

Synthesis and Characterization of 3-Benzothiazolthio-1-Propyltriethoxysilane and Its Reinforcement for Styrene–Butadiene Rubber/Silica Composites

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Received 13 March 2008; accepted 20 October 2008

DOI 10.1002/app.29634

Published online 12 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel block mercaptosilane (3-benzothiazolthio-1-propyltriethoxysilane) (Silane-M) was synthesized and characterized by Fourier transform infrared spectra, ^1H nuclear magnetic resonance, and elemental analysis. Styrene–butadiene rubber (SBR)/silica composites were prepared with Silane-M, and its effect on the properties of materials was studied. Results show that Silane-M can substantially improve the dispersion of silica and strengthen the reinforcement of silica for SBR vulcanizates like anchors of silica to

rubber matrix. As expected, it enhances the tensile, tear strength, dynamic compression property, and resistance to abrasion of SBR/silica composites. By adding Silane-M into the system, SBR/silica composites get superior skid resistance and high glass transition temperature (T_g). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1967–1973, 2009

Key words: characterization; silane; SBR; silica; reinforcement

INTRODUCTION

Silica, as a white reinforcing filler, has been used in the rubber industry for a long time. However, it cannot completely replace carbon black as the main filler in tire compound, in particular, tread compound. The reason is that it imparts poor processability and low failure properties to the filled rubber such as low stiffness and abrasion property and so on. Such behavior of silica in rubber have always been associated with its weak polymer–filler interactions and strong filler–filler interactions, both are mainly attributed to the siloxane and silanol groups on silica surface. Recently, the modification of silica surface with sulfur-containing silane coupling agents has aroused a significant amount of interest because they are able to enhance rubber–filler interaction via chemical linkage.^{1–4} Sulfur-containing silane coupling agents contain one or more of the following chemical bond types: S–H (mercapto), S–S (disulfide or polysulfide), O=C–S (carbonylthio), etc. They possess two functionally active end groups that can produce chemical bonding between silica and rubber. The readily hydrolyzable alkoxy group (such as $-\text{OCH}_3$ or $-\text{OC}_2\text{H}_5$) will react with silanols on the silica surface to form stable siloxane linkage. The sulfur-containing group can participate in sulfur

vulcanization leading to chemical linkage with the rubber.

Until now, several sulfur-containing silanes have been commercially developed for rubber industry. Their reinforcement for inorganic particle-filled vulcanizates and process capability and vulcanization specialty of rubber composites with them have reported.^{5–9} In this study, a novel blocked mercaptosilane (Silane-M) was synthesized, and its effect on the mechanical, abrasion, and dynamic mechanical properties of styrene-butadiene rubber (SBR)/silica composites was investigated. The chemical structure of Silane-M is given in Scheme 1.

EXPERIMENTAL

Materials

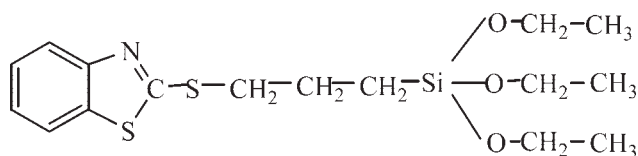
SBR (SBR1502) was obtained from Jilin Chemical Industry (Changchun, China); 2-mercaptobenzothiazole was purchased from Zhengbang Chemical (Zhengjiang, China). γ -Chloropropyltriethoxysilane was supplied by ShuGuang Group (Jiangsu, China); NaOH AR-grade was purchased from Tianjin Chemical (Tianjin, China). Precipitated silica with specific surface area of $140\text{ m}^2/\text{g}$ was purchased from Huiming (Jiangxi, China). Other materials were of industrial grade.

Synthesis of Silane-M

The synthesis of Silane-M was carried out in a three-necked round-bottomed flask equipped with an overhead stirrer, a thermometer, and a nitrogen gas

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50773021.



