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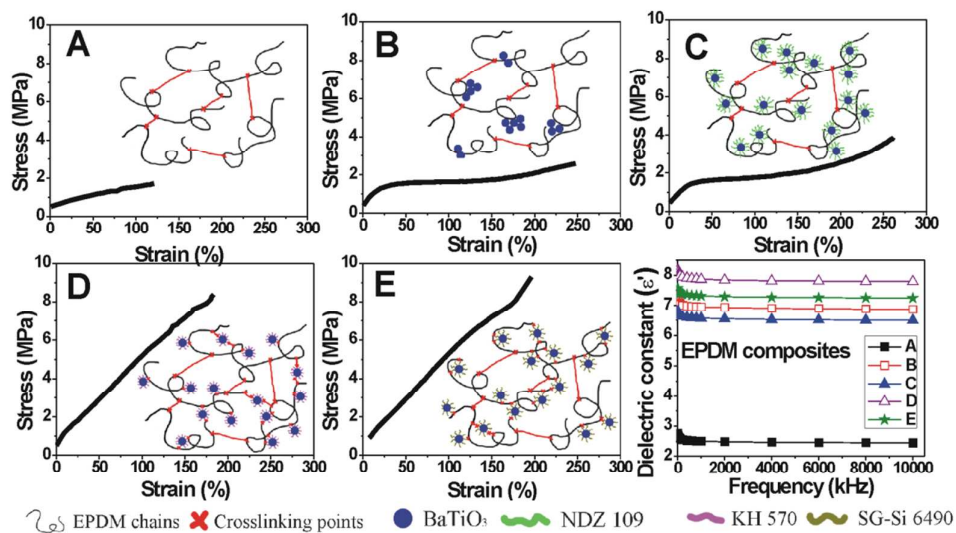
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A: EPDM contol; B: EPDM with untreated BaTiO<sub>3</sub>; C: EPDM with NDZ109 treated BaTiO<sub>3</sub>; D: EPDM with KH570 treated BaTiO<sub>3</sub>; E: EPDM with SG-Si6490 treated BaTiO<sub>3</sub>

Remarkable enhancement of mechanical and dielectric properties of flexible ethylene propylene diene monome (EPDM)/ Barium titanate (BaTiO<sub>3</sub>) dielectric elastomer by chemical modification of particles

Jun Su<sup>a,b</sup>, Jun Zhang<sup>1a</sup>,

<sup>a</sup> Department of Polymer Science and Engineering, College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, People's Republic of China

<sup>b</sup> College of Mechanics Engineering, Nanjing Institute of Industry Tecnology, Nanjing, 210023, People's Republic of China.

## Abstract

In this study, three types of coupling agents, titanium tris(dodecylbenzenesulfonate) isopropoxide (NDZ 109),  $\gamma$ -methacryloxypropyltrimethoxysilane (KH570) and vinyltrimethoxysiloxane homopolymer (SG-Si6490), were utilized to reduce the polar surface energy of Barium titanate (BaTiO<sub>3</sub>) particles from 37.53 mJ/m<sup>2</sup> to 0.77 mJ/m<sup>2</sup>, 16.52 mJ/m<sup>2</sup> and 5.46 mJ/m<sup>2</sup>, respectively. At 30 vol% filler loading, NDZ 109 treated BaTiO<sub>3</sub> with the lowest polar surface tension exhibited the remarkable compatibility with ethylene propylene diene monomer (EPDM) gum showed by bound rubber content. It is found that just 1% (by weight of BaTiO<sub>3</sub> amount) coupling agents SG-Si6490 can raise the tensile strength of EPDM with untreated BaTiO<sub>3</sub> composite from 1.94 MPa to 9.00 MPa, due to the C=C bonds from vinyl groups. In terms of electrical properties, when untreated BaTiO<sub>3</sub> loading was 30vol%, the dielectric constant of EPDM control can increase from about 2 to 7. Moreover, the SG-Si6490 treated BaTiO<sub>3</sub> further improved the dielectric constant of EPDM with untreated BaTiO<sub>3</sub> composite from 7 to around 8. EPDM with NDZ109 treated BaTiO<sub>3</sub> composite exhibited the lowest volume resistivity among EPDM composites.

**Keywords:** Barium titanate (BaTiO<sub>3</sub>), Ethylene propylene diene monomer (EPDM), Surface energy, Vulcanization, Mechanical and electrical properties

## 1. Introduction

Dielectric polymer/ceramic composites are widely used in electronic domain.<sup>1, 2</sup> For example, fluoride polymer/ceramic composites are commonly used as embedded and multilayer capacitors in electronic devices, because polar and rigid matrix of fluoride polymer.<sup>3,4</sup>

Another promising class of dielectric polymer/ceramic composites are dielectric elastomers with high actuated strain, which are capable of transforming under electric field over a wide range of frequency. Therefore, researchers are interested in developing artificial muscles and sensors by the use of dielectric elastomers.<sup>5,6</sup>

One of the commonly used ceramic particles is barium titanate (BaTiO<sub>3</sub>), which is ferroelectric material with perovskite structure and has both high dielectric constant and loss.<sup>7</sup> The disadvantage of BaTiO<sub>3</sub> is brittleness and high dielectric loss.<sup>8</sup>

In literature, polyurethanes have been studied as dielectric elastomers.<sup>9, 10</sup> Compared to them, ethylene propylene diene monomer (EPDM), with saturated and nonpolar backbone, not only has low dielectric constant and loss, but also has excellent resistance to heat, oxidation and solvent.<sup>11</sup> However, EPDM is non-self reinforced rubber. It was often incorporated with fillers, semi-crystallized resins or fibers to improve tensile strength.<sup>12, 13</sup>

Thus, it is interested to find whether the incorporation of EPDM and BaTiO<sub>3</sub> can overcome their individual drawbacks and obtain dielectric elastomers with high dielectric constant, low dielectric loss, enhanced tensile strength and retained flexibility.

Due to different polar surface energy between EPDM matrix and BaTiO<sub>3</sub> particles, the filler tends to aggregate and will influence the overall properties of EPDM composites. It is reported that the application of coupling agents improves the adhesion between rubber and fillers, and reduces agglomeration among fillers at the meantime.<sup>14, 15</sup>

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<sup>1</sup> Correspondence to: Jun Zhang ([zhangjun@njtech.edu.cn](mailto:zhangjun@njtech.edu.cn))

In this work, BaTiO<sub>3</sub> particles were treated by three types of coupling agents with different functional groups to reduce the surface energy and then improve the interactions between EPDM and BaTiO<sub>3</sub> particles. The aim is to select a coupling agent to produce a flexible EPDM/BaTiO<sub>3</sub> elastomer with high tensile strength, high dielectric constant and low dielectric loss. Other properties include polar surface tension, cure characteristics, bound rubber content, crosslink density, mechanical and dielectric properties.

## 2. Experimental

### 2.1 Materials

Ethylene propylene diene monomer (EPDM J-4045) containing 5-ethylidene-2-norbornene (ENB) as diene, was supplied by Jilin Petrochem., Sinopec, China. The EPDM was consisted of 52.0 wt% ethylene, 40.3 wt% propylene and 7.7 wt% ENB. Dicumyl peroxide (DCP), zinc oxide, stearic acid (SA) and 2-Mercapto benzimidazole (MB) were of reagent grade. The chemical names and structures of coupling agents were listed in Table 1. Coupling agents titanium tris(dodecylbenzenesulfonate) isopropoxide (NDZ109),  $\gamma$ -methacryloxypropyltrimethoxysilane (KH570) and vinyltrimethoxysiloxane homopolymer(SG-Si 6490) were supplied by Nanjing Shuguang Chemical Group Co., Ltd., China. Barium titanate (BaTiO<sub>3</sub>) particles were purchased from SongBao Electrically Functional Co., Ltd., Guangdong province, China.

(Table 1)

### 2.2 Sample preparation

#### 2.2.1 Surface modification of BaTiO<sub>3</sub>

NDZ109, KH570 and SG-Si6490 were used to modify the surface of the BaTiO<sub>3</sub> particles, respectively. The content of each coupling agent was 1% by weight (wt%) of BaTiO<sub>3</sub> amount. The 1.0g NDZ109 was firstly mixed with 100 mL isobutanol for 15min. BaTiO<sub>3</sub> (100 g) was then added into the above mentioned solution with a further 30 min stirring. Such mix was poured into the porcelain plate, which was placed into vacuum oven to dry for 4h. In this procedure, only isobutanol solution is vaporized, and all 1wt% coupling agents were physically or chemically adhered to the particle surface. Similarly, KH570 and SG-Si6490 on the BaTiO<sub>3</sub> surface were prepared by the same solution for 100g BaTiO<sub>3</sub> using the same procedure as described above.

Apart from FT-IR measurement, other experiments used the modified BaTiO<sub>3</sub> without further extraction. So, the content of coupling agents on BaTiO<sub>3</sub> surface in EPDM composites is 1wt% of BaTiO<sub>3</sub> mass.

#### 2.2.2 Preparation of EPDM/BaTiO<sub>3</sub> composites

The formulation of EPDM gum containing treated BaTiO<sub>3</sub> were listed in Table 2. The density of EPDM and BaTiO<sub>3</sub> is around 1.0g/cm<sup>3</sup> and 6.1g/cm<sup>3</sup>, respectively. Thus, volume fraction of BaTiO<sub>3</sub> in EPDM/BaTiO<sub>3</sub> composites was about 30vol% according to Table 2. Every EPDM composites were mixed by a two roll mixing mill (Shanghai Rubber Machinery Works, China), according to ISO2393. EPDM gums were vulcanized in an electrically heated press.

