Reduction of Volatile Organic Compound Emission. II. Use of Alkoxy-Modified Silsesquioxane for Compounding Silica-Filled Rubbers

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ABSTRACT: A class of alkoxy-modified silsesquioxane (AMS) containing less than 5 wt % of latent alcohol that can be used for compounding silica-filled rubbers is described. The AMS derived from octyl-triethoxysilane (OTES) behaves as a good shielding agent in silica-filled rubber to significantly reduce the compound Mooney viscosity and filler flocculation. The *co*-AMS prepared from OTES and 3-mercaptopropyl-trimethoxysilane yielded an effective shielding and coupling agent for reinforcing the silica-filled vulcanizates. The alcohols released as volatile organic compounds (VOC) are quantified during compounding and processing along with the compound properties of silica-filled vulcanizates containing various silicon compounds such as *bis*-(triethoxysilyl propyl) disulfide (TESPD), a polyhedral oligomeric silsesquioxanes (POSS), OTES, AMS, or *co*-AMS. Dynamic mechanical properties such as dependences of hysteresis on temperature (HTD) and storage modulus on strain (MSD) are discussed. Stronger HTD and weaker MSD were found in stocks containing *co*-AMS or a combination of AMS and a coupling agent when compared with that with TESPD. Stronger HTD and weaker MSD may benefit a tire compound with lower rolling resistance, more stable handling performance, as well as better wet traction. More importantly, the VOC released during the manufacture of rubber articles are significantly reduced in stocks containing AMS (or *co*-AMS) when compared with those with a silane. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 655–664, 2010

Key words: silsesquioxane; hysteresis; silica; filler-network; polymer-filler interactions; VOC; silane

INTRODUCTION

This is the second of the two papers on using various alkoxy-modified silsesquioxane (AMS) for reinforcing silica-filled rubbers. The first paper described the preparation of AMS and the elimination of about 95% of the alkoxy silane groups as a possible source of volatile organic compound (VOC) in subsequent uses.[1] Here, a comparison of the use of AMS to traditional alkoxysilyl containing reagents for the preparation of a silica-filled elastomeric composition will be made. Such coupling agents include *bis*-(triethoxysilyl propyl) polysulfides (e.g., tetrasulfide (TESPT) and disulfide (TESPD)),[2–6] combinations of octyltriethoxysilane (OTES) and 3-mercaptopropyl trialkoxy silanes[7] or thiooctanoyl propyl triethoxysilane[8] which have been employed to improve silica dispersion and processing as well to reinforcing the rubbers. However, all of these compounds are known to release VOC into the environment as a byproduct of their reactions. In addition, when rubbers are mixed with these silanes at lower temperatures, they require long mixing times or retain a considerable amount of unreacted alkoxysilyl groups that further react with the silica and moisture during storage, extrusion, tire building, and/or curing. Such a delayed reaction leads to the entrapment of the alcohol byproducts as blisters or tread porosity and results in an undesirable increase in the compound viscosity upon storage.[9] As a result of the delayed reaction, the speed of processing, mixing, and tread extrusion will be reduced, and thus significantly decrease the plant productivity. The use of alkoxy-modified silsesquioxane (AMS) compounds will be shown to alleviate the above issues. Such a use allows the advantages of traditional alkoxysilane-silica reaction to occur, with negligible alcohol released to atmosphere.

EXPERIMENTAL

Materials

The silica HiSil®190 (200–210 m²/g surface area) and Ciptane® 255LD which is a mercaptopropyl silane supported on silica were supplied by PPG Industries, (Pittsburgh, PA). The *bis*-(3-triethoxysilyl propyl) disulfide (TESPD), trade name of Silquest®

TABLE I
Silanes Used to Prepare AMS

Silane	Alkyl group in silane	Reactive group in silane
1	Octyl	Triethoxy
2	Octyl	Trichloro
3	3-Mercapto propyl	Trimethoxy
4	Thiooctanoyl propyl	Triethoxy

1859 was obtained from Witco Corp. (Greenwich, CT) or from Degussa–Hüls Corp.(Parsippany, NJ) under the trade name of Si75. The *n*-octyl triethoxysilane (OTES) was obtained from Dow Corning (Midland, MI). The 3-mercaptopropyl trimethoxysilane (MPTMS) and octyl trichloro silane were acquired from Gelest (Morrisville, PA). The thiooctanoyl propyl triethoxysilane (NXT™) was received from Crompton Corp. (Greenwich, CT). The polyhedral oligomeric silsesquioxanes (POSS)[10] were purchased from Hybrid Plastics (Hattiesburg, MS). All of these materials were used without further purification.