Scheme 1 Chemical structure of Silane-M.

inlet. 2-Mercaptobenzothiazole (16.7 g), 1 g NaOH, 28.9 g γ -chloropropyltriethoxysilane, and solvent were added into the flask to react under nitrogen atmosphere at a temperature of 50°C for 2 h. After the reaction, the reaction products were filtered and distilled under reduced pressure.

Structural characterization of Silane-M

Fourier transform infrared (FTIR) spectra of Silane-M were obtained with Nicolet FTIR spectrophotometer. ^1H Nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker AV 300 spectrometer with tetramethylsilane (TMS) as the internal reference. Elemental analysis was performed on ELEMENTAR vario elemental analysis instrument (Germany).

Preparation of SBR/silica composites

SBR and 50 phr (parts per hundred of rubber) precipitated silica were mixed for 10 min at room temperature with 1.6 phr sulfur, 5 phr ZnO, 2 phr stearic acid, 0–10 phr Silane-M, 0.5 g accelerator 1,3-diphenylguanidine, 1.5 phr antioxidant 4010NA (*N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine), and 1.8 phr accelerator *N*-cyclohexylbenzothiazole-2-sulfenamide in an ϕ (160 mm \times 330 mm open mill. The rotors operated at a speed ratio of 1 (front) : 1.22 (back). The compounds were vulcanized in an electrically heated press at 150°C for the optimum cure time (t_{90}), which is previously determined with rubber process analyzer (RPA 2000, Alpha Technologies) according to ISO3417 : 1991, to obtain the sheets and cylinders of SBR/silica composites (with Silane-M 0–10 phr). The content of Silane-M was changed to investigate the effect of Silane-M on the properties of composites.

The structural characterization and the determination of properties

The strain dependence of G' for silica-filled SBR unvulcanizate compounds was determined by RPA

(RPA 2000, Alpha Technologies). The condition of measurement is at a frequency of 1 Hz, a temperature of 60°C, and a strain range from 0.28 to 280%.

Transmission electron microscopy (TEM) images were taken with a JEM-100CX II at an acceleration voltage of 120 kV. Thin section (ca.100 nm) of the samples were cut out with a diamond knife at 120°C and used without staining.

The mechanical properties, such as tensile modulus at 300 and 500% elongation, tensile strength, and tear strength, were measured according to ISO/DIS37-1994 and ISO34-1-1994 specifications. U-CAN electron tensile testing machine was used with the crosshead speed of 500 mm/min. Akron abrasion loss was evaluated by a Gao-Tech abramer according to BS 903/A9-1988.

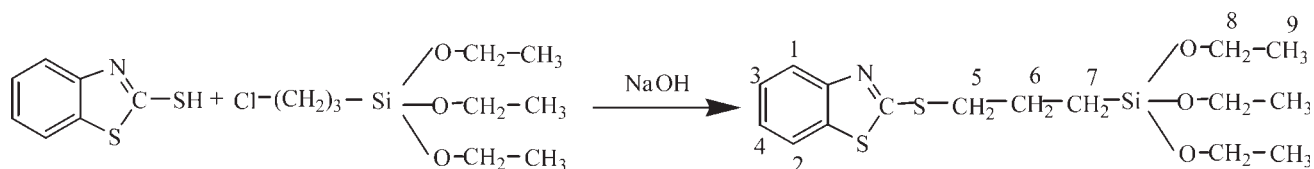
To study the heat buildup and permanent set at dynamic situation of these materials, U-CAN compression flexmeter was used for all compression testing and dynamic mechanical analysis (DMA). Cylindrical rubber specimens (25 mm in height and 17.5 mm in diameter) were subjected to repeated compression using a grip. The frequency of loading was 30 Hz, and the stroke (double amplitude) of imposed oscillation was 4.45 mm. The severity of the test was adjusted by varying the static compressive load applied to the sample, and compressive loadings of 24.5 kg were treated. The test procedures were terminated when the sample carried out about 25-min constant load or constant displacement fatigue.

