonding theory.<sup>5</sup> The bond formation of the agent with silica surface has been reported to be catalyzed by amines.<sup>6</sup> Plueddemann<sup>7</sup> has deduced a theory from a large amount of experimental results of the silane modifications: a dynamic equilibrium theory which is on the hypothesis of the equilibrium between bond formation and bond breaking at the interface of the agent and filler surface. Ground calcium carbonate surface, however, was shown to be less reactive towards silane coupling agent than silicates or silica surfaces by the reinforcing effects in resin castings.<sup>8</sup>

It was suggested that chemical bonds between calcium carbonate and the agent were unlikely. For grafting polymers, therefore, the agent has not been used on calcium carbonate but on silicate surfaces.<sup>9</sup>

Blyskosh et al.<sup>10</sup> grafted polystyrene onto a calcium carbonate surface by a mechanochemical method. Graft polymerization of methyl methacrylate or styrene on the surface was accomplished by the method of  $\gamma$ -ray preirradiation.<sup>11</sup> Sulfur dioxide-modified calcium carbonate was also used for the graft polymerization of vinylic compounds.<sup>12</sup>

In the course of the study on the graft polymerization of styrene on the silane-modified mineral fillers, gelation of the reaction mixture of the calcium carbonate was observed, just as in the clay system.<sup>13</sup> Our interest in the difference in the reactivity of the agent towards the two filler surfaces urged us to undertake this work. This paper will show that the polymeric silane coupling agent, prepared through the condensation of the monomeric agent on the filler surfaces and extracted with styrene monomer, acts as a primary crosslinking agent rather than the silane-modified filler particles. The catalyzed condensation of the agent by phosphoric acid-modified calcium carbonate and the improved physical properties of the rubbers loaded with the modified calcium carbonates are also discussed.

## EXPERIMENTAL

### Materials

Ground calcium carbonate (Bihoku Funka Ind. Inc., No. 2200) was shown to have a calcite structure by x-ray diffraction analysis.

ANAL. Found: Ig. loss; 44.09, SiO<sub>2</sub> + acid insol.; 0.20, Al<sub>2</sub>O<sub>3</sub>; 0.17, Fe<sub>2</sub>O<sub>3</sub>; 0.03, CaO; 55.22, MgO; 0.23%. Calcd. for calcite: CaO; 56.03%.

The surface area was determined to be 2.40 m<sup>2</sup>/g by the BET method. The average size of the particle diameter was 1.01  $\mu$ m by electron microscopic determination. The pH value of the aqueous suspension of calcium carbonate (5.0 g) was measured to be 9.30 at 25.0°C after being boiled in 100 ml water for 5 min.

The clay (Minerals & Chemicals Philipps Corp., ASP) used here was the same as in the preceding paper.<sup>13</sup> X-ray analysis showed kaolinite to be the principal mineral.

ANAL. Found: SiO<sub>2</sub>; 44.84, Al<sub>2</sub>O<sub>3</sub>; 39.59, Fe<sub>2</sub>O<sub>3</sub>; 0.36, TiO<sub>2</sub>; 1.12, CaO; 0.14, MgO; 0.06, Na<sub>2</sub>O; 0.07, K<sub>2</sub>O; 0.20, Ig. loss; 13.99%. Calcd. for kaolinite: SiO<sub>2</sub>; 46.54, Al<sub>2</sub>O<sub>3</sub>; 39.49, H<sub>2</sub>O; 13.96%.

The surface area and average diameter were determined to be 6.89 m<sup>2</sup>/g and 0.65  $\mu$ m, respectively. The pH value of aqueous suspension of the clay (0.05 g/ml) was 4.76 at 25.0°C.

The silane coupling agents used here were  $\gamma$ -methacryloxypropyltrimethoxysilane (A-174, Union Carbide Corp.) and  $\gamma$ -mercaptopropyltrimethoxysilane (A-189, Union Carbide Corp.), which were commercially obtained and used without any purification. Organic solvents or other reagents used were of reagent grade unless otherwise noted.