Preparations of AMS

The preparation of the AMSs and *co*-AMSs has been described previously.[1] The silanes used to prepare the AMSs and *co*-AMSs are listed in Table I. The AMS shown in Table II derived from silane **1** or **2** of Table I are designated as AMS **1**. The *co*-AMS was made by two silanes where the second silane is the minor component. For example, ***co*-AMS A** denotes an *co*-AMS in which OTES (silane **1**) is the major component and 3-mercaptopropyl trimethoxy silane (silane **3**) is the minor component at an 8 mol % level. Note that the second silane has a moiety to react with rubber and its composition is shown in Table II along with the latent ethanol content (EtOH) of every AMSs and *co*-AMSs. The detailed characterization of the AMSs and their proposed structures has been made.[1]

Rubber compound preparations

Two different rubber stocks were used for this study. One group contains only silica filler (Compound Group **A**), and the other contains about equal

TABLE II
Preparation of AMS or *co*-AMS

AMS or *co*-AMS	Silanes used to prepare AMS or *co*-AMS	mol % of 2nd silane	Latent EtOH (wt %)
AMS 1	**1**	n/a	3.5
***co*-AMS A**	**2 + 3**	8.0	4.39
***co*-AMS B**	**1 + 4**	9.1	4.05

TABLE III
Formulations Employed for Preparing the Rubbers

Ingredient	Compound group **A** all silica rubbers (phr[a])	Compound group **B** half silica rubbers (phr[a])
Natural rubber	0	25.0
SBR	100[b]	75.0[c]
Carbon black	0	35.0
Precipitated silica	65	30.0
Process oil	20 (Aromatic)	Various (Naphthenic)
Wax	1.7	1.5
Antioxidant[d]	0.95	0.95
Stearic acid	2.0	1.50
Silica dispersing agent (Silane, AMS)	Various	Various
Sulfur	2.8	Various
Accelerator 1[e]	1.17	1.5
Accelerator 2[f]	0.39	0.5
Zinc oxide	1.94	2.5

[a] Parts per 100 parts of rubber, by weight.
[b] Solution SBR (23.5% styrene, $T_g = -36°C$, $ML_4 = 58$).
[c] SSBR (20% styrene, 48% vinyl, $T_g = -33°C$, $ML_4 = 92$).
[d] *N*-(1,3 dimethylbutyl)-*N'*-phenyl-*p*-phenylene-diamine.
[e] *N*-Cyclohexyl-2-benzothiazolesulfenamine(CBS).
[f] Diphenyl guanidine (DPG).

amounts of carbon black and silica fillers (Compound Group **B**). The formulations for Groups **A** and **B** compounds are shown in Table III. The contributions of all compound ingredients are based on a total of 100 parts of the rubber or combination of rubbers (phr). Rubber compounds were mixed using the conditions and the loading sequence of ingredients described in Table IV in various mixing stages including a masterbatch (MB), a remill mix (R), and a final stage (F) if necessary. The silica-dispersing agents used for the preparation of the specific stocks investigated are listed in Table V.

Test conditions

Mooney viscosity (ML$_4$)

Mooney viscosity measurements were conducted according to procedures described in ASTM-D 1646-89[11] and in a previous publication.[9] The test was performed using a large rotor at 130°C for the filled rubbers and 100°C for gum rubbers. The sample was preheated at the test temperature for 1 min before the rotor started and then the Mooney viscosity (ML$_4$) was recorded as the torque after the rotor had rotated for 4 min at 2 rpm (average shear rate about 1.6 s^{-1}). After the rotor stopped rotating, the torque was continuously monitored over a period of time. The t_5 from this measurement is the time required to increase 5 Mooney units which is conventionally defined as the Mooney scorch.

TABLE IV
Mixing Procedures Employed for Preparing the Rubbers

Master Batch Stage (MB)	
Agitation speed	60 rpm
Initial temperature	100°C
Mixing at 0 sec	Charging polymers
Mixing at 30 sec	Charge carbon black (if added), 2/3 of the silica, and all pigments. Charge silanes or silica dispersing-agents (if added)
Mixing at 5 min	Drop
Target drop temperature (T_d)	155°C (stocks **1** and **4**) or 165°C (stocks **2**, **3**, **5**, **6**, **7**, and **8**)
Remill Batch Stage (R)	
Agitation speed	50 rpm
Initial temperature	90°C
Mixing at 0 sec	Charge masterbatch stock
Mixing at 30 sec	Charge the other 1/3 of the silica
Target drop temperature (T_d)	146°C (stocks **1** and **4**) or 155°C (stocks **2**, **3**, **5**, **6**, **7**, and **8**)
Final Batch Stage (if needed) (F)	
Agitation speed	50 rpm
Initial temperature	75°C
Mixing at 0 sec	Charge remilled stock
Mixing at 30 sec	Charge curing agent and accelerators
Target drop temperature (T_d)	100–105°C

Curing characterization

The Monsanto Rheometer MD2000 was used to characterize the filled stock curing process using a frequency of 1.67 Hz and a strain of 7% at 171°C. The testing procedures followed were those described in ASTM D 2084-81.[12] The t_{s2}, t_{10}, and t_{90} are the times at which the torque rises to 2%, 10% and 90%, respectively, of the total torque measured during the cure and are used to predict how optimum curing conditions.