(Table 2)

### 2.3 Testing procedures

#### 2.3.1 Fourier Transform Infrared Spectroscopy

The untreated, NDZ109 treated, KH570 treated and SG-Si6490 treated BaTiO<sub>3</sub> particles were firstly extracted by ether solvent in Soxhlet extractor for 4h at 70°C. Then, the extracted BaTiO<sub>3</sub> particles are dried at 40°C for 6 h.

Fourier Transform Infrared (FT-IR) spectra of such extracted BaTiO<sub>3</sub> were gained in Nicolet spectrometer (model NEXUS 670) by using KBr powder. The transmittance spectra of BaTiO<sub>3</sub> were recorded from 4000 to 400 cm<sup>-1</sup>, at the resolution of 2 cm<sup>-1</sup>.

#### 2.3.2 Water contact angle and surface tension

Static water contact angle was tested at 24°C by drop shape analysis system (model DSA 100), purchased by

Krüss, Germany. The contact angle was measured 10 s after the droplets fall on the material surface. Each value was an average of seven tests. The contact angle of diiodomethane was also measured. The surface tension was calculated by Owens and Wendt method, using the contact angles of above mentioned two solvents.

### 2.3.3 Curing characterizations

Curing properties of EPDM gums were tested by an Intelligent Computer Moving Die Rheometer (model MDR 2000), purchased by Wuxi Liyuan Electronic & Chemical Equipment Co., Ltd., China.

### 2.3.4 Crosslink density and bound rubber content

The solvent swell method was applied to measure the crosslink density of EPDM specimens. Samples were firstly immersed in toluene for 48 h at 24°C. The crosslink density was then calculated following Equation (1):

$$\nu = -\frac{1}{V} \left[ \frac{\ln(1-V_R) + V_R + \mu V_R^2}{V_R^{1/3} - \frac{V_R}{2}} \right] \quad (1)$$

where  $\nu$  is the crosslink density of EPDM composites ( $\text{mol} \cdot \text{cm}^{-3}$ ),  $V_R$  is the volume fraction of EPDM rubber after immersion in toluene,  $V$  is the molar volume of toluene solvent ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ),  $\mu$  is the interaction parameter between rubber and toluene solvent (0.49).<sup>16</sup>

The bound rubber content was calculated following Equation (2):

$$R_b(\%) = 100 \times [W_{fg} - W_t[m_f/(m_f+m_r)]] / W_t[m_r/(m_f+m_r)] \quad (2)$$

where  $R_b$  is the bound rubber content of EPDM gums,  $W_{fg}$  the total weight of BaTiO<sub>3</sub> and gel,  $W_t$  the weight of samples,  $m_f$  is the fraction of BaTiO<sub>3</sub> in the EPDM gums,  $m_r$  is the fraction of EPDM in the EPDM gums.

### 2.3.5 Scanning electron microscopy (SEM)

The dispersion of BaTiO<sub>3</sub> was observed with scanning electron microscope (model JEOL JSM-5900). The samples were firstly fractured in liquid nitrogen, and then the fracture surface sputtered with a layer of gold was scanned.

### 2.3.6 Mechanical properties

The tensile tests were completed by using electromechanical universal testing machine (model CMT 5254 type), purchased from Shengzhen SANS Testing Machine Co., Ltd., China, according to ISO37 and ISO34. The testing rate is 500mm/min. The testing temperature and humidity is 23°C and 50%RH. The Shore A hardness of the specimens was tested with a rubber Shore A hardness degree tester (model: LX-A), purchased from Jiangsu Mingzhu Testing Machinery Co., Ltd., China, following ISO 868.

### 2.3.7 Dielectric constant and dielectric loss

According to IEC 60250, the dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) were measured by Agilent Precision Impedance Analyzer (model 4294A), at 23°C and 50%RH. Samples with 20mm diameter were placed between silver electrode to test.

### 2.3.8 Volume and surface resistivity

According to IEC 60093, the volume and surface resistivity of EPDM composites were tested by a high-insulation resistance meter, purchased by Shanghai Precision & Scientific Instrument Co., Ltd., China.

## 3. Results and discussion

### 3.1 FT-IR analysis

The FT-IR spectra are used to detect the type of functional groups on the surface of BaTiO<sub>3</sub> particles before surface treatment and after extraction. The purpose of FT-IR spectra is to evaluate whether there is chemical adherence of coupling agents to the BaTiO<sub>3</sub> surface. In Figure 1, it is observed that three types of coupling agents all absorb at bands 2925 $\text{cm}^{-1}$  and 2854 $\text{cm}^{-1}$ . These two bands are assigned to asymmetric stretching vibration of

methylene and symmetric stretching vibration of methylene, respectively.<sup>1,4,17</sup>

Additionally, the coupling agent NDZ109 has characteristic peak at  $1601\text{cm}^{-1}$ , assigned to skeletal vibration of phenyl group.<sup>18</sup> As for KH570, a characteristic absorption peak appeared at  $1637\text{cm}^{-1}$  and is assigned to C=C stretching vibration. In terms of SG-Si6490, the band characteristically absorbs at  $1076\text{cm}^{-1}$ , assigned to Si-O-C rocking vibration.<sup>19-21</sup>

Figure 2 shows spectra of treated  $\text{BaTiO}_3$  after extraction. Although some of the characteristic peaks mentioned above are not obvious, the peaks at  $2925\text{cm}^{-1}$  and  $2854\text{cm}^{-1}$  can prove the adherence of coupling agents to the surface of  $\text{BaTiO}_3$  particles.

Moreover, there is a peak appearing at  $3525\text{cm}^{-1}$ , which is the stretching vibration of the -OH group.<sup>6,10</sup> In literature,<sup>22</sup> alkoxy groups can alcoholize with hydroxyl groups on particle surface and generate strong interaction between particles and coupling agents. Thus, it can confirm the adherence of coupling agents (NDZ109, KH570 and SG-Si6490) to  $\text{BaTiO}_3$  surface, respectively.

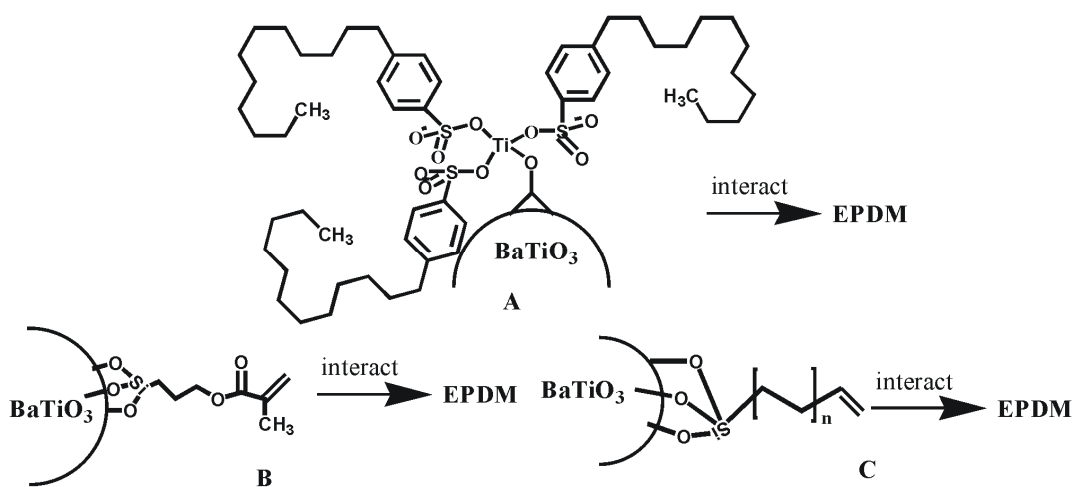
(Figure 1)

(Figure 2)

### 3.2 Water contact angle and surface tension measurement

Water contact angles and surface tension of  $\text{BaTiO}_3$  are listed in Figure 3 and Table 3, respectively. It is obvious that the water contact angle of untreated  $\text{BaTiO}_3$  can be greatly boosted by the surface modification. The polar surface tension, calculated by Owens and Wendt method, follows the order: untreated  $\text{BaTiO}_3 > \text{KH570}$  treated  $\text{BaTiO}_3 > \text{SG-Si6490}$  treated  $\text{BaTiO}_3 > \text{NDZ109}$  treated  $\text{BaTiO}_3$ . The results show that the polarity of functional groups in coupling agents follows the order: methacryloxypropyl groups from KH570  $>$  vinyl groups from SG-Si6490  $>$  dodecylbenzenesulfonate groups from NDZ109.

Scheme 1 illustrate the interaction of treated  $\text{BaTiO}_3$  with EPDM matrix. The reason for polarity differences is that the dodecylbenzenesulfonate group in NDZ109 has non-polar dodecyl and benzene groups, which can cover the surface of  $\text{BaTiO}_3$  particles to the most degree, changing the surface of  $\text{BaTiO}_3$  particles from hydrophilic to hydrophobic.<sup>2,11</sup> By comparison, oligomer SG-Si6490 possesses non-polar long carbon chains and polar vinyl groups rather than non-polar benzene groups, making the polar surface tension a little higher than NDZ109 treated  $\text{BaTiO}_3$ . In terms of methacryloxypropyl groups in KH570, due to the lack of long molecular chains and presence of polar acryloxy group, the polar surface tension of KH570 treated  $\text{BaTiO}_3$  is further increased.