### Graft Polymerization of Styrene

Modification with silane coupling agent of air-dried powder (20 g) was accomplished by the addition of the agent (2.38 ml) as aqueous methanolic solution (1.8 ml H<sub>2</sub>O, 100 ml methanol), followed by drying at 80°C for 3 hr. Phosphoric acid (85%, 1.0 g) was also treated as methanolic solution (100 ml methanol) soon after the solution was obtained.

Styrene monomer was fractionally distilled under 30 Torr just prior to reaction, and the main fraction (49.0°C) was used. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol.

A typical procedure for the graft polymerization is as follows. Calcium carbonate (2 g) modified as above and a magnetic stirring bar were placed in a test tube. The air in the tube was substituted with nitrogen, and the tube was sealed with a stopcock. About 2.0 ml of styrene monomer containing 40 mg of AIBN was added, and the tube was then sealed off. After the reaction suspension was confirmed to be well dispersed, it was heated at 80°C for the necessary period of time. The reaction was ceased by cooling in dry-iced methanol and poured into methanol. The resulting composite was filtered, dried *in vacuo*, and weighed.

### Gel-Permeation Chromatography

The molecular weight distribution of polymeric silane coupling agent (relative to polystyrene standards) was measured by gel-permeation chromatography (Yanagimoto, Model L-1100) with fractioning columns (Shodex GPC A-802, 500 mm; A-803 500 mm) and a uv detector. The mobile phase was tetrahydrofuran (THF) of chromatography grade.

### Infrared and Electron Photospectroscopy

Infrared spectra were obtained with a Japan Spectroscopic Co., Ltd., model IR-G. Electron photo spectra were measured by a Shimadzu electron photometer 650.

### Formulation and Properties Determination of EPDM and SBR

Modification of filler (105 g) with silane coupling agent (1.0 ml) was undertaken by a simple method of spraying the agent as aqueous methanolic solution (2 ml H<sub>2</sub>O, 8 ml methanol) using a V-shaped blender. Then the filler was spread on a tray and dried at 80°C for 2 hr. About 1.0 g of phosphoric acid (85%) was similarly treated as methanolic solution (14 ml) and dried.

Formulation of rubber was carried out on a 6 × 15-in. open roll mill by a standard procedure. Curing was performed by heating a sheet of the rubber under a pressure of 150 kg/cm<sup>2</sup> at 165°C for EPDM and 150°C for SBR. The physical properties of the vulcanized rubbers were measured by standard methods (Japanese Industrial Standards, JIS K 6301).

## RESULTS AND DISCUSSION

## Graft Polymerization onto Calcium Carbonate

In the presence of the silane-modified (A-174) calcium carbonate, styrene was polymerized in bulk using AIBN as a catalyst when the gelation of the reaction mixture was observed, just as in the polymerization of the silane-modified clay-styrene system.<sup>13</sup> The monomer conversion versus polymerization time curves for the two systems are shown in Figure 1. The closed symbols stand for the gel point of each system. The gelation of the clay system is shown to take place at an earlier stage in the reaction than that of the calcium carbonate system. The curve of the former system rises more steeply and at earlier stage than that of the latter system. This rapid increase in monomer conversion might be due to a gel effect of the reaction mixture.

Grafting polystyrene onto the agent, by bonding or at least adsorption onto calcium carbonate surface, is adequately feasible. The ungelled composite of polystyrene and silane-modified calcium carbonate obtained in the polymerization (reaction time, 20 min; conversion, 11%) was washed with hot benzene for 12 hr using a Soxhlet extraction apparatus, and the resulting residual solid was submitted to pyrolysis gas chromatography to determine the graft polystyrene. The weight ratio of the polystyrene to the polymer-powder composite was 0.0099.