Dynamic mechanical viscoelastic property measurements

The dynamic viscoelastic properties of cured stocks were obtained from temperature and strain sweep experiments using Rheometrics Dynamic Analyzer models RDA-700 and RDA-II. The strain sweep on unvulcanized rubbers stocks containing no curatives were performed using the RPA 2000 Rubber Process Analyzer (Alpha Technologies). Similar tests were also undertaken on selected final stocks containing curatives. Test conditions, the thermal annealing procedure, and sample preparations were described in a previous publication.[13] Rheological data such as storage modulus (G') and loss modulus (G''), strain, shear rate, viscosity, and torque were measured.

Tensile mechanical properties

The tensile mechanical properties were measured using the standard procedure described in ASTM-D 412[14] at 25°C. Force readings are expressed as engineering-stresses by reference to the original cross-sectional area of the test piece. The tensile test specimens were rings with 1.27 mm width, 1.91 mm thickness, and 15.7 mm inside diameter. A specific gauge length of 25.4 mm was used for the tensile test. Moduli measured at 50% (M50) and 300% (M300) of strains, the applied load at which test specimen broke (tensile strength), the elongation at break (E_b), and area under the stress–strain curve (tensile toughness) were recorded.

TABLE V
Silica-Dispersing Agent Employed for the Preparation of Stocks

Feature stock	Agent type	Agent (phr)	Ciptane® (phr)	Sulfur (phr)	Naphthenic oil	Compound group
1	0		0	2.8	N/A	A
2	**OTES**	6.67	0	2.8	N/A	A
3	**AMS 1**	4.1	0	2.8	N/A	A
4	**TESPD**	2.64	0	1.56	15.0	B
5	**AMS 1**	2.2	6.67	1.78	12.5	B
6	**POSS**	2.2	6.67	1.78	12.5	B
7	*co*-**AMS A**	2.35	0	1.78	13.5	B
8	*co*-**AMS B**	2.11	0	1.78	13.5	B

Tear strength measurement

The tear strengths of the vulcanized stocks were measured using the procedure following the ASTM-D 624-00[15] at 171°C. Test specimen geometry can take the form of a nicked ring, or ASTM-624 B nicked die, or ASTM-624 C non-nicked die. Test specimens are nicked rings with 6.4 mm width, 2.5 mm thickness, 44 mm inside diameter, and 57.5 mm outside diameter. The specimen was tested at the specific gauge length of 44.45 mm. The force required to produce a new surface is measured as the tear strength.

The rebound test

The Zwick rebound resilience tester measures Rebound Resilience as a very basic dynamic-test. The test piece is subjected to one half-cycle of deformation. Sample geometry is round with a dimension of 38 mm diameter and 19 mm thickness. The specimen is strained by impacting the test piece with an indentor which is free to rebound after the impact. Rebound resilience is defined as the ratio of mechanical energies before and after impact. Samples were preheated to the selected temperature for 30 min before testing.

Bound rubber content determination

The bound rubber content test is used to determine the percent of polymer bound to filler particles in filled stocks. The detailed procedure of measuring Bound rubber is described in the previous publication.[16] The bound rubber content is determined following Bernnan's procedure.[17]

Latent alcohol measurements

Quantitative determination of the amount of alcohol that can be released by complete hydrolysis of the residual alkoxy silane ([ROSi]) was measured. The released alcohol (latent alcohol) measurements were made in AMS and in stocks as a function of mixing stages and thermal treatments. The detailed procedure to measure the latent alcohol in rubbers was described in previous publications.[9,18]

RESULTS AND DISCUSSIONS

Processing assessment on using AMS for compounding silica-filled rubbers

For the first evaluation of AMS as a silica-dispersing, silica-shielding, or silica-processing agent in an all silica formulation, the first three stocks (**1**, **2**, and **3**) of Table V were prepared from which a list of selected critical properties from the uncured stocks

TABLE VI
Properties of the Uncured Rubber Compounds

Stock	1	2	3
ML_4	Over torque	52	58
t_5 (min)	N/A	>60	43
$\delta(\Delta G')$ (MPa)	6.68	1.92	3.23

were tabulated in Table VI. An effective silica dispersion, shielding, or processing agent should be able to interact with silica filler during preparation of rubber compounds such that workable rubber slabs are produced for extrusion and tire formation. Either a bifunctional polysulfane of TESPT and TESPD[2–6] or a monofunctional silane of OTES[9,18,19] or the physical processing aids such as sugar fatty acid esters[20,21] are capable of coating the silica aggregates during the mixing stage that effectively reduces the compound Mooney viscosity (ML_4) for processing. Comparisons of these stocks show that the AMS (stock **3**) and the OTES (stock **2**) containing stocks had similar ML_4 values that were significantly lower than stock **1**, which contained no silica-dispersing or shielding agent. Note that OTES has been shown to be an effective silica-shielding agent.[9,18,19] Therefore, AMS has a similar shielding effect to that of OTES for compounding silica containing rubbers. A reduced compound ML_4 is advantageous because it provides better processibility and handling, especially during the extrusion and tire build processes. The ML_4 reduction is most dramatically seen when compared with stock **1**, which did not contain either a silica-coupling agent or a silica-shielding agent and thus resulted in a ML_4 too high to process.

