

# Phosphate Coupling Agents for Calcium Carbonate Filler

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## Synopsis

Phosphate coupling agents, i.e., alkyl dihydrogenphosphates containing functional groups such as olefinic, chloro, methacryloxy, and mercapto, were synthesized and allowed to react with calcium carbonate filler suspended in an aqueous medium. The modification provided the filler with good dispersibility in mineral oil. Physical properties of the vulcanized rubbers loaded with the modified fillers were found to be influenced by the functional group introduced. For example, in peroxide-cured ethylene-propylene-diene rubber (EPDM), the methacryloxy group was most effective, and the mercapto group significantly enhanced the physical properties of sulfur-cured styrene-butadiene rubber (SBR), while a saturated aliphatic phosphate was ineffective in both curing systems. Deposition of the coupling agent as calcium salt onto calcium carbonate surface was observed by scanning electron microscopy. This novel approach for the surface modification of calcium carbonate filler is discussed in relation to the reinforcing effects on rubbery materials.

## INTRODUCTION

In the preceding report<sup>1</sup> dealing with the reaction of alkyl dihydrogenphosphates and calcium carbonate in aqueous medium, it was shown that a large alkyl dihydrogenphosphate molecule such as octyl dihydrogenphosphate reacts with calcium carbonate to give the dibasic calcium salt of the phosphate, which deposits onto the calcium carbonate surface and provides the surface with hydrophobicity. Thus, a large alkyl dihydrogenphosphate molecule could be an effective surface modifier of calcium carbonate filler. Therefore, the synthesis of the dihydrogenphosphates of alcohols having some reactive functional groups and their uses as surface modifiers have become our interest.

In this article, five types of functional groups are discussed: saturated and unsaturated aliphatic, chloro, mercapto, and methacryloxy groups. Modification effects derived from the phosphate treatments are discussed in correlation with the physical properties of rubber vulcanizates compounded with the modified calcium carbonate fillers. In a given curing system, the selection of the appropriate functional group of the phosphate is shown to be significant to obtain improvement in reinforcement of elastomers by calcium carbonate. The alkyl dihydrogenphosphates used here are termed phosphate coupling agents.

## EXPERIMENTAL

### Alcohol

All the alcohols, except for one, used in this work were available commercially and used without purification: octanol, 3,7-dimethyl-6-octenol, bicyclo[2,2,1]-hept-5-en-2-methanol, 2-(methacryloxy)propanol, and 6-chlorohexanol. 6,6'-Dithiodihexanol was prepared by treating 6-chlorohexanol with sodium disulfide.<sup>2</sup>

ANAL. Calcd. for  $C_{12}H_{26}O_2S_2$ : C, 54.09; H, 9.84. Found: C, 54.00; H, 9.87; mp 31–32°C.

### Calcium Alkyl Phosphate Dihydrate

The alcohols were phosphorylated in a Dry-Ice ethanol bath by a conventional method<sup>3</sup> using phosphoryl trichloride and pyridine, hydrolyzed with water, followed by the addition of calcium chloride solution and neutralization with sodium hydroxide. The obtained crude dibasic calcium alkyl phosphate dihydrate was treated with hydrochloric acid, extracted with ether, and reformed from the extracted solution. After the repetition of this procedure, the salt was filtered, washed with water and acetone, and dried *in vacuo*. In the case of preparation of calcium 6-mercaptohexyl phosphate dihydrate, 6,6'-dithiodihexanol was phosphorylated and the resulting diphosphate was reduced with zinc powder and hydrochloric acid.

The results of elemental analyses for the calcium salts obtained are summarized as follows:

ANAL. Calcd. for calcium octyl phosphate dihydrate ( $C_8H_{21}O_6PCa$ ): C, 33.80; H, 7.45; P, 10.89. Found: C, 33.65; H, 7.72; P, 11.19. Calcd. for calcium 3,7-dimethyl-6-octenyl phosphate dihydrate ( $C_{10}H_{23}O_6PCa$ ): C, 38.70; H, 7.47; P, 9.98. Found: C, 38.64; H, 7.73; P, 9.86. Calcd. for calcium bicyclo[2,2,1]hept-5-en-2-methyl phosphate dihydrate ( $C_8H_{15}O_6PCa$ ): C, 34.53; H, 5.43; P, 11.13. Found: C, 34.52; H, 5.31; P, 11.11. Calcd. for calcium 2-(methacryloxy)propyl phosphate dihydrate ( $C_7H_{15}O_8PCa$ ): C, 28.19; H, 5.07; P, 10.38. Found: C, 28.22; H, 4.91; P, 10.56. Calcd. for calcium 6-mercaptohexyl phosphate dihydrate ( $C_6H_{17}O_6PCaS$ ): C, 24.99; H, 5.94; P, 10.74. Found: C, 24.97; H, 5.84; P, 10.59. Calcd. for calcium 6-chlorohexyl phosphate dihydrate ( $C_6H_{16}O_6PCaCl$ ): C, 24.79; H, 5.55; P, 10.65. Found: C, 24.55; H, 5.60; P, 10.78.

### Phosphate Coupling Agent

Phosphate coupling agents were obtained by the acidolysis of the corresponding calcium salts with hydrochloric acid, followed by ether extraction, drying with anhydrous sodium sulfate, and evaporation of the ether. The coupling agents obtained were confirmed to be chromatographically pure. Thin-layer chromatography was carried out on silica gel. The developing solvent system used was  $CHCl_3:CH_3OH:CH_3COOH:H_2O = 25:15:4:2$  v/v %.  $R_f$  values of the coupling agents are summarized in Table I.

### Calcium Carbonate

Ground calcium carbonate having a calcite structure and an average specific surface area of  $7.74 \text{ m}^2/\text{g}$  was supplied by Bihoku Funka Co., Ltd.

ANAL. Calcd. for calcite: CaO, 56.03. Found: CaO, 55.28; MgO, 0.38;  $SiO_2$ , 0.13;  $Al_2O_3$ , 0.08;  $Fe_2O_3$ , 0.05; P, 0.009; ignition loss, 43.99.

TABLE I  
*R<sub>f</sub>* Values of Phosphate Coupling Agents

Phosphate coupling agent	Abbrev.	<i>R<sub>f</sub></i> <sup>a</sup>
Octyl dihydrogenphosphate	OP	0.57
3,7-Dimethyl-6-octenyl dihydrogenphosphate	CP	0.62
Bicyclo[2,2,1]hept-5-en-2-methyl dihydrogenphosphate	NMP	0.52
2-(Methacryloxy)propyl dihydrogenphosphate	MPP	0.51
6-Mercaptohexyl dihydrogenphosphate	MHP	0.53
6-Chlorohexyl dihydrogenphosphate	CHP	0.52

<sup>a</sup> Thin-layer chromatography was carried out on silica g.c.l. Developing solvent system was  $\text{CHCl}_3:\text{CH}_3\text{OH}:\text{CH}_3\text{COOH}:\text{H}_2\text{O} = 25:15:4:2$  (v/v %).

### Phosphate Treatment

About 110 g of the ground calcium carbonate was suspended in 300 ml distilled water. Under vigorous stirring, 1.0 g of phosphate coupling agent in 50 ml water was added. After 30 min, the filler was filtered, washed with a small amount of acetone, and dried at 80°C for 4 h. The dried cake was crushed with a mortar to provide a filler.

### Scanning Electron Micrography

The modified surface of the precipitated calcium carbonate of reagent grade having a calcite structure and an average specific surface area of 0.98 m<sup>2</sup>/g was observed with a Hitachi Scanning Electron Micrograph, HFS-2.

### Absorptiometry

The phosphate coupling agents attached to the surface of the calcium carbonate were determined by decomposition with nitric acid and sulfuric acid, followed by absorptiometry using ammonium molybdate and ascorbic acid according to the procedure of Fogg and Wilkinson.<sup>4</sup> The values obtained were corrected by that for the blank calcium carbonate.

### Physical Properties of Rubber Vulcanizates

Compounding was carried out on a 6 × 15-in. open roll mill. Curing was performed by heating a sheet of rubber compound under a pressure of 150 kg/cm<sup>2</sup> at 150°C for SBR, 160°C for epichlorohydrin rubber (CHC), and 165°C for EPDM. The physical properties of the vulcanizates were measured by standard methods (Japanese Industrial Standards, JIS K 6301).