The dynamic mechanical spectra of the samples were obtained by using TA 2890 (TA Instrument, USA) DMA. The specimens were analyzed in tensile mode at a constant frequency of 10 Hz, a strain of 0.1%, and a temperature range from –110 to 90°C at a heating rate of 5°C/min. Mechanical loss factor ($\tan \delta$) was measured as a function of temperature for the samples under identical conditions.

RESULTS AND DISCUSSION

Synthesis and characterization of Silane-M

The synthetic mechanism for Silane-M is shown in Scheme 2. The chemical structure of Silane-M was confirmed by FTIR, ^1H NMR, and elemental analysis.



Scheme 2 The synthetic mechanism of Silane-M.

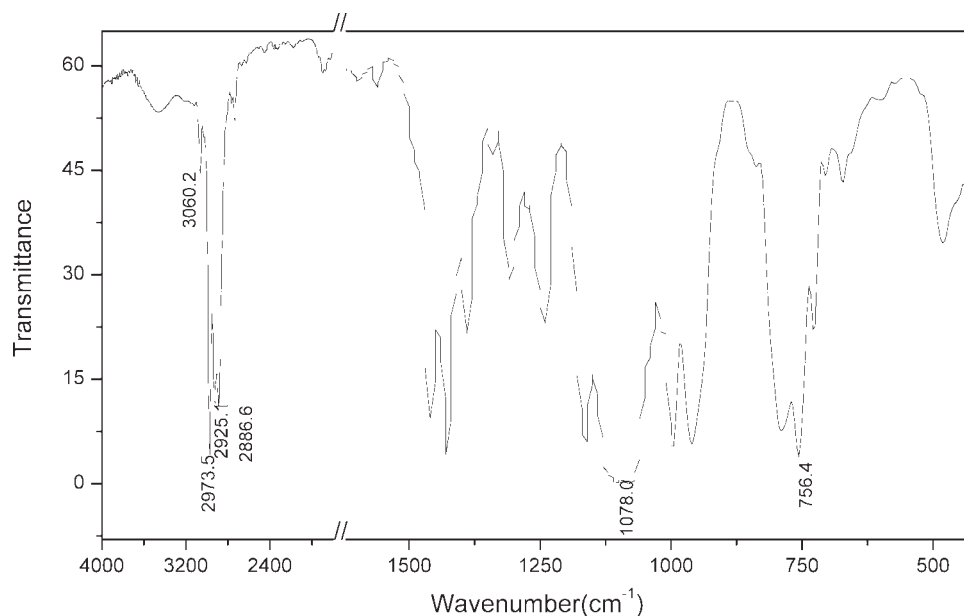


Figure 1 FTIR spectra of Silane-M.

Figure 1 shows the FTIR spectra of Silane-M. A strong absorption band at 1078.0 cm^{-1} is observed, corresponding to the Si—O stretching vibration. Bands at 2973.5 , 2925.1 , and 2886.6 cm^{-1} are attributed to the C—H asymmetric and symmetric stretching vibrations of CH_3 and CH_2 on the structure of Silane-M, respectively. Three sharp bands at 3060.2 cm^{-1} are associated with stretching vibrations of benzenoid group. Bands at 756.4 cm^{-1} are characteristic of *ortho*-bisubstitutional benzene ring.

Figure 2 shows the ^1H NMR spectrum of Silane-M. ^1H NMR (300 MHz, CDCl_3): δ (TMS, ppm) 7.71 (m, 2H, Ar—H), 7.24 (m, 2H, Ar—H), 3.34 (t, 2H, S— CH_2), 1.94 (m, 2H, CH_2), 0.80 (t, 2H, Si— CH_2),

3.78 (q, 6H, O— CH_2), 1.18 (t, 9H, CH_3). Anal Calcd for Silane-M: C, 51.75; H, 6.74; N, 3.77; found: C, 51.36; H, 6.66; N, 3.75.

The chemical structure of Silane-M was confirmed by FTIR, ^1H NMR, and elemental analysis.