Moreover, increasing values of ML_4 is an important issue since it is desirable to maintain a near constant compound ML_4 during rubber processing at elevated temperatures such as extrusion. To evaluate the stock ML_4 stability issue, the t_5 data obtained from the Mooney test measured at 130°C shown in Table VI were used as an indicator to predict how fast compound viscosity will rise during processing at elevated temperatures. Since the testing conditions of t_5 data are close to the highest processing temperature that a normal tire plant will use, it was chosen as a way of assessing this issue. The t_5 value of 43 min for stock **3** containing AMS seemed acceptable for normal plant processing operation. The increased ML_4 values in the filled compound at an elevated temperature is primarily due to the filler flocculation process,[9,18] although it may be argued that some degrees of vulcanization may occur during the Mooney scorch measurement. The filler flocculation process in silica stocks strongly depends upon thermal histories, humidity, and types of silica dispersing agents added.[9,18] However, in a well silica-shielded compound such as in stock **2**, which
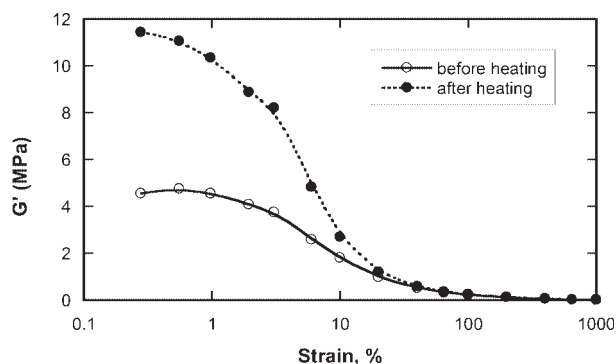
Figure 1 The G' strain dependences of the uncured stocks **1** before (○) and after (●) thermal annealing at 171°C for 15 min. The measurement was conducted at 50°C at 1 Hz.

contained OTES, the extent of ML_4 increase is so small that the resulting t_5 value was greater than 60 min of the maximum test time used for measurements. Apparently, filler flocculation and vulcanization contribute little to the t_5 increase in this stock. Therefore, the t_5 may also be used to assess the degree of filler flocculation in a compound at an elevated temperature and in turn to evaluate the effectiveness of the silica-shielding agent.

An alternative way to evaluate the effectiveness of a silica-shielding agent is to directly examine the filler network change after thermally annealing a compound containing no curatives under conditions that mimicked cure (171°C for 15 min). The measurements can be done conveniently by examining the G' strain dependences of the uncured stocks **1**–**3** with different thermal histories as shown in Figures 1–3. A large increase in G' after heating was observed for stock **1** in Figure 1 when compared with those of stocks **2** (Fig. 2) and **3** (Fig. 3). The change in $G'(\delta G')$ before and after thermal annealing as a function of strain of stocks **1**–**3** are plotted in Figure 4, where a bigger and stronger G' strain dependence was found in stock **1** when compared with others. Meanwhile, similar results were seen
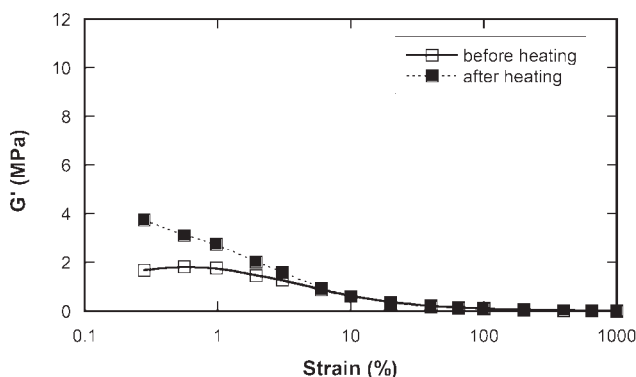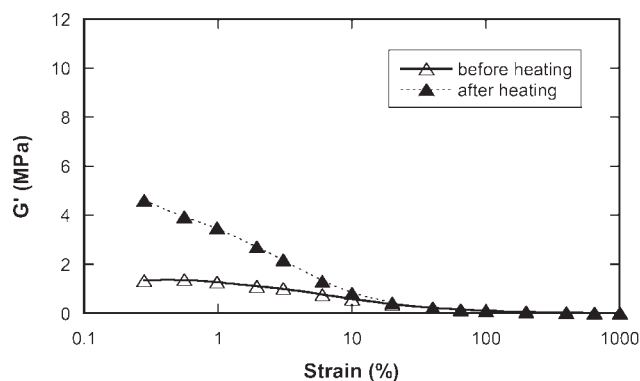

Figure 3 The G' strain dependences of the uncured stocks **3** before (△) and after (▲ solid triangles) thermal annealing at 171°C for 15 min. The measurement was conducted at 50°C at 1 Hz.