### Viscosity of CaCO<sub>3</sub>-Dispersed Mineral Oil

The relative viscosity of the calcium carbonate-dispersed mineral oil (Di-anaprocess KL-1, Idemitsu Kohsan Co., Ltd.) was measured at 25.0°C with a Tokyo Keiki Mfg. Co. B-Type Viscometer, BH.

TABLE II  
Determination of the Attached Agents and Specific Surface Area of  $\text{CaCO}_3$

Phosphate coupling agent	Treated, wt %	Attached, wt %	Conversion, %	Specific surface area, $\text{m}^2/\text{g}$
Control	none	none	—	7.74
OP	0.92	0.73	79	9.70
CP	0.92	0.75	82	9.94
NMP	0.92	0.53	58	10.02
MPP	0.92	0.30	33	9.16
MHP	0.92	0.44	48	9.72
CHP	0.92	0.38	41	9.46

## RESULTS AND DISCUSSION

### Calcium Carbonates Modified with Phosphate Coupling Agents

The amounts of the attached coupling agents and the specific surface areas of the modified calcium carbonates are indicated in Table II. Relatively larger alkyl groups in the phosphates appear to enhance the conversion of the agent because of lower hydrophilicity. This tendency roughly correlates with the  $R_f$  values of the agents as shown in Figure 1. This result is consistent with that obtained in the previous work.<sup>1</sup>

The deposition of the calcium salt of MPP on the precipitated calcium carbonate is clearly shown in the scanning electron micrographs of Figures 2 and 3. The precipitated calcium carbonate was employed to definitely display the modified morphology. Compared with nonmodified calcium carbonate, on the modified surface scalelike precipitates are recognized. The other phosphate coupling agents also produced similar forms.

The data on the specific surface areas of the modified calcium carbonates in Table II show that the treatment with the agent generally results in an increase in the area. This can be ascribed to the surface erosion and/or to the calcium salt formation.

In every case, the modified calcium carbonate exhibited hydrophobicity. The relative viscosities of the OP-modified calcium carbonate-dispersed mineral oil in Figure 4 indicate that a steep viscosity increase was observed over a filler

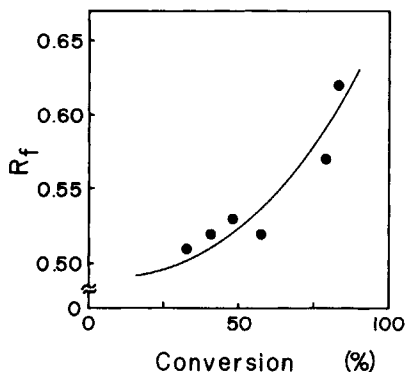


Fig. 1. Relationship between  $R_f$  values and conversion of phosphate coupling agents.

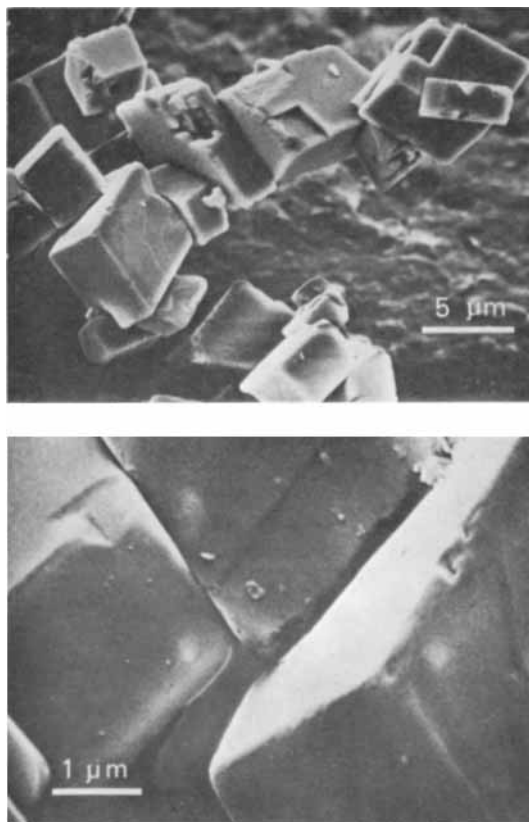


Fig. 2. Scanning electron micrographs of nonmodified calcium carbonate.

volume fraction of 0.20. Rapid increases in the interaction among the filler particles would account for the phenomenon. In contrast, the nonmodified calcium carbonate coagulated in the oil under the same conditions, resulting in nonfree flow. In the latter case, the relative viscosity rose sharply over a filler volume fraction of 0.11. The improved dispersion derived from the phosphate modification is also to be expected for rubbery or molten plastic materials having a nonpolar nature or small polarity.