Vulcanization properties of SBR/silica composites

Figure 3 shows the vulcanization curve of SBR/silica compounds with different contents of Silane-M. As can be seen, with 2-phr Silane-M, the torque of silica-filled SBR compound is highest of all, and it is attributed to that Silane-M can chemically react with

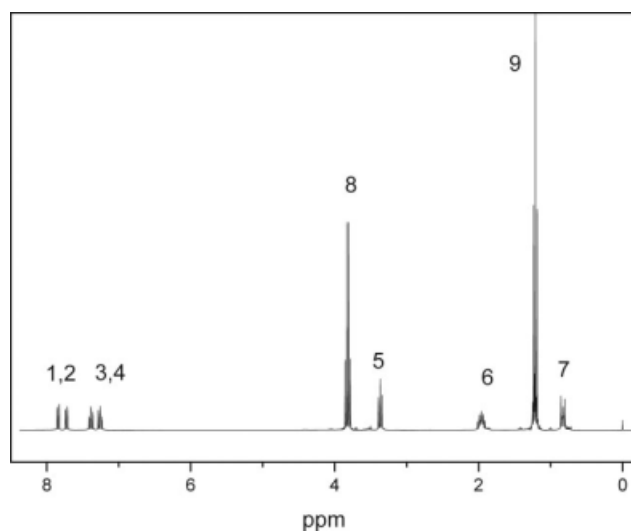


Figure 2 ^1H NMR spectrum of Silane-M.

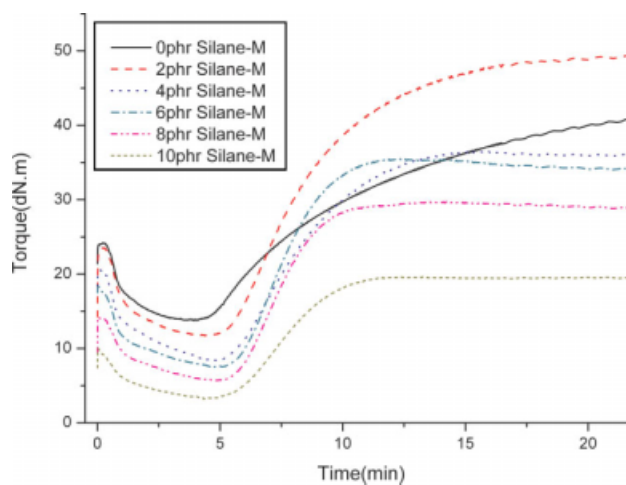


Figure 3 Curing curve of SBR/silica compounds with different content of Silane-M. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

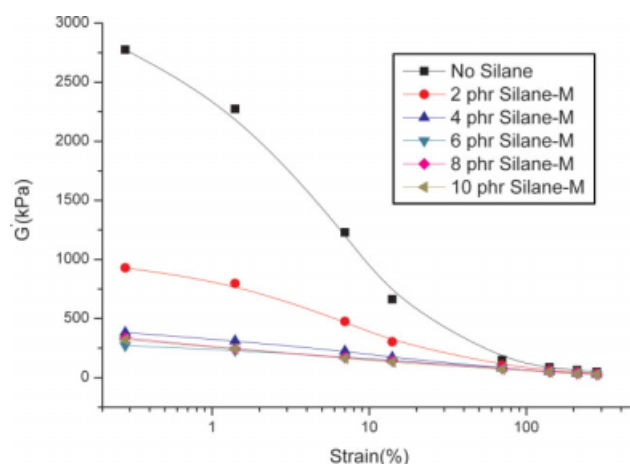


Figure 4 Effect of Silane-M on strain dependence of G' for silica-filled SBR unvulcanizate compounds. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

both silica and rubber and improve the filler–rubber interactions to increase the crosslinking density of composites. However, with further addition of more Silane-M, the excessive moieties of Silane-M serve as plasticizer in composite to reducing torque. The plasticizing effect of Silane-M was convinced by the latter DMA results.