between the AMS containing stock **3** and the OTES containing stock **2**. The data from Figures 1–4 can be collectively expressed as the change in Payne effect ($\delta(\Delta G')$) of a sample before and after thermal annealing.[16,18] The $\Delta G'$ was measured as the difference in G' at low (0.2%) and high (1000%) strains from an uncured sample in the absence of curatives and it is commonly used as an indicator of degree of filler networking in compounds (Payne effect).[22–24] The $\delta(\Delta G')$ data have been shown to be a convenient way to measure the filler flocculation, which in turn, is a measure of the effectiveness of a silica-shielding agent to process silica containing rubbers.[16,18] The $\delta(\Delta G')$ data listed in Table VI show the lower $\delta(\Delta G')$ values for stocks **2** and **3** compared with stock **1** indicating that the silica aggregates were shielded well in **2** and **3** resulting in lower degree of filler flocculation upon heating in these stocks. The $\delta(\Delta G')$ data along with those of ML_4 and t_5 suggest that AMS is as effective a silica-shielding agent as a silane to disperse silica and to reduce the filler flocculation upon heating. AMS is therefore useful for compounding silica filled rubbers.
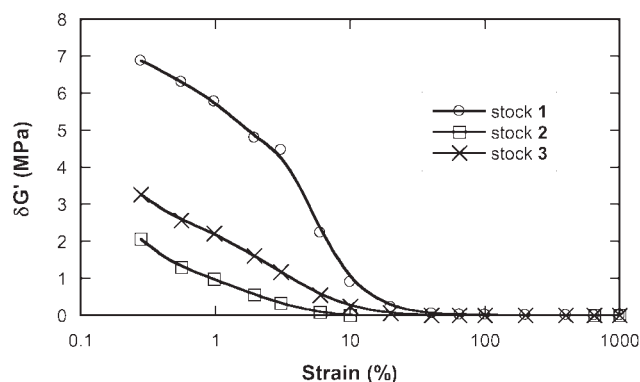

Figure 2 The G' strain dependences of the uncured stocks **2** before (□) and after (■) thermal annealing at 171°C for 15 min. The measurement was conducted at 50°C at 1 Hz.

Figure 4 The dependences of change in G' ($\delta G'$) before and after thermal annealing on the applied strain for the uncured stocks **1** (○), **2** (□), and **3** (X). The measurement was conducted at 50°C at 1 Hz.

It should be noted that the slight differences in lower compound ML_4 and $\delta(\Delta G')$ along with longer t_5 data were found in stock **2** when compared with stock **3**. Stocks **2** and **3** were prepared with nearly equal molar concentration of siloxane functionality (24.1 mmoles for stock **2**, and 24.8 mmoles for stock **3**) for the sake of comparing their shielding effectiveness as well as the VOC emission discussed in the next section. The differences in these data suggest the OTES is more effective in shielding the silica with the conditions used than is AMS. The advantage of using OTES is likely attributed to the lower reactivity of the cleavage of silsesquioxane linkages in AMS resulting in a lower degree of silanization reaction during compounding. The silsesquioxane in AMS does open more effectively with slight processing changes or by using a promoter to enhance silica reaction during compounding. The details of this approach will be described in a future publication.

VOC emission and latent alcohol during processing and cure

Another important issue with silica compounds in plant processing is the latent alcohol retained in the stocks before and after curing. The latent alcohol could potentially cause blistering in the rubber slabs that significantly reduces the extrusion speed as well as producing cavities in the final cured stocks. Additionally, the alcohol emitted as VOC during the rubber preparation is an environmental concern.

The alcohol content of various stocks was quantitatively determined by total hydrolysis.[1,9,18] The latent alcohol results of stocks **2** and **3** were shown previously[1] where the alcohol emitted as VOC during compounding with **AMS 1** was negligible when compared with that of stock **2** containing OTES. Moreover, the AMS-containing uncured stock **1** retained almost no additional latent alcohol available for release as VOC during further processing of the rubber into tire components. In addition to the retained latent alcohol in the final stocks, they were also followed on the rubbers that were mixed at different mixing stages. These are demonstrated in Table VII from stocks **4** to **8**. The same trend shown above for alcohol emission was seen. Stock **4**, containing TESPD, showed a significant evolution of ethanol in both the **MB** (masterbatch) and **R** (remill) mixing stages. Even after cure, about 15% of the initially added latent alcohol present in the silane still remained. In contrast, the AMS containing stocks (**5**, **7**, and **8**) showed almost no alcohol emission or latent alcohol retention during these same steps. The limited amount of available unreacted alkoxysilane groups, from the AMS, during and after mixing, eliminates the possibility of blistering of rubber compounds during vulcanization. The lower latent alcohol content in

TABLE VII
Latent Ethanol from Processing and Cure

Stock	4	5	6	7	8
Charged (wt %)	0.810	0.041	0.00	0.054	0.045
MB (wt %)	0.514	0.035	0.002	0.049	0.022
R (wt %)	0.282	0.033	0.001	0.052	0.022
F, before cure (wt %)	0.269	0.029	0.001	0.045	0.022
F, after cure (wt %)	0.121	0.031	0.002	0.041	0.021

rubber then allows faster processing such as extrusion and production of cured tires without producing porosity. In addition to the processing advantages, the use of AMS apparently allows for a significant increase in the amount of silica that can be used for reinforcement without sacrificing plant productivity. Some of the advantages possible with silica-filled stocks can be seen in the next section.