The solid was then decomposed by a solution of THF and dilute hydrochloric acid, and the resulting materials were washed with THF. The infrared spectrum of the grafting material thus obtained is shown in Figure 2, indicating that the polymer is the copolymer of the silane coupling agent and styrene monomer. The broad carbonate band (at about  $1400\text{ cm}^{-1}$ ) shows that the small part of the calcium carbonate has survived the hydrolysis. Condensation of the silane coupling agent is also suggested by the broad band at  $1000\text{--}1200\text{ cm}^{-1}$ .

However, it seems to be difficult to explain the easy gelation only by the crosslinking of the silane-modified powder. Thus further studies on the extracts from the silane-modified surface were undertaken as explained below.

The amount of silane coupling agent extracted was determined first. To 2.0 g of the silane-modified powder, 30 ml of THF was added, and the suspension

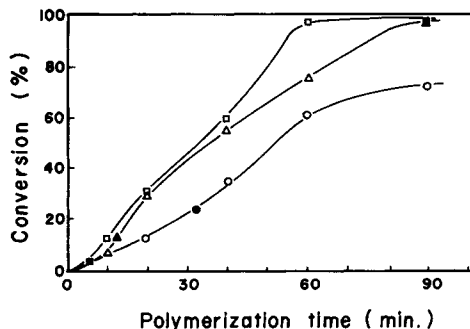


Fig. 1. Polymerization of styrene in the presence of  $\text{CaCO}_3$  (O), P- $\text{CaCO}_3$  ( $\Delta$ ), and clay ( $\square$ ), treated with silane coupling agent. Closed symbols stand for the gel points. Polymerization temperature was  $80^\circ\text{C}$ .

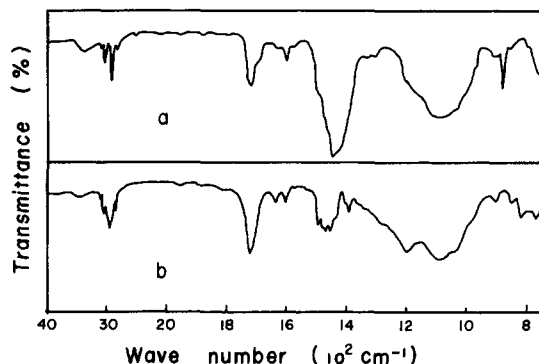


Fig. 2. Infrared spectra of the graft polystyrene on silane-modified calcium carbonate (a) and of the equimolar polymerized product of the partially hydrolyzed silane coupling agent and styrene (b). Both polymers were insoluble in benzene.

was stirred at room temperature for 30 min. After centrifugal separation (7600 rpm, 10 min), the organic supernatant was submitted to infrared spectroscopic determination. The silane coupling agent in the extract of styrene monomer was similarly determined. These data are summarized in Figure 3. In both the cases of THF extracts and of styrene monomer extracts, ca. 70% of the agent is shown to be extracted, and the difference in their amounts in the clay and calcium carbonate surfaces is unclear.

The drying treatment of the silane coupling agent on the filler surface was found to result in the evaporation of a fairly large proportion of the agent. Through the decomposition with dilute hydrochloric acid of the calcium carbonate (2.0 g), which had been modified with silane coupling agent (0.227 g), 0.165 g of the agent was recovered by uv spectrometric determination. Therefore, almost all of the silane coupling agent that was not extracted had evaporated during the drying procedure. By dilute hydrochloric acid decomposition of the residual calcium carbonate from which the agent had been extracted with THF, the unextracted agent was determined to be 0.002 g. A similar evaporation of the silane coupling agent under drying is assumed for the case of treatment on the clay surface.