The RPA analysis on silica-filled SBR unvulcanizate compounds

Figure 4 shows a plot of elastic modulus versus the logarithm of strain of silica-filled SBR unvulcanizate compounds. As can be seen, with increasing strain, the modulus of the filled SBR compounds without silane decreases and shows a typical nonlinear behavior, which is generally termed the “Payne effect,” whereas it does not change significantly for the compounds with 4-phr Silane-M. It is also observed that the moduli of all compounds at high-strain amplitude are close. It has widely been accepted that the Payne effect is mainly related to the filler network formed in the rubber matrix. The rubber trapped or caged in the filler network would at least be partially “dead,” behaving like a filler. Therefore, the effective volume of the silica would increase substantially upon filler networking. However, with the addition of Silane-M, the networking of silica is weakened much and so is the Payne effect.

Morphology of SBR/silica composites

The TEM images of SBR/silica composites with different contents of Silane-M are shown in Figure 5. Some silica particles aggregate together forming micron-grade grain without Silane-M. Silane-M improves the distribution and dispersion of silica in

polymer phase because it can react with silanols on the surface of silica, reduce the hydrogen bond effect between silica particles, and lessen filler agglomeration. This result correlates very well with the mechanical property. Thus, the improvement of silica dispersion and distribution is one of the reason that Silane-M can improve the properties of SBR/Silica composite.

Effect of Silane-M on mechanical properties of SBR/silica composites

As shown in Figures 6 and 7, with the addition of Silane-M into SBR/silica composites, tensile strength and tensile modulus M300 and M500 (stress at 300 and 500% elongation) increase progressively. However, tear strength grows to a maximum at around 6-phr Silane-M content and then decreases. It can be attributed to that Silane-M possess two functional groups that can chemically react with both silica and rubber. The readily hydrolyzable alkoxy group will react with silanols on the silica surface to form stable siloxane linkage. The benzothiazolthio group can participate in sulfur vulcanization leading to chemical linkage with the rubber. The interaction between rubber and silica is reinforced when Silane-M is added to the composite system. While the amount of Silane-M is over 6 phr, the excessive moieties injure the tear strength as a plasticizing agent.¹⁰

Effect of Silane-M on dynamic compression property for SBR/silica composites

Figure 8 shows the rapid drop of heat buildup and permanent set with increasing Silane-M content. It can be explained that in the absence of Silane-M, the silica particles aggregate and form into a developed but weak filler network in the matrix because of hydrogen bond among the high population of silanol groups on the face of particles. In repeated compression, the network is broken down and reformed continuously, which cause high energy dissipation as heat. The face modification of inorganic filler by Silane-M strengthens interface force of composites, lessens aggregate agglomeration between particles, and weakens the filler network. Thus, it reduces the repeat destruction and reconstruction of the network resulting in lower heat buildup. In addition, the more intense mutual interaction between filler and rubber reinforced by Silane-M leads into the smaller permanent set.

As can be observed in Figure 9, with increasing Silane-M content, Akron abrasion of composites get lower, and at 6-phr concentration of Silane-M, SBR/silica composites get its superior abrasion resistance. With more Silane-M adding into the system, the resistance to abrasion of materials hardly improves. This observation may be attributable to the