Reinforcing the silica-filled rubbers with AMS and *co*-AMS

Compounding silica-filled rubbers with AMS and a coupling agent

To reinforce the silica-filled rubber, it is desirable to add a coupling agent with the addition of one or more groups that are able to bind to the elastomer. The widely used TESPD or TESPT[2–6] served as the bifunctional silane to aid compound processing as well as to reinforce the silica-filled rubbers. Alternatively, an individual processing aid or silica-dispersing agent can be added in the presence of a small amount of sulfur containing coupling agent such as mercapto alkyl silanes[7] or blocked mercapto alkyl silanes for reinforcing the rubbers.[8] Since the AMS is shown to be an effective silica-shielding agent in the previous section, the combination of AMS and a small amount of coupling agent such as MPTMS in silica-filled rubbers was expected to reinforce rubbers well when compared with the bifunctional silanes traditionally used. To reduce the VOC and odor issues in using MPTMS for compounding, a commercial product containing MPTMS supported on silica (Ciptane® 255LD, a 3-mercaptopropyl silane (MPTMS) fixed to silica with substantially no trialkoxysilane present) was used. When the Ciptane® is used, the amount of silica in the rubber compound can be adjusted for the added silica from the Ciptane® to give the desired total amount of silica in the formulation.

Stocks containing silica and carbon black (Group **B**) were prepared by using TESPD (stock **4**), Ciptane® 255LD with either **AMS 1**(stock **5**) or POSS (stock **6**). The use of POSS in rubber compound had been reported.[25] For the sake of comparison, the stock containing POSS was included in order to compare with those of the AMS. Note that the POSS

TABLE VIII
Processing and Curing Characteristics of Uncured Stock

Stock	4	5	6	7	8
Mooney Scorch measurement at 130°C					
ML_4	68.29	71.47	96.97	84.84	70.65
t_5 (min)	22.3	20.2	16.3	16.4	19.1
Curing characterization at 160°C					
MH-ML (kg_f-cm)	15.96	14.30	17.00	16.02	15.21
t_{s2} (min)	4.91	4.61	3.62	3.17	4.22
t_{10} (min)	4.64	4.07	3.27	2.63	3.51
t_{90} (min)	13.96	16.58	22.68	26.16	23.97
Others					
$\delta(\Delta G')$ (MPa)	2.01	1.61	2.64	2.06	1.41
Bound rubber content (%)	45	46	45	48	42

Figure 5 The G' strain dependences of the uncured stocks **4** (○, containing TESPD), **5** (□, containing **AMS 1**), and **6** (X, containing POSSS). The measurement was conducted at 50°C at 1 Hz.

has the perfect closed structure[10] of silicon–oxygen bond when compared with those of AMS.[1] The amount of MPTMS in Ciptane® 255LD used for stocks **4** and **5** is about 0.3 phr, a relatively small dosage used when compared with those using the TESPD. The formulation and ingredients used to prepare stocks **4**, **5**, and **6** are listed in Tables III and V. The processibility of these stocks is assessed by examining the ML_4, t_5, as well as the curing characteristics shown in Table VIII. Higher ML_4 and $\delta(\Delta G')$ values, as well as shorter t_5 values of stock **6** indicated that POSS does not act as an effective silica-shielding agent. Apparently, the silicon–oxygen polyhedral structure in POSS cannot react with silica well enough to prevent silica agglomeration after mixing or after thermal annealing. In contrast, the chosen level of **AMS 1** with Ciptane® (stock **5**) gave processing and curing characteristics similar to an optimized stock containing the TESPD (stock **4**), but with less filler flocculation upon heating as seen by the lower $\delta(\Delta G')$ data.