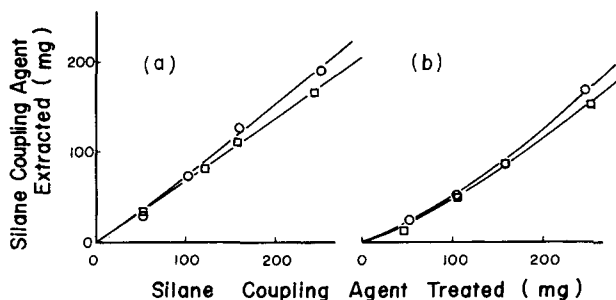


Fig. 3. (a) Relation between the amount of silane coupling agent treated on the fillers and that extracted with THF: CaCO<sub>3</sub> (O) and clay (□). Ester band of the agent (1716 cm<sup>-1</sup>) was used for the determination by calibration method. (b) The relation was obtained for styrene monomer extracts: CaCO<sub>3</sub> (O) and clay (□).

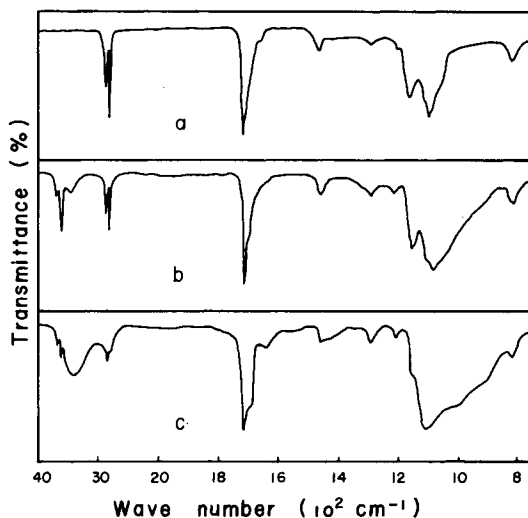


Fig. 4. Infrared spectra of silane coupling agent in styrene monomer (a), in styrene monomer extract from the silane-modified  $\text{CaCO}_3$  (b) and the silane-modified clay (c).

Although nearly the same amount of silane coupling agent was extracted with styrene monomer from clay and calcium carbonate surfaces (Fig. 3), the infrared spectra of the two were significantly different in the region of  $1000\text{--}1200\text{ cm}^{-1}$  (Fig. 4). The broad bands suggest that the extracts with styrene monomer contain the polymeric silane agent linked with siloxane bonds.

To obtain more information on this point, GPC analysis was applied to the THF extracts. GP chromatograms are depicted in Figures 5 and 6 for calcium carbonate and clay systems, respectively. Figures 5 and 6 clearly show that the silane coupling agent extracted from clay surface is predominantly a polymeric one of higher molecular weight than that from calcium carbonate surface and that the amount of monomeric agent in the clay system is too small to be observed. Treatment with much more agent, even on a clay surface, tolerated the peak shift to the lower-molecular-weight side. From the infrared spectral results

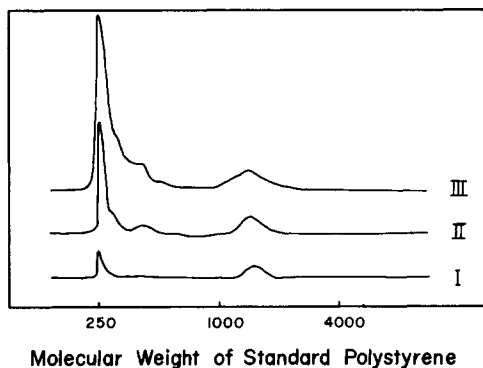


Fig. 5. GPC curves for THF extracts from  $\text{CaCO}_3$  (2.0 g) treated with silane coupling agent: I, 51 mg; II, 160 mg; III, 325 mg.

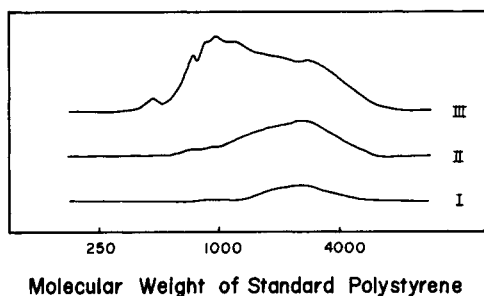


Fig. 6. GPC curves for THF extracts from clay (2.0 g) treated with silane coupling agent: I, 53 mg; II, 156 mg; III, 302 mg.

described above, a similar molecular weight distribution appeared to hold for the agent in styrene monomer extracts.