#### **Coupling Effects on Reinforcing EPDM Cured with Peroxide**

The physical properties of peroxide-cured EPDM compounded with the modified calcium carbonates are shown in Table III, indicating the functional effects of the phosphate coupling agents on the reinforcement. A saturated alkyl dihydrogenphosphate, OP, was found to be ineffective for reinforcing improvement in spite of better wetting toward the polymer and improved dispersion in the polymer matrix. A similar phenomenon was also found in the studies on silane-treated silica-SBR system<sup>5,6</sup> and silane-treated clay-EPDM system.<sup>7</sup>

Olefinic or methacryloxy groups in CP or MPP, however, afforded considerable increases in the moduli and very small permanent sets. It is probable that the increased bondings between the rubber molecules and the functional groups attached to the filler surface caused such improvements. The increased hardness

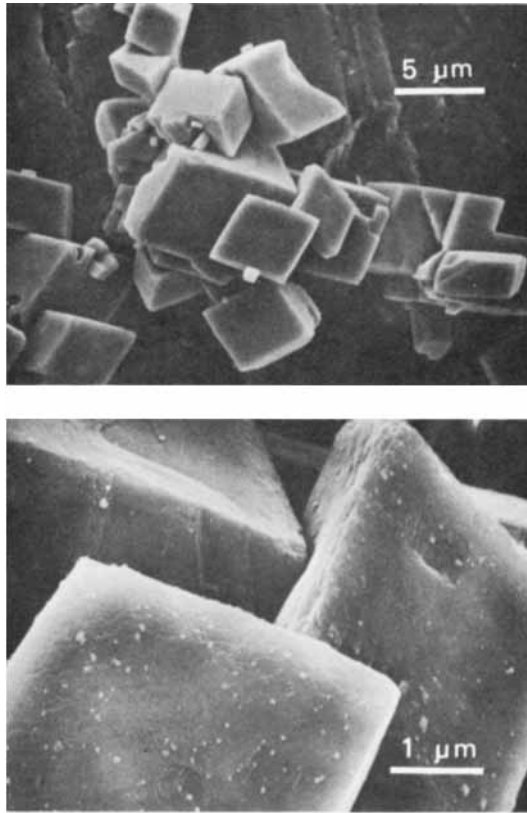


Fig. 3. Scanning electron micrographs of calcium carbonate treated with 7 wt % MPP.

and tear strength as well as large reduction of the elongation are also accounted for by the increased bonding. Some behaviors were indicated by the study on the immobilized rubber layer around silica particles in the silica-loaded 1-chlorobutadiene-butadiene rubber vulcanizates cured with  $\gamma$ -aminopropyltriethoxysilane.<sup>8</sup>

Thus, the incorporation of groups reactive toward the curing agent into the

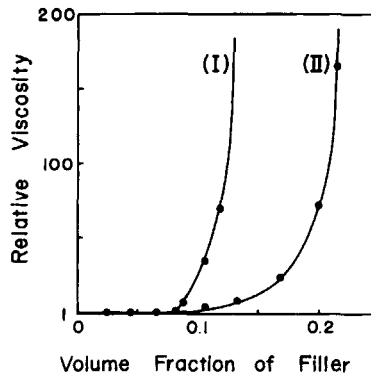


Fig. 4. Relative viscosities of mineral oil dispersed with nonmodified calcium carbonate (I) and OP-modified calcium carbonate (0.37 wt %) (II) at 25.0°C.