The rubber reinforcement in stocks **5** and **6** compared with stock **4** were assessed by bound rubber data, G' strain dependence measured on uncured stocks (Fig. 5), viscoelastic properties (Table IX), and tensile mechanical properties (Table X) that were measured on cured stocks. The comparable bound rubber contents among stocks **4**, **5**, and **6** suggest all rubbers are equally reinforced in the uncured stocks. The G' strain dependences of stocks **4**, **5**, and **6** are shown in Figure 5 where slightly higher G' were found in stock **5** when compared with those of stock **4** as the applied strain was greater than 2% (inset in Fig. 5). It has been shown that when a higher degree of polymer-filler (P-F) interaction is present in a sample, lower low-strain G' but higher high-strain G' are usually found upon deformation.[13,16,18,26] Apparently, filled rubber with a less developed filler network will give lower low-strain G'. Meanwhile, the higher high-strain G' is believed due to the presence of the stronger filler network woven by P-F interac-
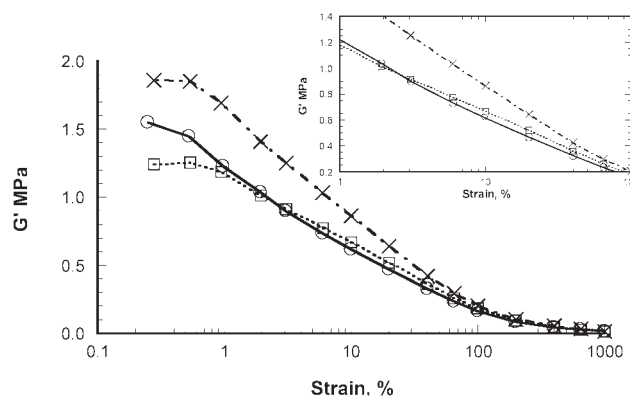
tions that are more resistant to the applied deformation.[16,18] Therefore, it is apparent that stock **5** which contains the silica-shielding agent, **AMS 1**, and a small amount of coupling agent, MPTMS, had a marginally less developed but stronger filler network and had slightly higher P-F interaction compared with that of stock **4** containing TESPD.

The tan δ temperature spectra of cured stocks **4**, **5**, and **6** are shown in Figure 6 where stronger dependences were observed in stocks containing the MPTMS (stocks **5** and **6**) compared with the TESPD stock **4**. The result in lower 50°C tan δ found in stocks **5** and **6** but with comparable 0°C tan δ to the stock **4**. The 0°C and 50°C tan δ from Figure 6 along with G' at −20°C and 50°C rebound values were tabulated in Table IX. The tan δ values measured at different temperatures are usually used to predict several tire performances. For example, tire rolling resistance and wet traction are both dictated by the energy losses from the tire service, but encompass different deformation magnitudes and frequencies.[27–30] These energy losses can be conveniently measured by the dynamic viscoelastic properties of the rubber in a frequency range of 1–10 Hz with strain levels selected as a function of temperature from −100°C to 100°C.[31] Thus, use of tan δ at 0°C as a predictor of tire wet traction, tan δ at 50°C as a

TABLE IX
Rebound Data and Viscoelastic Properties Measured from Temperature Sweep

Stock	4	5	6	7	8
G' at −20°C (MPa)	33.25	30.85	38.53	25.69	26.84
tan δ at 0°C	0.3263	0.3384	0.3242	0.2991	0.3071
tan δ at 50°C	0.2052	0.1839	0.1917	0.1859	0.1887
50°C Rebound (%)	55.8	57.6	54.6	55.6	56.4

TABLE X
Tensile Mechanical and Tear Properties

Stock	4	5	6	7	8
Tensile mechanical measurement at 25°C					
M50 (MPa)	1.33	1.14	1.28	1.13	1.14
M300 (MPa)	10.15	8.53	8.81	8.3	8.26
Strength (MPa)	17	16.28	15.71	15.18	16.36
E_b (%)	441	467	457	458	480
Toughness (MJ/m^3)	32.21	31.37	30.72	29.25	32.61
Tear strength measurement at 171°C					
Tear strength (kN/mm)	11.42	10.87	9.93	10.81	12.42
Tear strength (E_b %)	159	178	133	165	187

predictor of rolling resistance, and G' at −20°C as a predictor of snow traction are widely practiced in the tire industry. Therefore, stock **5** (containing **AMS 1**) was predicted to have better snow traction and lower rolling resistance (RR) without sacrifice of wet traction, compared with stock **4** that contained TESPD. The lower RR prediction for stocks **5** and **6** were consistent with the rebound data measured at 50°C shown in Table IX. Note that rebound test is another means to measure the energy loss as described in the test section. The higher number of the rebound test results indicate less energy loss during the deformation process imparted by impacting the rubber with an indentor. Therefore, lower RR is predicted for a tire tread tested with higher rebound values. In addition, the stronger tan δ temperature dependences measured at lower strains (0.5% (−60 to −30°C) and 2% (−30 to 60°C)) in stocks **5** and **6** may suggest higher degrees of P-F in these stocks.[13,16,26] When the strain level increased from 5 to 100% with these stocks, stock **6** with POSS shows higher tan δ for applied strain greater than 2% (Fig. 7). Note that tan δ is the normalized G'' which is the energy loss at a constant strain[26,28] di-

vided by compound G'. The lower low-strain tan δ found in stock **6** is mainly due to its higher compound G'. By examining the energy loss strain spectra of these stocks in Figure 8, the highest energy losses were found in stock **6**, whereas stock **5** had the least energy losses over the entire measured strain range. Therefore, the POSS-MPTMS stock is expected to give a higher rolling resistance than the AMS-MPTMS stocks when they are subjected to larger applied strain deformations.