Hydrolysis and subsequent condensation of alkoxy silyl groups are known to be catalyzed by acid as well as base. Recently Fourier transform infrared spectroscopy was developed to study the condensation of silane coupling agent with each other or with surface silanol groups on glass fiber.<sup>14</sup> From the results of Figures 5 and 6, the acidic sites on the clay surface<sup>15</sup> seemed to catalyze the homocondensation of the agent on the surface. Therefore, it was assumed that the treatment of calcium carbonate with acid, e.g., phosphoric acid, might enhance the catalysis of the polycondensation.

The treatment of calcium carbonate with a methanolic solution of phosphoric acid gave calcium carbonate contaminated with calcium hydrogen phosphate (P-CaCO<sub>3</sub>), which was identified by x-ray diffraction analysis (interplanar spacings of intensive lines: found; 2.93, 3.35, 3.37. ASTM card for CaHPO<sub>4</sub>, 9-80; 2.96, 3.35, 3.37 Å) and by electron photospectroscopy (peak for P2p<sub>3/2</sub>: found; 133.0 eV authentic CaHPO<sub>4</sub>·2H<sub>2</sub>O, 133.0 eV).

GPC data of the extracted silane coupling agent from P-CaCO<sub>3</sub> are shown in Figure 7, where some data in Figures 5 and 6 are reproduced for comparison. It can be noticed for the extracts from P-CaCO<sub>3</sub> that the relative amount of polymeric silane coupling agent to that of monomeric one has increased as compared

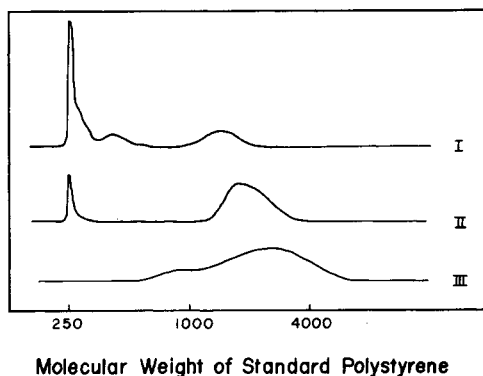


Fig. 7. GPC curves for THF extracts from CaCO<sub>3</sub> (2.0 g, I), P-CaCO<sub>3</sub> (2.0 g, II), and clay (2.0 g, III) treated with 160, 164, and 156 mg of silane coupling agent, respectively.

TABLE I  
Acidic and Basic Properties of Fillers

Filler	pH of aqueous suspension, at 25 °C	Surface acidity ( $H_0 \leq 6.8$ ), $\mu\text{mol/g}$
CaCO <sub>3</sub>	9.30	0.2
P-CaCO <sub>3</sub>	7.73	1.6
Clay	4.76	35.4

with the corresponding data for calcium carbonate. Moreover, the molecular weight of the polymeric agent from P-CaCO<sub>3</sub> is shown to be larger than that from calcium carbonate. The total amount of the agent extracted from P-CaCO<sub>3</sub> with THF was found to be nearly the same as that from calcium carbonate by a comparison of the peak area on the chromatograms.

The results described above suggest that the P-CaCO<sub>3</sub> surface might have some catalytic activity for the polymerization of the agent and that the active sites might correlate with the phosphate moiety on the surface. Thus the amount of the acid on the surface, having an acidity function of  $H_0 \leq 6.8$ , was determined by the titration of 0.01 mol/l. butylamine in benzene using neutral red as an indicator (Table I). Washings of P-CaCO<sub>3</sub> with water did not diminish the phosphate peak in the electron photo spectrum, suggesting that the phosphate was not easily washed away. Furthermore, no significant chemical shift of the peak was observed through the treatment of silane coupling agent. It would be reasonable to assume that the active site for the reaction is the phosphate moiety and that the bond formation between the agent and the surface is negative.