Scheme 1 Interaction of treated  $\text{BaTiO}_3$  with EPDM matrix: A. NDZ109 treated  $\text{BaTiO}_3$ ; B. KH570 treated  $\text{BaTiO}_3$ ; C. SG-Si6490 treated  $\text{BaTiO}_3$ .

(Figure 3)

(Table 3)

### 3.3 Effect of coupling agents on dispersion properties of BaTiO<sub>3</sub> in organic solvents

Figure 4 shows dispersion of untreated BaTiO<sub>3</sub> and treated BaTiO<sub>3</sub> in two-phase solvent. Due to higher density, distilled water is at the bottom, while n-octane is at the upper layer. It is observed that the untreated BaTiO<sub>3</sub> shows hydrophilic properties, while treated BaTiO<sub>3</sub> all show oleophilic properties. This is because untreated BaTiO<sub>3</sub> has -OH group on particle surface. The alkoxy groups from NDZ109, KH570 and SG-Si6490 all can react with -OH group on the surface of BaTiO<sub>3</sub> particle, making the surface of BaTiO<sub>3</sub> particles full of dodecyl, vinyl and acryloxy, respectively. Thus, the treated BaTiO<sub>3</sub> particles all suspended well in n-octane solvent.

(Figure 4)

### 3.4 Effect of coupling agents on bound rubber of EPDM gums

The bound rubber content of EPDM gums are listed in Table 4. The bound rubber content of EPDM gums follows the order: EPDM with untreated BaTiO<sub>3</sub> < EPDM with KH570 treated BaTiO<sub>3</sub> < EPDM with SG-Si6490 treated BaTiO<sub>3</sub> < EPDM with NDZ109 treated BaTiO<sub>3</sub>. It has been discussed that the surface modification can bring functional groups on the surface of BaTiO<sub>3</sub>, lowering the polar surface energy of BaTiO<sub>3</sub> particles. Because EPDM matrix is a nonpolar material, BaTiO<sub>3</sub> particles which have lower polar surface energy are more compatible with EPDM matrix.

It is observed in scheme 1 that NDZ109 possesses non-polar dodecyl and benzene groups, so the bound rubber of EPDM with NDZ109 treated BaTiO<sub>3</sub> is the highest.<sup>8</sup> Although oligomer SG-Si6490 has polar vinyl groups, it also long hydrocarbon chains. Like dodecyl groups, such polar and long hydrocarbon chains can physically entangle with EPDM matrix to increase the compatibility with EPDM, leading to the relatively higher bound rubber content.<sup>5,9</sup> Because of the lack of long molecular chains, the polar acryloxy group mainly reduce the compatibility of KH570 treated BaTiO<sub>3</sub> with EPDM matrix. In this way, the bound rubber content of EPDM with NDZ109 treated BaTiO<sub>3</sub> further decreases..

(Table 4)

### 3.5 Effect of coupling agents on cure properties of EPDM gums

The cure characteristics of EPDM with BaTiO<sub>3</sub> treated by three types of coupling agents are shown in Figure 5 and Table 5. The first decline of torque cure is due to the softening of EPDM gums at 170°C. Because of the generation of cross-linking bonds among macromolecular chains, the torque gradually grows.<sup>23</sup>

It is observed that ultimate cure state of mixes indicated by maximum torque ( $M_H$ ) and cure rate, obeys the sequence: EPDM with KH570 treated BaTiO<sub>3</sub> > EPDM with SG-Si6490 treated BaTiO<sub>3</sub> > EPDM with NDZ109 treated BaTiO<sub>3</sub> > EPDM with untreated BaTiO<sub>3</sub> > EPDM control.

Generally, the rise of  $M_H$  and cure rate can be ascribed to two possible reasons: increased physical entanglement of particles with rubber gums and increased chemical bonds formed.<sup>3</sup> The incorporation of untreated BaTiO<sub>3</sub> particles can increase the  $M_H$  and cure rate of EPDM composites. This is because that untreated BaTiO<sub>3</sub> can partially and physically adhere to the EPDM matrix. As for NDZ109 treated BaTiO<sub>3</sub>, the physical adherence of particles to EPDM matrix is much stronger than untreated BaTiO<sub>3</sub>, proved by bound rubber content measurement.<sup>7</sup> So the  $M_H$  and cure rate of EPDM with NDZ109 treated BaTiO<sub>3</sub> are higher than those of EPDM with NDZ109 treated BaTiO<sub>3</sub>.

It has been proved that surface modification of BaTiO<sub>3</sub> can endow particle surface with certain functional groups from coupling agents.<sup>22</sup> In terms of SG-Si6490, the C=C of vinyl groups can cleave and generate active carbon radicals to form extra chemical crosslink bonds, making the  $M_H$  and cure rate of EPDM with SG-Si6490 treated BaTiO<sub>3</sub> higher than those of EPDM with NDZ109 BaTiO<sub>3</sub> particles.<sup>12</sup>

Similarly, KH570 introduces methoxy groups that can dehydrate with hydroxyl on the surface of BaTiO<sub>3</sub>,

introducing C=C groups at the same time. The C=C groups from KH570 can participate into cure process and react with unsaturated groups in EPDM, leading to the rise of  $M_H$  and cure rate.<sup>15</sup>

Although both KH570 and SG-Si6490 have the C=C groups, the differences between  $M_H$  and cure rate of them are greater. SG-Si6490 is oligomer, so there is lower concentration of C=C groups in SG-Si6490 than that in KH570. Therefore, there are less C=C groups in SG-Si6490 to generate chemical cross-linking points, making the  $M_H$  and cure rate of EPDM with SG-Si6490 treated  $BaTiO_3$  lower than those of EPDM with KH570 treated  $BaTiO_3$ .<sup>13</sup>

Scorch time indicates the premature vulcanization of EPDM matrix. It is observed from the Table 5 that the addition of untreated and treated  $BaTiO_3$  can all shorten scorch time, meaning the reduced scorch safety of EPDM composites.<sup>23, 24</sup>

(Figure 5)

(Table 5)

### 3.6 Effect of coupling agents on crosslink density of EPDM composites

The crosslink density of EPDM control and EPDM/ $BaTiO_3$  composites are listed in Table 6 and follow the order: EPDM with KH570 treated  $BaTiO_3$  > EPDM with SG-Si6490 treated  $BaTiO_3$  > EPDM with NDZ109 treated  $BaTiO_3$  > EPDM control  $\approx$  EPDM with untreated  $BaTiO_3$ . This result partially confirms the trend of  $M_H$ .

Although EPDM with untreated  $BaTiO_3$  has higher  $M_H$  value than EPDM control, the crosslink density of EPDM with untreated  $BaTiO_3$  is almost the same as that of EPDM control. The reason is that the  $M_H$  value is not only correlated with the variation of chemical crosslink density but also affected by the physical entanglement of  $BaTiO_3$  particles with EPDM gums. It seems that the incorporation of untreated  $BaTiO_3$  can partially enhance the physical entanglement with EPDM gums and then boost the  $M_H$ , without affecting the chemical crosslink density of EPDM composites.<sup>25</sup>

In terms of NDZ109, the dodecyl can physically entangle with EPDM matrix, making  $BaTiO_3$  particles physically adhere to the EPDM matrix. In this way, such physical entanglement slightly increases crosslink density of EPDM with NDZ109 treated  $BaTiO_3$ .<sup>13</sup>

When the surface of  $BaTiO_3$  has been modified by KH570 and SG-Si6490, the functional groups adhered to the surface of filler particles can participate into the vulcanization process and form chemical bonds between  $BaTiO_3$  particles and EPDM matrix, raising both  $M_H$  value and chemical crosslink points.<sup>25, 26</sup>

(Table 6)

### 3.7 Effect of coupling agents on $BaTiO_3$ dispersion in EPDM composites

Scanning electron micrographs (Figure 6) are utilized to illustrate the effect of coupling agents on  $BaTiO_3$  particles dispersion. Due to strong hydrogen bonding formed by hydroxyl on  $BaTiO_3$  particles surface, the untreated  $BaTiO_3$  has a trend to agglomerate. After surface treatment by KH570 and SG-Si6490, it is observed that  $BaTiO_3$  can be embedded in the EPDM matrix to some extent, showing the improvement of interfacial adhesion. The reason is that the functional groups of KH570 and SG-Si6490 on surface of  $BaTiO_3$  particles can generate chemical bonds with EPDM matrix, proved by crosslink density results. This is also consistent with earlier reports,<sup>27, 28</sup> in which coupling agents can improve the filler dispersion and reduce agglomeration of particles.

(Figure 6)



### 3.8 Effect of coupling agents on mechanical properties of EPDM composites

Data of mechanical properties of EPDM with three types of coupling agents treated BaTiO<sub>3</sub> are listed in Table 7. The addition of untreated BaTiO<sub>3</sub> can greatly increase the hardness, but slightly increase the 100% modulus and tensile strength. Moreover, the surface modification of BaTiO<sub>3</sub> by coupling agents can further increase the hardness, 100% modulus and tensile strength of EPDM composites to some degree.