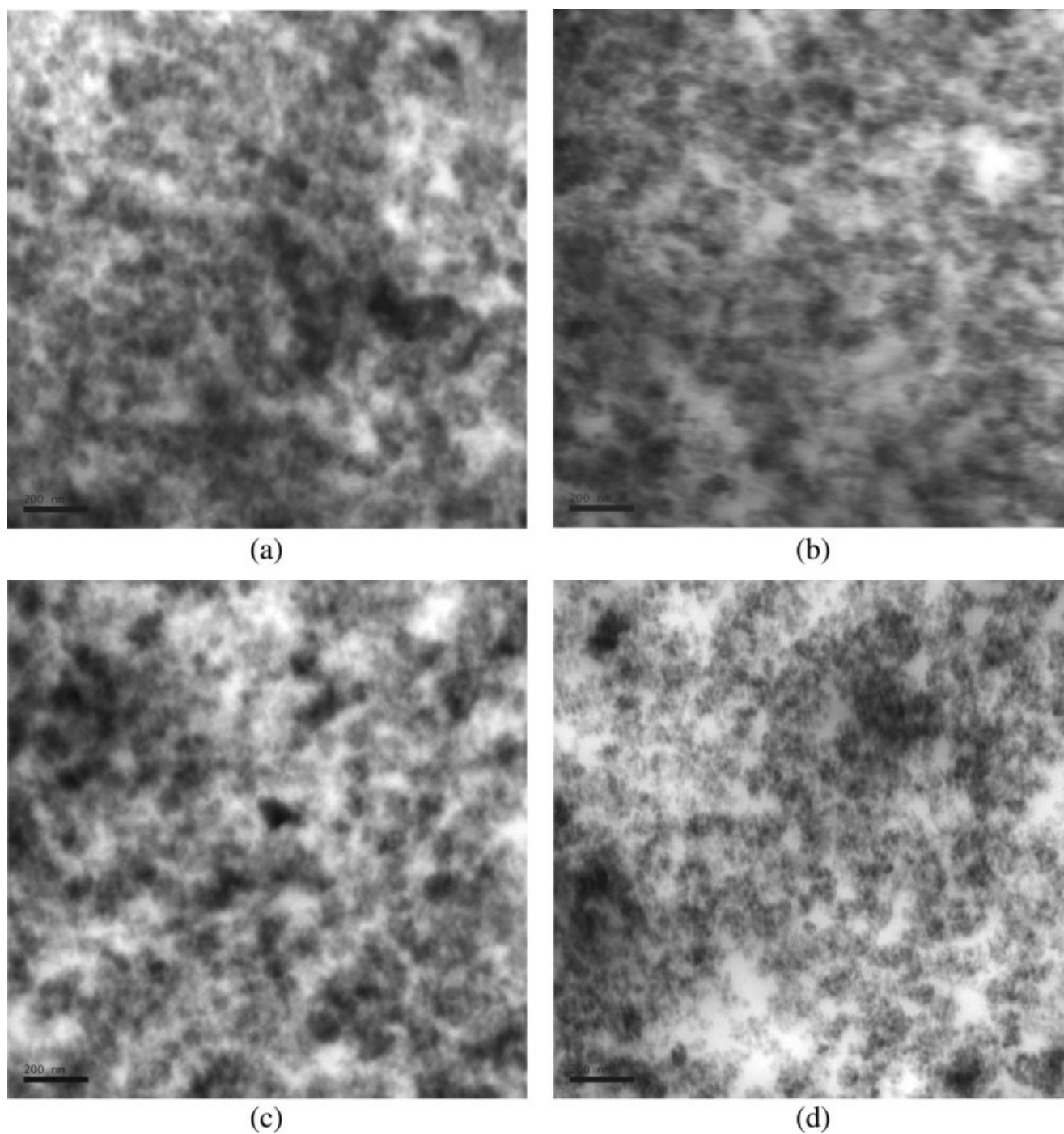


Figure 5 TEM photomicrograph of SBR/silica composites: (a) SBR/silica composite without Silane-M; (b) SBR/silica composite with 2-phr Silane-M; (c) SBR/silica composite with 4-phr Silane-M; (d) SBR/silica composite with 6-phr Silane-M.

reinforcement of rubber–filler interactions with Silane-M, but redundant Silane-M serves as plasticizer and is not able to improve the abrasion property too much.

Effect of Silane-M on dynamic mechanical property of SBR/silica composites

From the viscoelastic property point of view, an ideal material applied in tire tread, which is able to

meet the requirements of a high-performance tire, should give a lower $\tan \delta$ at a temperature of 80°C and demonstrate high hysteresis at 0°C to reduce rolling resistance and obtain high skid resistance. Generally, it is difficult to obtain the balance between rolling resistance and skid resistance. Accordingly, the ratio between $\tan \delta$ at 0°C and 80°C can be used to evaluate the composite dynamic properties for automotive tire tread rubber.