Results for the graft polymerization in the presence of the silane-modified P-CaCO<sub>3</sub> are also shown in Figure 1. The gelation tendency of the reaction mixtures apparently has a good correlation with both the amount and molecular weight of the polymeric silane coupling agent extracted. Even the silane coupling agent adsorbed on the powder surface may link the polystyrene; however, it is thought to be reasonable that the polymeric silane coupling agent extracted with styrene monomer acts as a primary crosslinking agent in the gelled products.

### Silane-Modified Calcium Carbonate Fillers for EPDM and SBR

Ground calcium carbonate has been extensively used in the rubber industry as a cost-reducing filler having a clean white color and good electric properties; hence it is of importance to make the filler have some reinforcing effects.

There have been many works on the reinforcing mechanisms of silane coupling agent in rubbery materials.<sup>16</sup> From dynamic equilibrium theory, it is implied that the polymeric silane coupling agent is favorable for good adhesion to a hydrophilic surface, since the polymer has many interaction groups in the chain with the surface.

Adhesion of silane coupling agent to a glass surface was reported to be much improved by controlled partial prehydrolysis of the agent.<sup>17</sup> Linear polymeric silane coupling agent was also found to be effective in improving the compatibility between inorganic fillers having surface hydroxy groups and thermosetting plastics.<sup>18</sup> Such advantages of the polymeric agents would be the case for calcium



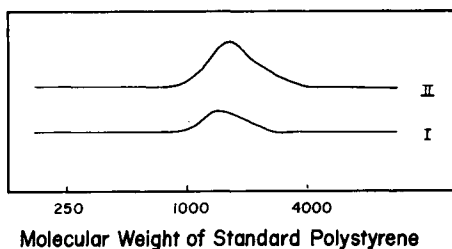


Fig. 8. GPC curves for THF extracts from  $\text{CaCO}_3$  (105 g, I) and P- $\text{CaCO}_3$  (105 g, II) treated with silane coupling agent (1.0 ml) as aqueous methanol (8.0 ml MeOH, 2.0 ml  $\text{H}_2\text{O}$ ) and dried at  $80^\circ\text{C}$  for 2 hr.

carbonate filler, although having a surface much less active towards the agent. The extracts of THF from the silane-modified P- $\text{CaCO}_3$  filler and from the silane-modified calcium carbonate filler exhibited similar GPC patterns to the results in Figure 7 without the monomer peaks (Fig. 8).

After the simple treatments of calcium carbonate filler with a well-diluted phosphoric acid solution and with the silane coupling agent, the effects of the modified fillers on the physical properties of the rubbers were investigated. Table II shows the recipe and physical properties of the peroxide-cured EPDM rubber. The more modifications undertaken in the filler, the larger the average size filler particles would be; however, significant improvement of the physical properties by treatment with phosphoric acid is recognized. For EPDM rubber loaded with clay in place of calcium carbonate filler, the improvement by silane modification was reported to be more striking.<sup>19</sup>

Improvement of the physical properties by acid modification, the etching effect of acid on the filler surface—where silane coupling agent anchor themselves, seems to be possible. However, from the GPC observations above (Fig. 8), it might be said that the formation of polymeric silane coupling agent is the primary factor involved in the improvement. Thus a larger amount and higher molecular weight of the agent was formed on P- $\text{CaCO}_3$  than on calcium carbonate surface. The drying of the silane-modified fillers, spread on a tray, appeared to force the monomeric agent to evaporate almost completely.