Figure 7 illustrates the strain-stress curves of EPDM composites as well as the dispersion models of BaTiO<sub>3</sub> particles in EPDM matrix. The addition of untreated BaTiO<sub>3</sub> can not increase the 100% modulus and tensile strength of EPDM composites because of the agglomeration of BaTiO<sub>3</sub> particles in EPDM matrix. It is also observed that the weak and physical adherence of untreated BaTiO<sub>3</sub> particles to EPDM matrix can increase the elongation at break from 119% to 252%.

The treatment of coupling agent NDZ109 brings slight increase on mechanical properties of EPDM composites, because the crosslink density of EPDM with NDZ109 treated BaTiO<sub>3</sub> is slightly higher than that of EPDM with untreated BaTiO<sub>3</sub>. The dodecyl on BaTiO<sub>3</sub> particles can not only prevent BaTiO<sub>3</sub> from agglomerating, but also can physically entangle with EPDM matrix. In this way, the elongation at break and tensile strength of EPDM with NDZ109 treated BaTiO<sub>3</sub> have a little increase compared with EPDM with untreated BaTiO<sub>3</sub>.<sup>9, 29</sup>

In addition, EPDM with KH570 and SG-Si6490 treated BaTiO<sub>3</sub> all show higher tensile and tear strength than EPDM with untreated and NDZ109 treated BaTiO<sub>3</sub>. This is because both KH570 and SG-Si6490 have C=C bonds, which can generate chemical cross-linking points between BaTiO<sub>3</sub> particles and EPDM matrix. Thereby, crosslink density, modulus at 100% and tensile strength of EPDM composites all increase. In addition, the functional groups of SG-Si6490 on BaTiO<sub>3</sub> has long hydrocarbon chains, which have more physical entanglement with EPDM matrix than KH570 treated BaTiO<sub>3</sub>. In this way, although EPDM with SG-Si6490 treated BaTiO<sub>3</sub> has lower crosslink density than EPDM with KH570 treated BaTiO<sub>3</sub>, the tensile strength of the former is a little higher than the latter.

Compared to EPDM with untreated BaTiO<sub>3</sub>, surface treatment of BaTiO<sub>3</sub> with KH570 and SG-Si6490 can lower the elongation at break. This can be explained by the fact that the extra formed C-C linkage are much rigid.<sup>12</sup> Thus, EPDM with KH570 and SG-Si6490 treated BaTiO<sub>3</sub> exhibit lower value of elongation at break than EPDM with untreated BaTiO<sub>3</sub>.

(Table 7)

(Figure 7)

### 3.9 Effect of coupling agents on dielectric properties

EPDM is generally used as an insulator because of its non-polar backbone structure.<sup>30</sup> In literature, the addition of inorganic fillers can enhance the conductivity of polymer.<sup>31</sup> Figure 8 and 9 show curves of relative dielectric constant and dielectric loss of EPDM composites in the following order: EPDM with KH570 treated BaTiO<sub>3</sub> > EPDM with SG-Si6490 treated BaTiO<sub>3</sub> > EPDM with untreated BaTiO<sub>3</sub> > EPDM with NDZ109 treated BaTiO<sub>3</sub> > EPDM control.

Due to the presence of BaTiO<sub>3</sub> particles, there is interfacial polarization at the interface between BaTiO<sub>3</sub> and EPDM matrix. Generally, the relative dielectric constant is mainly correlated with the ability to polarize. The relative dielectric constant can change with the variation of polarizability. Thus, the results of surface tension of functional groups on the surface of BaTiO<sub>3</sub> can support the results of relative dielectric constant of EPDM composites.<sup>20, 21</sup>

The surface modification of BaTiO<sub>3</sub> can increase the dielectric loss of EPDM composites. The dielectric loss values of EPDM composites follow the order: EPDM with KH570 treated BaTiO<sub>3</sub> > EPDM with SG-Si6490 treated BaTiO<sub>3</sub> > EPDM with NDZ109 treated BaTiO<sub>3</sub> ≈ EPDM with untreated BaTiO<sub>3</sub> ≈ EPDM control. The dielectric loss tangent is ascribed to the viscous drag of BaTiO<sub>3</sub> particles which correlates with polar surface tension of particles. The higher the polarity on surface of BaTiO<sub>3</sub> particles can cause higher value of dielectric loss tangent.

In addition, the relative dielectric constant of EPDM with various coupling agents remain almost unchanged in the frequency range of 20 kHz ~ 10 MHz, while dielectric loss decline in that range.

Fig.10 shows the dielectric loss factor (defined as  $\tan\delta=\varepsilon''/\varepsilon'$ ) of EPDM composites. It is shown that the dielectric loss factors of EPDM composites are close to each other, and that EPDM with KH570 treated BaTiO<sub>3</sub> has the highest dielectric loss factor among all EPDM composites.

In literatures, Cole-Cole model and Debye relaxation are often used to evaluate the dielectric properties of composites.<sup>32-36</sup> Cole-Cole semicycles are often shown by the plot of dielectric constant versus dielectric loss.<sup>29</sup> Fig.11 illustrates the curves of dielectric loss versus dielectric constant of EPDM samples. There are Cole-Cole semicycles found for EPDM with untreated BaTiO<sub>3</sub>, EPDM with KH570 treated BaTiO<sub>3</sub> and EPDM with SG-Si6490 treated BaTiO<sub>3</sub> composites. Every semicycle can be correlated to one Debye relaxation, due to the interfacial polarization. NDZ109 treated BaTiO<sub>3</sub> possesses the lowest polar surface energy, so there is not obvious semicycle found in curves of EPDM with NDZ109 treated BaTiO<sub>3</sub> composites, meaning the interfacial polarization between NDZ109 treated BaTiO<sub>3</sub> and EPDM matrix is the lowest.

(Figure 8)

(Figure 9)

(Figure 10)

(Figure 11)

### 3.10 Effect of filler loading on surface and volume resistivity of EPDM composites

Resistivity can indicate the resistance of materials to the passing of current carrier.<sup>25, 26</sup> Table 8 shows the surface and volume resistivity of EPDM composites. It is observed that the incorporation of 30vol% untreated BaTiO<sub>3</sub> can greatly decrease the volume resistivity of EPDM control by two orders of magnitude. Only EPDM with NDZ109 treated BaTiO<sub>3</sub> further decreases one order of magnitude of volume and surface resistivity. This is correlated with bound rubber content. Higher bound rubber content means more EPDM matrix adhere to the particle surface, leading to more electric passage. In this way, the volume resistivity decreases.

(Table 8)

## 4. Conclusions

The incorporation of treated BaTiO<sub>3</sub> in EPDM can both enhance tensile strength and dielectric constant without greater increase of dielectric loss. It is found that just 1% (by weight of BaTiO<sub>3</sub> amount) coupling agents SG-Si6490 can raise the tensile strength of EPDM with untreated BaTiO<sub>3</sub> from 1.94 MPa to 9.00 MPa, because the C=C bonds from vinyl groups in SG-Si6490 can participate into cure process and generate chemical bonds between BaTiO<sub>3</sub> particles and EPDM matrix, greatly enhancing crosslink density of EPDM composites.

When the filler loading of untreated BaTiO<sub>3</sub> is at 30vol%, the dielectric constant of EPDM control can increase from around 2 to 7 at 10 MHz. Moreover, KH570 and SG-Si6490 treated BaTiO<sub>3</sub> particles can further increase the dielectric constant from 7 to around 8. However, compared to untreated BaTiO<sub>3</sub>, NDZ109 treated BaTiO<sub>3</sub> particles can decrease the dielectric constant and loss of EPDM composites. As for some EPDM composites, there are Cole-Cole semicycles shown in curves of dielectric constant versus dielectric loss, due to strong interfacial polarization.

The surface treatment of BaTiO<sub>3</sub> with coupling agents can introduce functional groups to particle surface and reduce the polar surface tension of BaTiO<sub>3</sub> particles, shown by the contact angle results. The non-polar dodecyl and benzene groups in NDZ109 can lower the polar surface energy of BaTiO<sub>3</sub> from 37.53 mJ/m<sup>2</sup> to 0.77 mJ/m<sup>2</sup>.

The decreased polar surface tension can increase the bound rubber content of EPDM gum and decrease the volume resistivity of EPDM to the greatest extent. The dispersion properties show that treated BaTiO<sub>3</sub> change from hydrophilic to oleophilic. The SEM results show that the interaction between filler and EPDM has been improved.