TABLE III  
Coupling Effects on Peroxide-Cured EPDM<sup>a</sup>

Phosphate coupling agent	Control, none	OP	CP	NMP	MPP
Treated, wt %	0	0.92	0.92	0.92	0.92
Attached, wt %	0	0.73	0.75	0.53	0.30
Tensile strength, MPa	4.5	4.4	4.7	6.0	7.4
100% Modulus, MPa	2.2	1.9	2.8	3.1	3.4
200% Modulus, MPa	2.6	2.2	3.9	4.9	5.5
Elongation, %	370	370	290	280	310
Hardness <sup>b</sup> (JIS)	66	64	68	68	67
Tear <sup>b</sup> (JIS-B), kN/m	10	8	11	11	11
Set <sup>b</sup> %	8	8	4	2	4

<sup>a</sup> Recipe: EPDM (Sumitomo Esprene 502), 100; CaCO<sub>3</sub>, 100; ZnO, 5.0; dicumyl peroxide (97%), 2.7. Cure: 165°C, 15 min.

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

TABLE IV  
Coupling Effects on Sulfur-Cured SBR<sup>a</sup>

Phosphate coupling agent	Control none	OP	CP	MHP	
				0.46	0.92
Treated, wt %	0	0.91	0.92	0.46	1.83
Attached, wt %	0	0.73	0.71	0.24	1.01
Tensile strength, MPa	3.6	4.8	4.8	5.7	5.8
100% Modulus, MPa	1.3	1.3	1.4	1.6	2.1
200% Modulus, MPa	1.5	1.4	1.5	1.8	2.5
300% Modulus, MPa	1.8	1.7	1.8	2.1	2.9
Elongation, %	480	530	570	530	510
Hardness <sup>b</sup> (JIS)	58	59	61	60	63
Tear <sup>b</sup> (JIS-B), kN/m	16	15	18	20	20
Set, <sup>b</sup> %	7	9	11	8	7
Swelling, <sup>c</sup> %	327	328	324	294	261

<sup>a</sup> Recipe: SBR (Nipol 1502), 100; CaCO<sub>3</sub>, 100; ZnO, 5.0; stearic acid, 1.0; sulfur, 2.0; 2-benzothiazoyl disulfide, 1.5; diphenyl guanidine, 0.5. Cure: 150°C, 15 min.

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

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



TABLE V  
Effects of Phosphate Coupling Agent (CHP) on Properties of Calcium Carbonate-Filled  
Epichlorohydrin Rubber Vulcanizate<sup>a</sup>

	Control	CHP-Modified, 0.38 wt %
Tensile strength, MPa	5.9	6.6
300% Modulus, MPa	2.0	4.0
Elongation, %	670	660
Hardness <sup>b</sup> (JIS)	56	62
Tear <sup>b</sup> (JIS-B), kN/m	14	22
Set, <sup>b</sup> %	19	8

<sup>a</sup> Recipe: epichlorohydrin rubber (CHC, Gechron 2000), 100; CaCO<sub>3</sub>, 100; zinc stearate, 0.8; 2-mercaptoimidazoline, 1.5; trilead tetroxide, 5.0. Cure: 160°C, 30 min.

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

alkyl group of the phosphate is thought to be essential for the reinforcing modification. In radical initiation and subsequent crosslinking processes, the unsaturation moiety attached to the filler surface would compete with the unsaturation in the polymer matrix. The high effectiveness of MPP or NMP in filler reinforcement suggests that the methacryloxy or bicyclo[2,2,1]hept-5-en-2-methyl group participates effectively in the reaction process. This was evident by the good copolymerizability of the groups with the unsaturation in the polymer molecules.

A large number of mechanisms have been proposed to interpret the filler reinforcing phenomena.<sup>5,9</sup> For the rubber compound loaded with the relatively large-size filler of ground calcium carbonate, the interfacial bond formation between the rubber and the filler is convincingly thought to be a predominant factor for reinforcing the rubber vulcanizate rather than an improvement of the surface wettability or the dispersibility.

### Coupling Effects on Reinforcing SBR Cured with Sulfur

Some functional effects of the phosphate coupling agent on SBR reinforcement were also recognized in the sulfur curing system. Physical properties of the modified filler-compounded SBR vulcanizates are summarized in Table IV. The increased surface wetting and dispersibility attributed to OP treatment appears to be useless for reinforcing the sulfur-cured SBR. Although CP carries an unsaturation in the alkyl group, improvement on reinforcement is small. The unsaturation seems to be somewhat less effective in sulfur curing than in peroxide curing. Similarly low responsiveness of the unsaturation was reported on reinforced EPDM by silane-modified clay<sup>7</sup> and talc.<sup>10</sup>

High modulus accompanying relatively low permanent set and low benzene swelling caused by MHP modification shows that mercapto is an effectual group in the sulfur curing system. Green strength of SBR compounded with calcium carbonate (100 phr) increased from 0.44 to 0.60 MPa upon MHP modification (0.41 wt %). This should be ascribed to the additions of the mercapto groups to the unsaturated groups in the polymer chains. Although the real mechanism of mercapto participation in the crosslinking reaction is not clear, these bonds between the filler surface and rubber seem to afford these improvements.