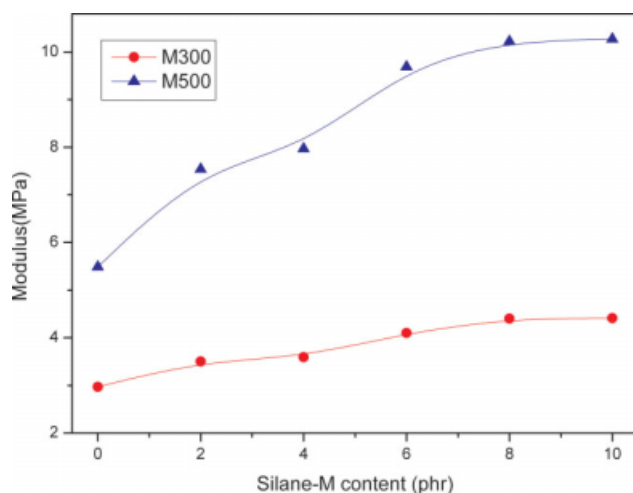


Figure 6 Effect of Silane-M on the tensile modulus at 300 and 500% elongation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

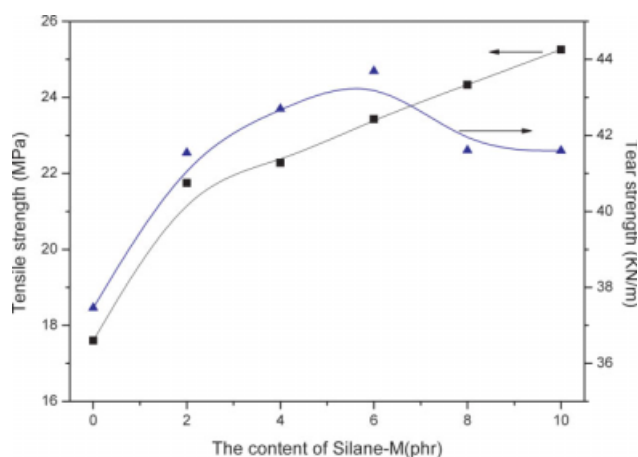


Figure 7 Effect of Silane-M on the tensile strength and tear strength. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

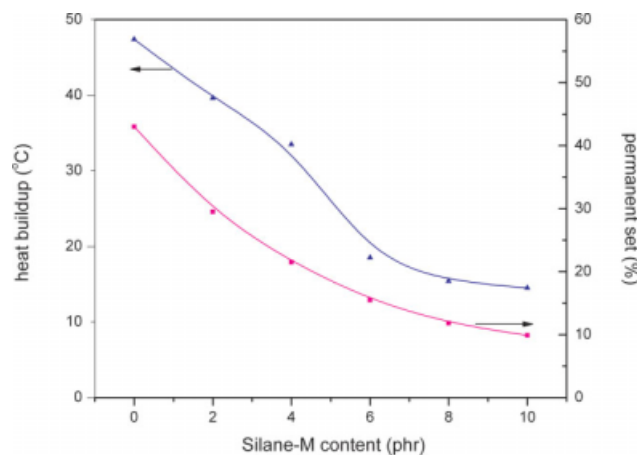


Figure 8 Effect of Silane-M on heat buildup and permanent set at dynamic compression. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

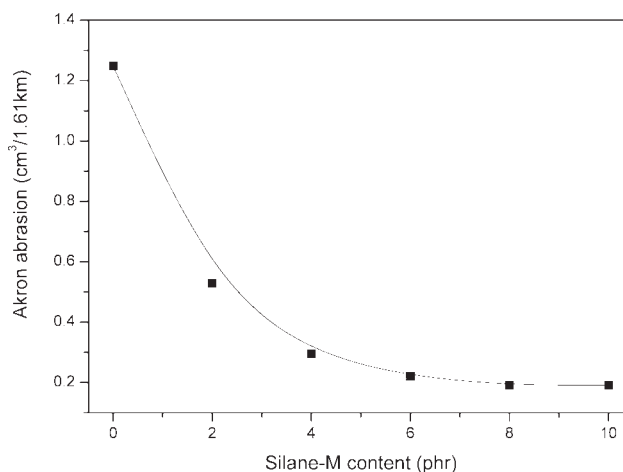


Figure 9 Effect of Silane-M on abrasion loss.