## Acknowledgements

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1. A. Allahbakhsh and S. Mazinanib, *RSC Adv.*, 2015, **5**, 46694-46699.
2. C. Jia, Z. Shao, H. Fan and J. Wang, *RSC Adv.*, 2015, **5**, 15283.
3. S. Liu, S. Xiao, S. Xiu, B. Shen, J. Zhai and Z. An, *RSC Adv.*, 2015, **5**, 40692.
4. B. Chen, N. Ma, X. Bai, H. Zhang and Y. Zhang, *RSC Adv.*, 2012, **2**, 4386-4689.
5. W. Lei, R. Wang, D. Yang, G. Hou, X. Zhou, H. Qiao, W. Wang, M. Tiana and L. Zhang, *RSC Adv.*, 2015, **5**, 47429.
6. P. Dey, K. Naskar, B. Dash, S. Nair, G. Unnikrishnanb and G. B. Nando, *RSC Adv.*, 2014, **4**, 35879.
7. S. Liu and J. Zhai, *RSC Adv.*, 2014, **4**, 40973.
8. M.-F. Lin, V. K. Thakur, E. J. Tanb and P. S. Lee, *RSC Adv.*, 2011, **1**, 576-578.
9. Y. Kim, O. N. L. Smith, M. Kathaperumal, L. R. Johnstone, M.-J. Panc and J. W. Perry, *RSC Adv.*, 2014, **4**, 19668.
10. C. Ehrhardt, C. Fettkenhauer and J. Glenneberg, *RSC Adv.*, 2014, **4**, 40321.
11. X. Hu, H. Gao, X. Zhou, Y. Cui and H. Ge, *RSC Adv.*, 2014, **4**, 13662.
12. J. Su, S. Chen, J. Zhang and Z. Xu, *Polym. Test.*, 2009, **28**, 419-427.
13. J. Su, S. Chen, J. Zhang and Z. Xu, *Polym. Test.*, 2009, **28**, 235-242.
14. S. O. Pongdhorn, T. Uthai and H. Kannika, *Polym. Test.*, 2004, **23**, 397-403.
15. N. Alkadasi, D. G. Hundiwale and U. R. Kapadi, *Polym. Plast. Technol. Eng.*, 2006, **45**, 415-420.
16. J. Brandrup, E. H. Immergut and E. A. Grulke, *Polymer Handbook*, 1999, Wiley-Interscience, New York.
17. S. Chen, J. Zhang and J. Su, *J. Appl. Polym. Sci.*, 2009, **114**, 3110-3117.
18. Q. Zhao, X. Li and J. Gao, *Polym. Degrad. Stab.*, 2007, **92**, 1841-1846.
19. W. Z. Wang and B. J. Qu, *Polym. Degrad. Stab.*, 2003, **81**, 531-537.
20. Z. D. Liu, Y. Feng and W. L. Li, *RSC Adv.*, 2015, **5**, 29017.
21. H. Luo, D. Zhang, L. Wang, C. Chen, J. Zhou and K. Zhou, *RSC Adv.*, 2015, **5**, 52809.
22. K. Nagata, Y. Takahashi, S. Shibusawa and Y. Nakamura, *J. Adhes. Sci. Technol.*, 2002, **16**, 1017-1026.
23. H. K. Rahiman, G. Unnikrishnan, A. Sujith and C. K. Radhakrishnan, *Mater. Lett.*, 2005, **59**, 633-639.
24. C. Nakason, P. Wannavilai and A. Kaesaman, *Polym. Test.*, 2006, **25**, 34-41.
25. J. Su, S. Chen, J. Zhang and Z. Xu, *J. Reinf. Plast. Comp.*, 2010, **29**, 2946-2960.
26. J. Su, S. Chen, J. Zhang and Z. Xu, *J. Appl. Polym. Sci.*, 2010, **117**, 1741-1749.
27. S. O. Pongdhorn, S. Chakrit, T. Uthai and H. Kannika, *Polym. Test.*, 2004, **23**, 871-879.
28. S. O. Pongdhorn, S. Chakrit, H. Kannika and T. Uthai, *Polym. Test.*, 2005, **24**, 439-446.

29. K. Hayashida, *RSC Adv.*, 2013, **3**, 221-227.
30. W. Zheng and S. C. Wong, *Compos. Sci. Technol.*, 2003, **63**, 225-235.
31. J. Su, S. Chen, J. Zhang and Z. Xu, *J. Appl. Polym. Sci.*, 2010, **122**, 3277-3289.
32. S. Bandyopadhyay and A. Dutta, *RSC Adv.*, 2015, **5**, 65123-65132.
33. C. Grosse, *J. Colloid Interf. Sci.*, 2014, **419**, 102-106.
34. M. Ramar, P. Tyagi, C. K. Suman and R. Srivastava, *RSC Adv.*, 2014, **4**, 51256-51261.
35. M. Smari, H. Rahmouni, N. Elghoul, I. Walha, E. Dhahri and K. Khirouni, *RSC Adv.*, 2015, **5**, 2177-2184.
36. K. Sasaki, K. Wake and S. Watanabe, *Radio Sci.*, 2014, **49**, 459-472.

Table 1 Chemical/commercial names and structures of three coupling agents

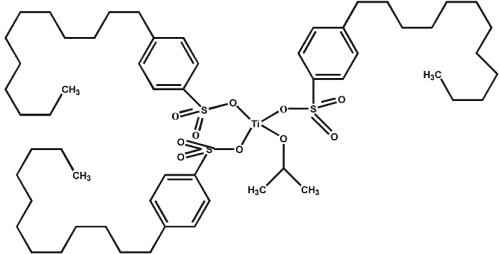
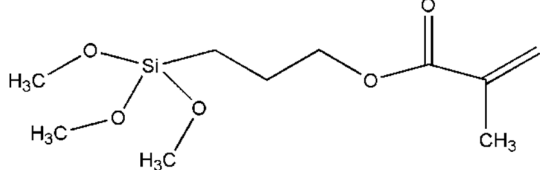
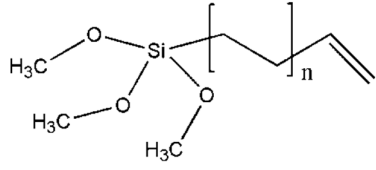
Chemical/commercial name	Molecular formation and structure
<p style="text-align: center;">Titanium tris(dodecylbenzenesulfonate)isopropoxide (NDZ 109)</p>	<p style="text-align: center;"><math>C_{57}H_{94}O_{10}S_3Ti</math></p> 
<p style="text-align: center;"><math>\gamma</math>-methacryloxypropyltrimethoxysilane (KH570)</p>	<p style="text-align: center;"><math>C_{10}H_{20}O_5Si</math></p> 
<p style="text-align: center;">vinyltrimethoxysiloxane homopolymer(SG-Si6490)</p>	

Table 2 Formulation of EPDM/BaTiO<sub>3</sub> composites used in this study (phr)

EPDM	Control	Untreated BaTiO <sub>3</sub>	NDZ109 treated BaTiO <sub>3</sub>	KH570 treated BaTiO <sub>3</sub>	SG-Si 6490 treated BaTiO <sub>3</sub>	ZnO	SA	DCP	MB
100						5	1	4	1
100		260				5	1	4	1
100			260			5	1	4	1
100				260		5	1	4	1
100					260	5	1	4	1

Table 3 Surface tension of untreated and treated BaTiO<sub>3</sub>

Sample	Surface tension (mJ/m <sup>2</sup> )		
	$\gamma_s$	$\gamma_s^d$	$\gamma_s^p$
Untreated BaTiO <sub>3</sub>	75.37	37.84	37.53
109-treated BaTiO <sub>3</sub>	37.19	36.42	0.77
570-treated BaTiO <sub>3</sub>	77.51	60.99	16.52
6490-treated BaTiO <sub>3</sub>	36.48	31.02	5.46

$\gamma_s$ : solid surface tension;  $\gamma_s^d$ :dispersive solid surface tension;  $\gamma_s^p$ :polar solid surface tension.

Table 4 Bound rubber content of EPDM gums

Sample	Bound rubber content (%)
EPDM with untreated BaTiO <sub>3</sub>	26
EPDM with NDZ109 treated BaTiO <sub>3</sub>	35
EPDM with KH570 treated BaTiO <sub>3</sub>	29
EPDM with SG-Si6490 treated BaTiO <sub>3</sub>	32



Table 5 Cure characteristics of EPDM with and without BaTiO<sub>3</sub>

Sample	M <sub>L</sub> N·m	t <sub>ML</sub> min	M <sub>H</sub> N·m	t <sub>MH</sub> min	t <sub>s2</sub> min	t <sub>90</sub> min	Cure rate N·m·min <sup>-1</sup>
EPDM control	0.097	0.68	1.11	14.90	1.40	7.90	0.0713
EPDM with untreated BaTiO <sub>3</sub>	0.13	0.17	1.93	14.98	0.90	7.22	0.1215
EPDM with NDZ109 treated BaTiO <sub>3</sub>	0.16	0.47	2.52	14.82	0.93	7.13	0.1643
EPDM with KH570 treated BaTiO <sub>3</sub>	0.16	0.18	2.80	14.53	0.97	7.27	0.1843
EPDM with SG-Si6490 treated BaTiO <sub>3</sub>	0.21	0.23	2.49	15.00	0.91	9.73	0.1572

M<sub>L</sub>: minimum torque; t<sub>ML</sub>: time to minimum torque; M<sub>H</sub>: maximum torque; t<sub>MH</sub>: time to maximum torque; t<sub>s2</sub>: scorch time; t<sub>90</sub>: optimum cure time; Cure rate: (M<sub>H</sub> - M<sub>L</sub>) / (t<sub>90</sub> - t<sub>s2</sub>).