TABLE VI  
Physical Properties of SBR Vulcanizates<sup>a</sup>  
Compounded with MHP-Spray-Dried CaCO<sub>3</sub><sup>b</sup>

Phosphate coupling agent	Control, none	MHP
Treated, wt %	0	0.94
Attached, wt %	0	0.60
Tensile strength, MPa	3.2	4.1
100% Modulus, MPa	1.3	1.9
200% Modulus, MPa	1.4	2.3
300% Modulus, MPa	1.7	2.6
Elongation, %	480	460
Hardness <sup>c</sup> (JIS)	58	62
Tear <sup>c</sup> (JIS-B), kN/m	16	24
Set, <sup>c</sup> %	7	6
Swelling, <sup>d</sup> %	325	271

<sup>a</sup> Recipe: SBR (Nipol 1502), 100; CaCO<sub>3</sub>, 100; ZnO, 5.0; stearic acid, 1.0; sulfur, 2.0; 2-benzothiazoyl disulfide, 1.5; diphenyl guanidine, 0.5. Cure: 150°C, 15 min.

<sup>b</sup> Aqueous methanolic solution (MeOH:H<sub>2</sub>O = 9:1 v/v) of MHP was sprayed using V-shaped blender.

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

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

### Coupling Effects on Reinforcing CHC Vulcanizates

Mercapto silane-treated silica has been found to have a good reinforcing ability toward epichlorohydrin rubber cured with 2-mercaptoimidazoline.<sup>11</sup> In this curing system, the chloroalkyl group in CHP was found effective for physical improvement.

Table V indicates the data of the physical properties of epichlorohydrin rubber vulcanizates loaded with CHP-modified calcium carbonate. The chloroalkyl groups on the filler are reasonably assumed to chemically react with the polymer to afford interfacial crosslinks according to the estimated curing mechanism.<sup>12</sup>

TABLE VII  
Physical Properties of EPDM Vulcanizates<sup>a</sup>  
Compounded with Barium Sulfates With and Without Treatment<sup>a</sup>

	Control, none	MPP-Modified, 0.19 wt %
Tensile strength, MPa	2.8	5.5
100% Modulus, MPa	1.8	2.5
200% Modulus, MPa	2.3	4.8
Elongation, %	270	240
Hardness <sup>b</sup> (JIS)	59	61
Tear <sup>b</sup> (JIS-B), kN/m	9	11
Set, <sup>b</sup> %	3	1

<sup>a</sup> Recipe: EPDM (Sumitomo Esprene 502), 100; BaSO<sub>4</sub>, 100; ZnO, 5.0; dicumyl peroxide (97%), 2.7. Cure: 165°C, 15 min. Mixing ratio of BaSO<sub>4</sub> and CaCO<sub>3</sub> was 100:10 by weight; the specific surface area of the BaSO<sub>4</sub> was 3.47 m<sup>2</sup>/g.

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

### Using Phosphate Coupling Agent

Some other techniques for the modification with the phosphate coupling agents were developed. The spray-dry method employed earlier<sup>13</sup> also proved to be simple and useful. Physical properties of SBR vulcanizates compounded with MHP-spray-dried calcium carbonate are shown in Table VI. Significant improvement in the properties was obtained by using small amounts of the agent.

A further application technique using phosphate coupling agent inherently correlates with the modification process. The agent was treated in a solvent with small amounts of calcium carbonate in the presence of another kind of filler. For example, barium sulfate was mixed with calcium carbonate (100:10 wt/wt) and treated with MPP in water. The modification effects on the EPDM vulcanizates are shown in Table VII.

Thus, the deposition of the calcium salt of the phosphate coupling agent onto inorganic material surface has been revealed to be a novel and effective approach toward the surface activation for chemical reactions such as crosslinking reactions.

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