Polymeric silane coupling agent, which was obtained by the hydrolysis in a

TABLE II  
Effect of Silane<sup>a</sup> Modification on Vulcanizate Properties of  $\text{CaCO}_3$ -Loaded EPDM<sup>b</sup>

Filler	$\text{CaCO}_3$	$\text{CaCO}_3$ / silane	P- $\text{CaCO}_3$ / silane	$\text{CaCO}_3$ / polym. silane <sup>c</sup>
Tensile Strength, $\text{kg/cm}^2$	52	61	71	64
Elongation, %	330	280	240	290
200% Modulus, $\text{kg/cm}^2$	25	47	62	47
Hardness <sup>d</sup>	68	70	71	70
Tear (JIS-B), <sup>d</sup> $\text{kg/cm}$	14	14	16	14
Set, <sup>d</sup> %	10.3	6.9	3.9	8.1

<sup>a</sup>  $\gamma$ -Methacryloxypropyltrimethoxysilane (A-174, Union Carbide Corp.).

<sup>b</sup> Recipe: EPDM (Mitsui EPT 3045) 100, filler 100, zinc oxide 5.0, dicumyl peroxide 3.0. Cure:  $165^\circ\text{C}$ , 15 min.

<sup>c</sup>  $\bar{M}_w$  relative to standard polystyrene was  $4.7 \times 10^3$ .

<sup>d</sup> Tested by the method of Japanese Industrial Standards (JIS K 6301).

TABLE III  
Effect of Silane<sup>a</sup> Modification on Vulcanizate Properties of CaCO<sub>3</sub>-Loaded SBR<sup>b</sup>

Filler	CaCO <sub>3</sub>	CaCO <sub>3</sub> / silane	P-CaCO <sub>3</sub> / silane	P-CaCO <sub>3</sub> /(EtO) <sub>4</sub> Si/ silane <sup>c</sup>
Tensile strength, kg/cm <sup>2</sup>	47	39	47	56
Elongation, %	520	480	440	440
300% Modulus, kg/cm <sup>2</sup>	19	23	33	40
Hardness <sup>d</sup>	60	61	64	64
Tear (JIS-B), <sup>d</sup> kg/cm	13	15	15	19
Set, <sup>d</sup> %	8.7	7.4	5.2	4.3
Swelling, <sup>e</sup> %	321	279	257	252

<sup>a</sup>  $\gamma$ -Mercaptopropyltrimethoxysilane (A-189, Union Carbide Corp.).

<sup>b</sup> Recipe: SBR (Nipol 1502) 100, filler 100, zinc oxide 5.0, stearic acid 1.0, sulfur 2.0, 2-benzothiazoyl disulfide 1.5, diphenyl guanidine 0.5. Cure: 150°C, 10 min.

<sup>c</sup> One ml of (EtO)<sub>4</sub>Si was treated as methanolic solution (8.0 ml MeOH).

<sup>d</sup> Tested by the method of Japanese Industrial Standards (JIS K 6301).

<sup>e</sup> Weight increase after immersion in benzene for 48 hr at room temperature.

large excess of water prior to the treatment of filler surface, is shown to be slightly effective (last column in Table II). The poor improvement is probably due to the formation of a three-dimensional polymer, which is undesirable for subsequent treatment to the filler surface.

Furthermore, for sulfur-cured SBR, the silane-modified P-CaCO<sub>3</sub> was shown to provide a considerable improvement in the physical properties of the rubber (Table III). In this case,  $\gamma$ -mercaptopropyltrimethoxysilane (A-189) was employed as a coupling agent.

One of the further modifications suggested from the catalysis of the P-CaCO<sub>3</sub> surface is the coating of the filler with siloxane polymer networks by hydrolyzing of silanetetraalkoxide, since the silica surface is well known to have a good response towards silane coupling agent. Silanetetraethoxide was treated by a simple spraying method of aqueous methanolic solution. The filler was dried once and followed by the treatment of the agent. Although the filler treated with silanetetraethoxide might be larger particles, a considerable improvement of the physical properties of the rubber is shown to be achieved. Such a coating modification with siloxane polymer may serve a new use for ground calcium carbonate filler.

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