Table 6 Crosslink density of mixes with various coupling agents

Sample	Crosslink density ( $\text{mol}\cdot\text{cm}^{-3}$ )
EPDM control	0.000155
EPDM with untreated $\text{BaTiO}_3$	0.000147
EPDM with NDZ109 treated $\text{BaTiO}_3$	0.000185
EPDM with KH570 treated $\text{BaTiO}_3$	0.000530
EPDM with SG-Si6490 treated $\text{BaTiO}_3$	0.000493

Table 7 Mechanical properties of EPDM with and without BaTiO<sub>3</sub>

Sample	Hardness Shore A	Modulus at 100% MPa	Tensile strength MPa	Elongation at break %	Tear strength kN/m
EPDM control	51	1.34±0.06	1.45±0.18	119±30	8.73±1.58
EPDM with untreated BaTiO <sub>3</sub>	65	1.53±0.11	1.94±0.48	252±32	9.53±0.79
EPDM with NDZ109 treated BaTiO <sub>3</sub>	68	1.59±0.06	3.23±0.44	251±17	9.26±1.15
EPDM with KH570 treated BaTiO <sub>3</sub>	74	4.88±0.14	8.29±0.89	182±7	19.87±2.15
EPDM with SG-Si6490 treated BaTiO <sub>3</sub>	74	4.21±0.08	9.00±0.52	196±9	21.06±2.48

Table 8 Surface and volume resistivity of EPDM composites

Sample	EPDM Control	EPDM with untreated BaTiO <sub>3</sub>	EPDM with NDZ109 treated BaTiO <sub>3</sub>	EPDM with KH570 treated BaTiO <sub>3</sub>	EPDM with SG-Si6490 treated BaTiO <sub>3</sub>
Volume resistivity (Ω·m)	$1.57 \times 10^{15}$	$1.49 \times 10^{13}$	$2.87 \times 10^{12}$	$3.38 \times 10^{13}$	$1.42 \times 10^{13}$
Surface resistivity (Ω)	$5.01 \times 10^{12}$	$1.46 \times 10^{12}$	$3.85 \times 10^{11}$	$3.47 \times 10^{11}$	$1.93 \times 10^{11}$

**Figure captions**

Fig.1 FT-IR spectra of three coupling agents

Fig.2 FT-IR spectra of treated BaTiO<sub>3</sub> after extraction

Fig.3 Water contact angles of BaTiO<sub>3</sub>

Fig.4 Dispersion of powders in a two-phase solvent, the bottom layer solvent is deionized water and the upper layer solvent is *n*-octane: A. Untreated BaTiO<sub>3</sub>; B. NDZ109 treated BaTiO<sub>3</sub>;C.

KH570 treated BaTiO<sub>3</sub>;D. SG-Si6490 treated BaTiO<sub>3</sub> .

Fig. 5 Cure curves of EPDM composites

Fig. 6 SEM micrographs of EPDM vulcanizates with various coupling agents, A: EPDM with untreated BaTiO<sub>3</sub>; B: EPDM with NDZ109 treated BaTiO<sub>3</sub>; C: EPDM with KH570 treated BaTiO<sub>3</sub>;

D: EPDM with SG-Si6490 treated BaTiO<sub>3</sub>

Fig. 7 Strain-stress curves and dispersion models of BaTiO<sub>3</sub> particles in EPDM composites, A:

EPDM control; B: EPDM with untreated BaTiO<sub>3</sub>; C: EPDM with NDZ109 treated BaTiO<sub>3</sub>; D:

EPDM with KH570 treated BaTiO<sub>3</sub>; E: EPDM with SG-Si6490 treated BaTiO<sub>3</sub>

Fig.8 Relative dielectric constant of EPDM with treated BaTiO<sub>3</sub>

Fig.9 Dielectric loss of EPDM with treated BaTiO<sub>3</sub>

Fig.10 Dielectric loss factor of EPDM composites

Fig.11 Curves of dielectric constant versus dielectric loss of EPDM composites

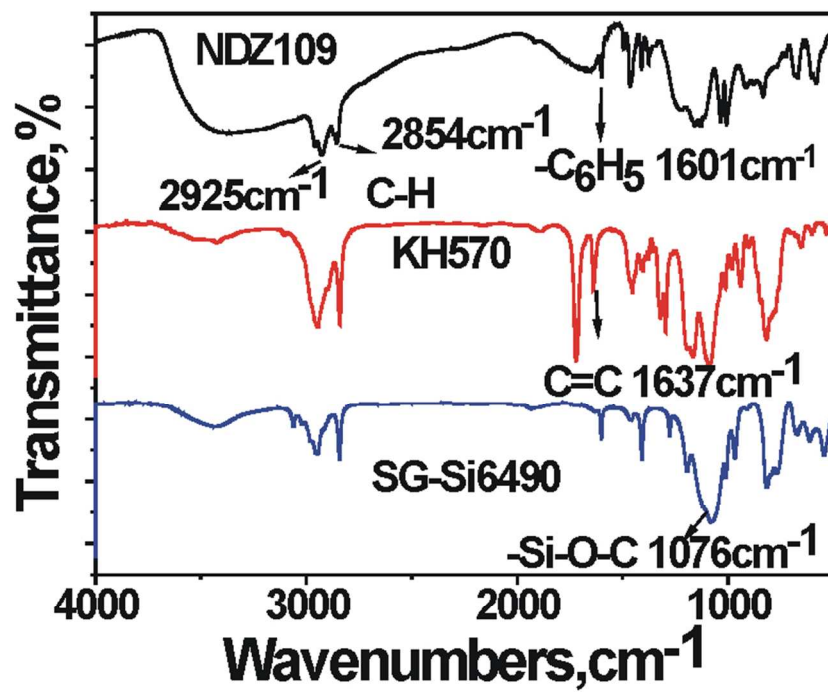


Fig.1 FT-IR spectra of three coupling agents  
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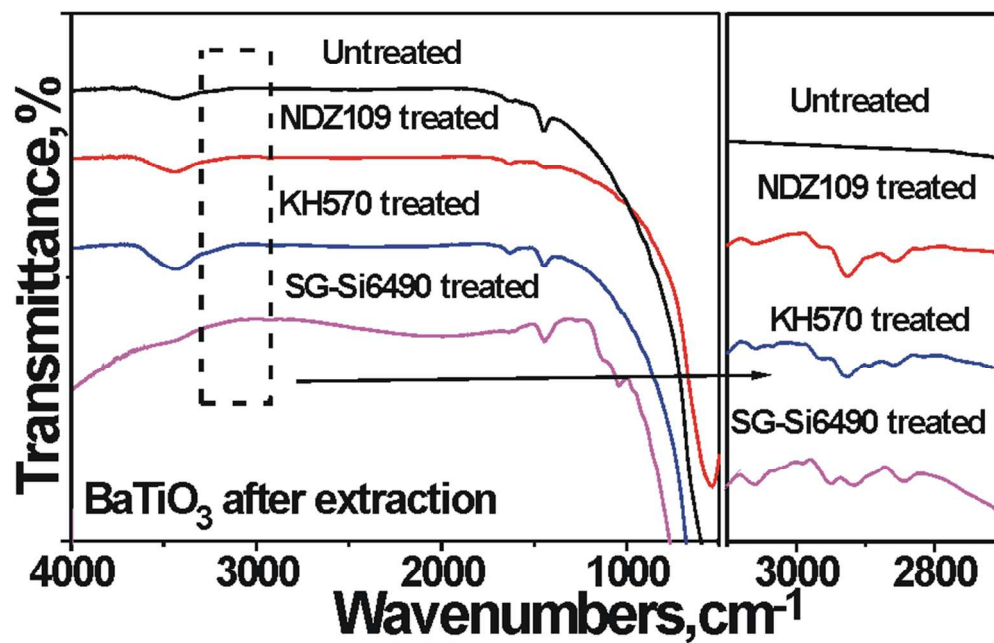


Fig.2 FT-IR spectra of treated BaTiO<sub>3</sub> after extraction  
79x56mm (300 x 300 DPI)

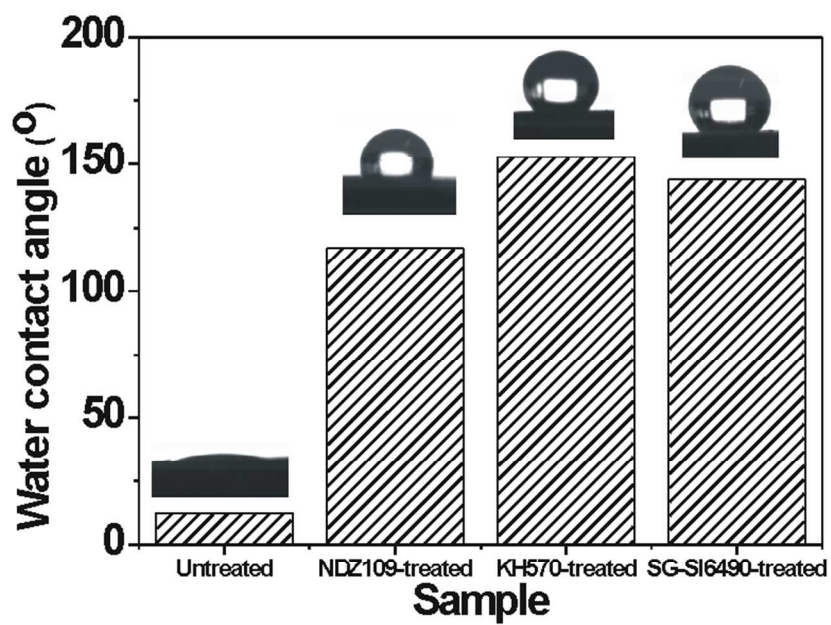


Fig.3 Water contact angles of BaTiO<sub>3</sub>  
79x56mm (300 x 300 DPI)