It can be seen from Figure 10 and Table I, as Silane-M increases, the skid resistance become better but rolling resistance augment. The ratio between $\tan \delta$ at 0°C and 80°C get its maximum at 2 phr of Silane-M. Table I also shows that the glass transition temperature (T_g) of SBR/silica composites rises first and then drop with the increase of Silane-M. This is believed that Silane-M can promote the mutual interaction between rubber and silica to increase the content of bound rubber whose T_g is higher than polymer matrix around silica surface. The excessive Silane-M like plasticizer that injure filler-matrix interaction and improve the mobility of rubber chain in composite can slightly debase T_g .

CONCLUSIONS

In this work, 3-benzothiazolthio-1-propyltriethoxysilane (Silane-M) was successfully synthesized and characterized by FTIR, ^1H NMR, and elemental

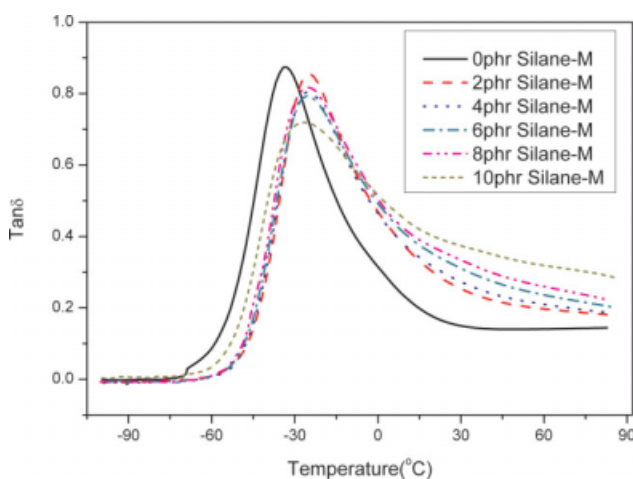


Figure 10 Plots of $\tan \delta$ versus temperature of SBR/silica composites from DMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
 T_g and $\tan \delta$ of SBR/silica Composites with Different Concentrations of Silane-M from DMA

Sample	Without Silane-M	Silane-M (2 phr)	Silane-M (4 phr)	Silane-M (6 phr)	Silane-M (8 phr)	Silane-M (10 phr)
$\tan \delta$ at 0°C	0.332	0.471	0.485	0.494	0.498	0.516
$\tan \delta$ at 80°C	0.143	0.182	0.191	0.208	0.227	0.295
Ratio, 0°C/80°C	2.32	2.59	2.54	2.38	2.19	1.75
T_g (°C)	-31.8	-25.4	-25.1	-25.6	-26.2	-26.6

analysis. SBR/silica composites were prepared with Silane-M, and its effect on properties of composites was studied. It can be observed from the experiments that Silane-M is acting as the anchors of silica to SBR matrix. It is concluded from the investigation that Silane-M can improve the separation and distribution of silica in rubber matrix and strengthen the reinforcement of silica for SBR vulcanizates to enhance the tensile, tear strength, dynamic compression property, and resistance to abrasion of SBR/silica composites. As the cost of modifier is considered, at the 6-phr content of Silane-M, the composites get superior properties. The DMA results indicate that with the addition of Silane-M, SBR/silica composites get better skid resistance and high T_g . However, the excessive portion of Silane-M injures the filler-matrix interaction and slightly debases T_g like plasticizing agent.

The authors express their sincere appreciation to the College of Materials Science and Engineering of the South China Uni-

versity of Technology for supporting the group in undertaking the project.

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