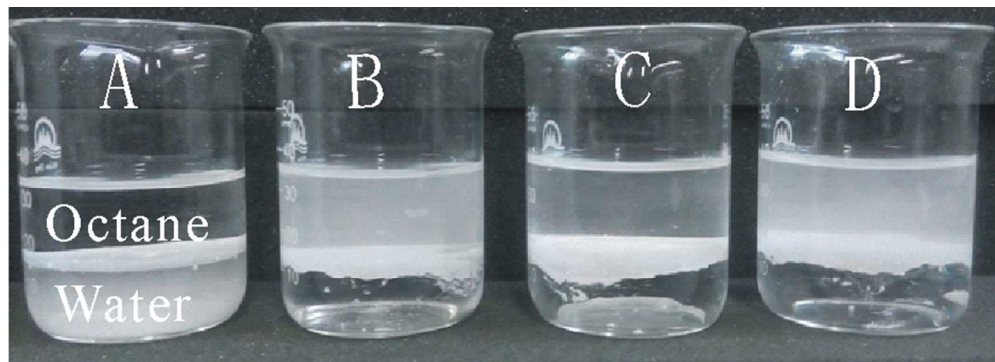


Fig.4 Dispersion of powders in a two-phase solvent, the bottom layer solvent is deionized water and the upper layer solvent is n-octane: A. Untreated BaTiO<sub>3</sub>; B. NDZ109 treated BaTiO<sub>3</sub>;C. KH570 treated BaTiO<sub>3</sub>;D. SG-Si6490 treated BaTiO<sub>3</sub> .  
79x28mm (300 x 300 DPI)

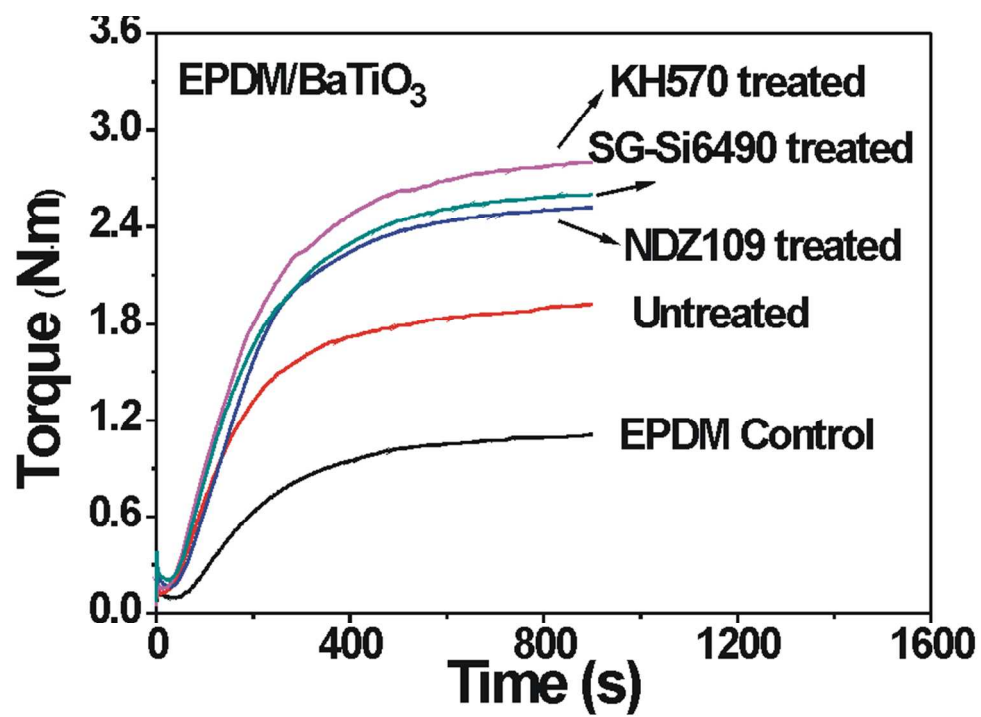


Fig. 5 Cure curves of EPDM composites  
79x56mm (300 x 300 DPI)

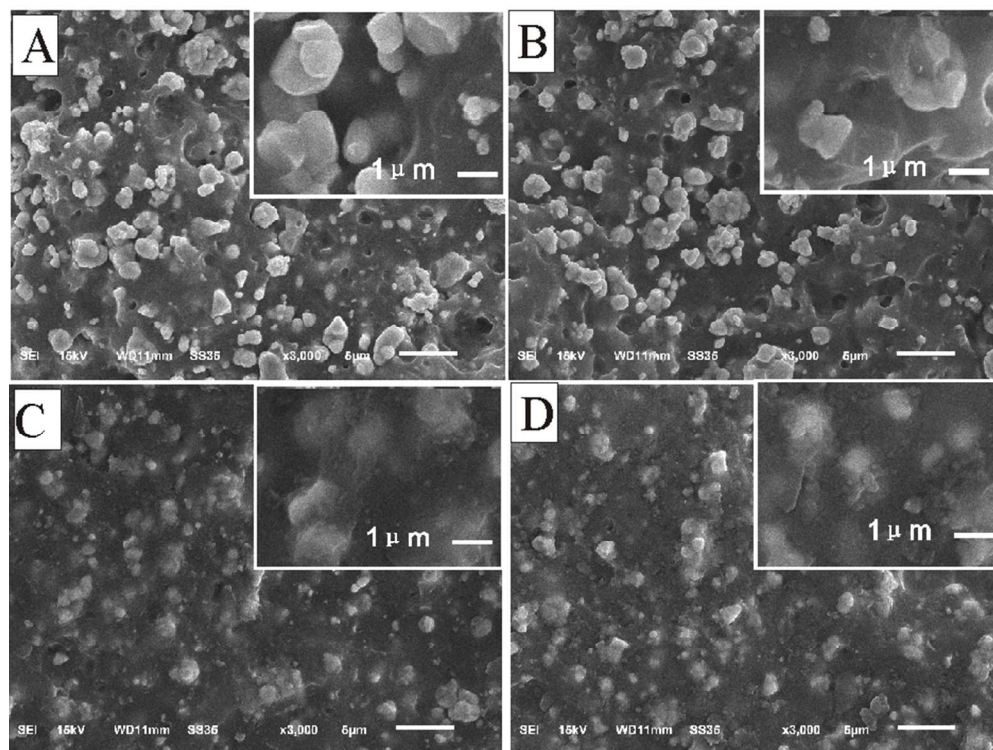


Fig. 6 SEM micrographs of EPDM vulcanizates with various coupling agents, A: EPDM with untreated BaTiO<sub>3</sub>; B: EPDM with NDZ109 treated BaTiO<sub>3</sub>; C: EPDM with KH570 treated BaTiO<sub>3</sub>; D: EPDM with SG-Si6490 treated BaTiO<sub>3</sub>  
79x59mm (300 x 300 DPI)

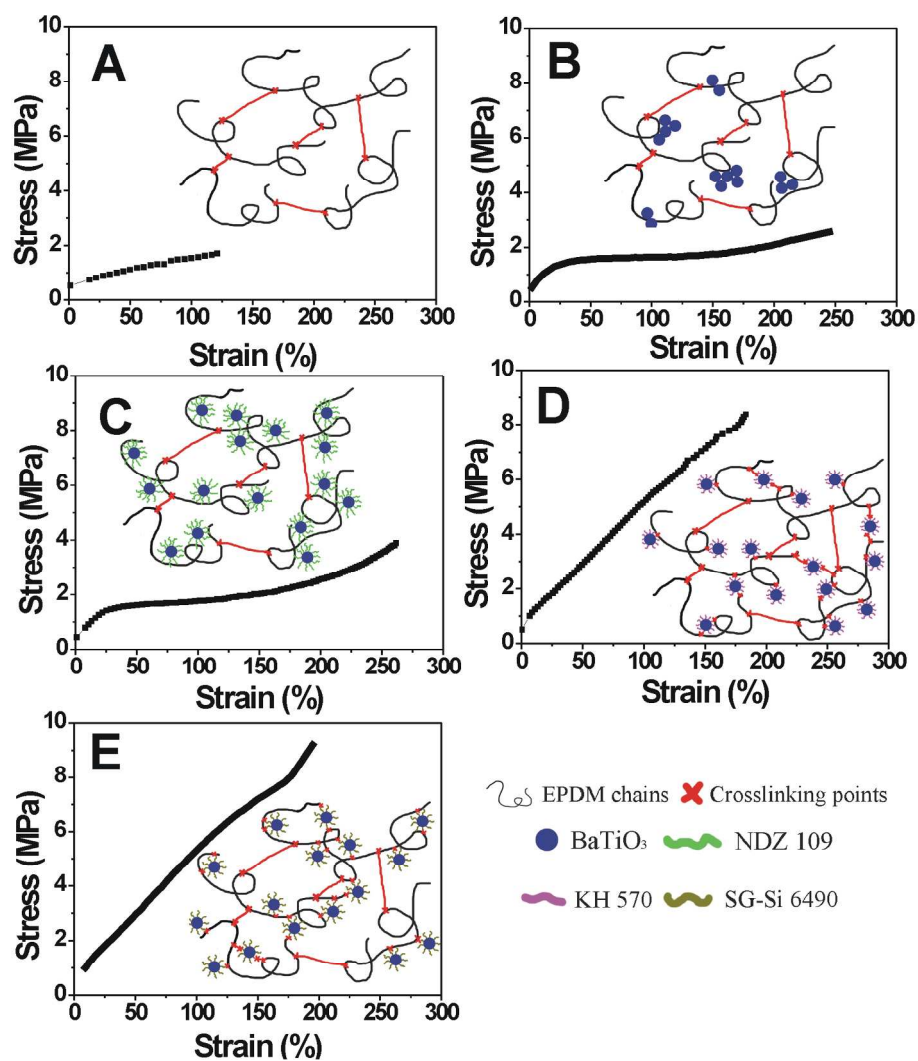


Fig. 7 Strain-stress curves and dispersion models of BaTiO<sub>3</sub> particles in EPDM composites, A: EPDM control; B: EPDM with untreated BaTiO<sub>3</sub>; C: EPDM with NDZ109 treated BaTiO<sub>3</sub>; D: EPDM with KH570 treated BaTiO<sub>3</sub>; E: EPDM with SG-Si6490 treated BaTiO<sub>3</sub>  
179x193mm (300 x 300 DPI)

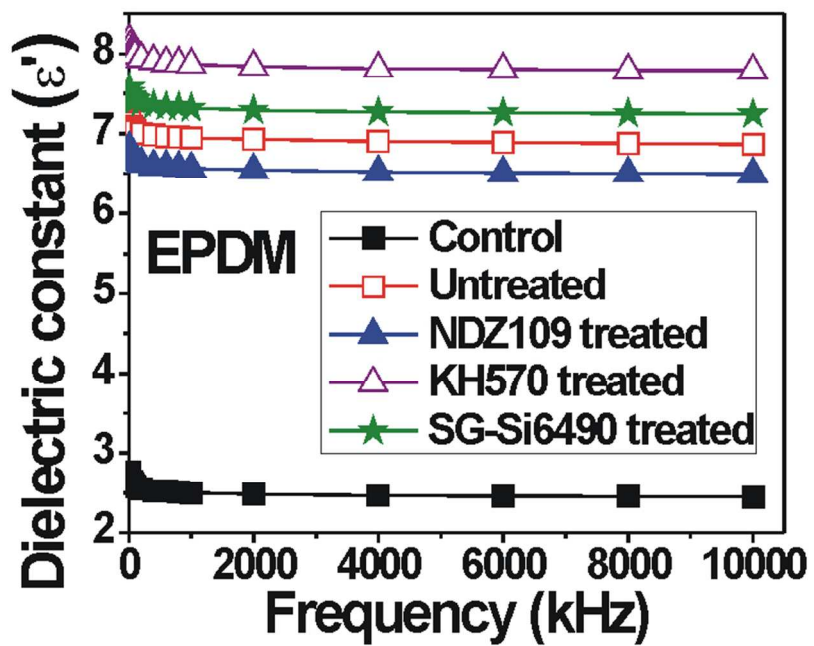


Fig.8 Relative dielectric constant of EPDM with treated BaTiO<sub>3</sub>  
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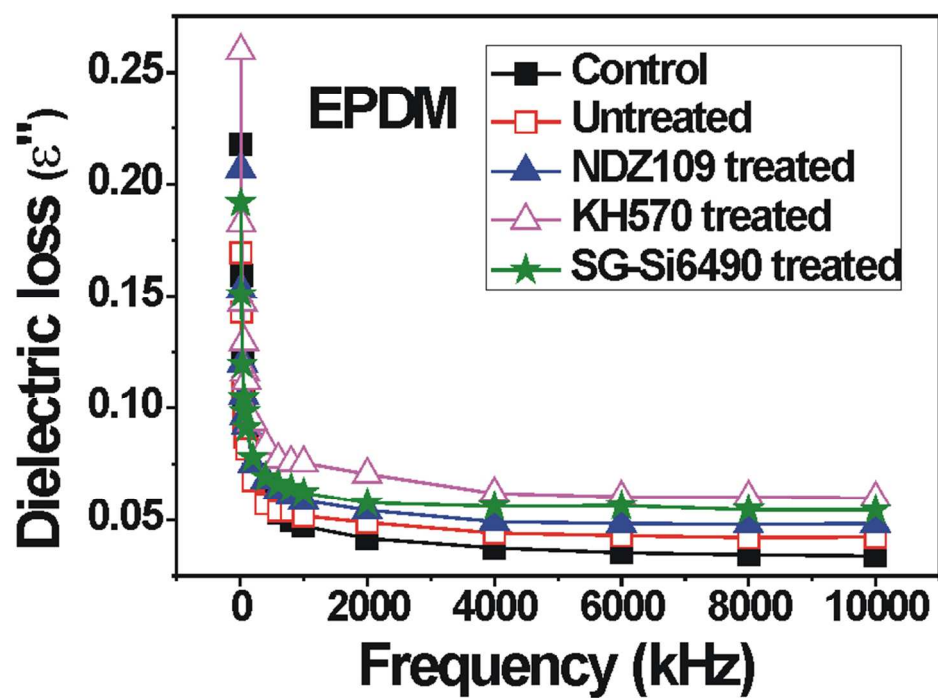


Fig.9 Dielectric loss tangent of EPDM with treated BaTiO<sub>3</sub>  
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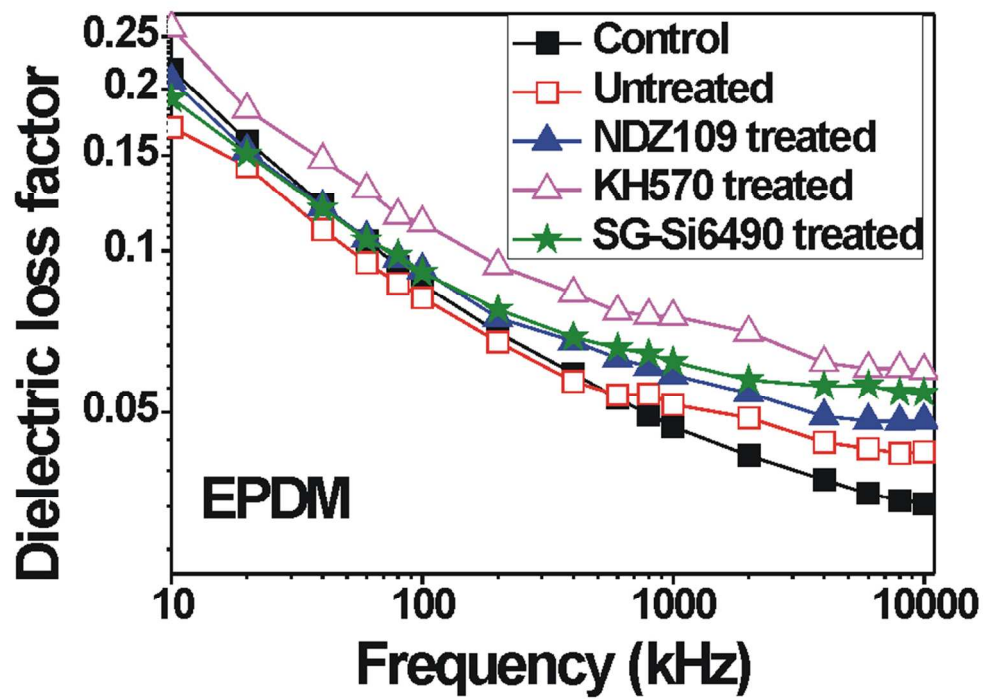


Fig.10 Dielectric loss factor of EPDM composites  
79x56mm (300 x 300 DPI)

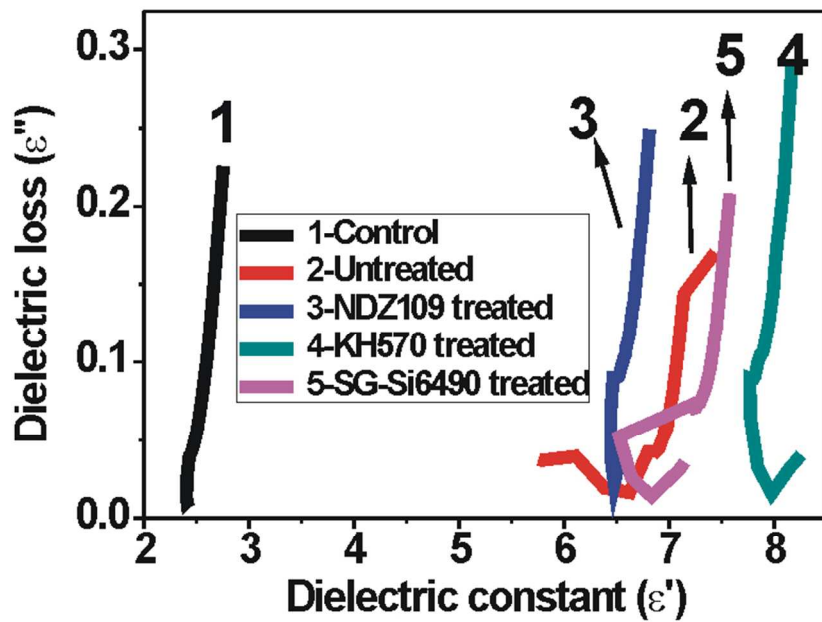


Fig.11 Curves of dielectric constant versus dielectric loss of EPDM composites  
79x56mm (300 x 300 DPI)