The tensile mechanical and tear properties for stocks **4**, **5**, and **6** are listed in Table X. The properties in stocks **4** and **5** were apparently comparable. Although slightly lower high-strain moduli (M300) were found in stock **5**, further optimization of these mechanical properties has been obtained and will be the subject of a subsequent publication.

Compounding silica-filled rubbers with a functional *co*-AMS

Although a combination of AMS and a coupling agent in silica-filled rubber gives properties comparable to those prepared by the use of TESPT or
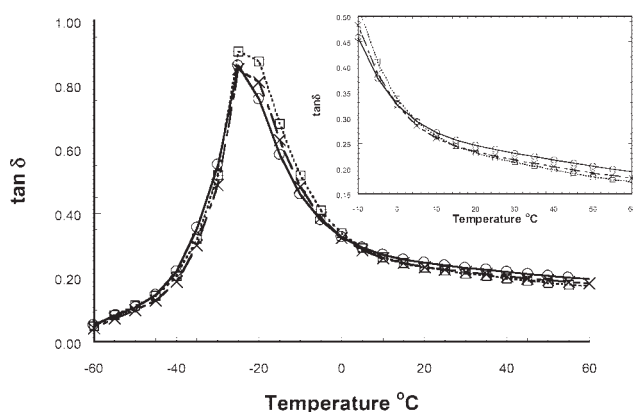

Figure 6 The tan δ temperature dependences of the cured stocks **4** (○, containing TESPD), **5** (□, containing **AMS 1**), and **6** (X, containing POSS).

Figure 7 The tan δ strain dependences of the cured tocks **4** (○, containing TESPD), **5** (□, containing **AMS 1**), and **6** (X, containing POSSS) measured at 50°C.

Figure 8 The G'' and G' (inset) strain dependences of the cured tocks **4** (○, containing TESPD), **5** (□, containing **AMS 1**), and **6** (X, containing POSSS) measured at 50°C.
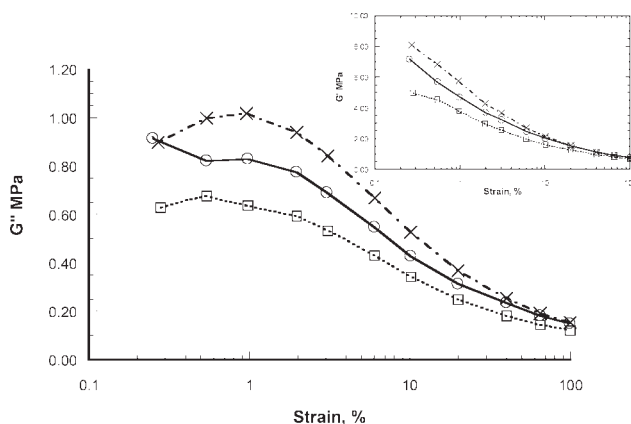
TESPD, a more desirable use of this technology would be the incorporation of the coupling and silica-dispersing agents into the same AMS. For this a functional co-AMS was prepared from silane **1** with either silane **3** or silane **4**.[1] Compounded silica-filled rubbers with the functional co-AMS, stocks **7** and **8** were prepared with **AMS A** and **AMS B**, respectively. Note that **AMS A** contains mercapto functionality, whereas blocked mercapto groups were incorporated in **AMS B**. The silane **1** part of the co-AMS then can be used as the silica-dispersing agent to disperse and to process the silica-filled rubbers, whereas the coupling part derived from silane **3** (mercapto) or silane **4** (blocked mercapto) can be utilized for rubber reinforcement. Results similar to what was obtained from **AMS 1** and a coupling agent in the stock **5** were obtained with the exception of higher compound ML_4 found in stock **7**. The physical properties of stocks **7** and **8** show similarities to stock **5** in Tables IX and X. The higher ML_4 of stock **7** may be attributed to the higher degree of reaction between the mercapto group in **AMS A** and rubber. Further optimization in the design of co-AMS, such as the composition of mercapto functionality, the dosage used for compounding, and the mixing conditions employed may be needed to address the issues. However, the results described above suggest the presence of a higher degree of P-F interaction, and/or a higher degree of silica hydrophobation in the rubbers and are consistent with those findings in the preceding section.

CONCLUSIONS

The compounding, processing, and physical properties of silica-filled rubbers containing a class of alkoxy-modified silsesquioxane (AMS) compounds have been described. The structure of AMS is moisture stable and hydrocarbon soluble but still retains enough alkoxysilane functionality so that a silica reactive product is obtained and allow for the compounding of improved vulcanizates from silica-filled rubbers. The silica-filled rubbers containing AMS with a coupling agent or just the co-AMS as a coupling agent have also been demonstrated. The test data has shown the enhanced rubber reinforcement, increased polymer-filler interaction, and lowered compound viscosity without sacrificing favorable compound properties. Therefore, the use of AMS as a silica shielding agent or co-AMS as a coupling agent should allow the production of tires having improved silica dispersion and improved tire performances including lower rolling resistance, better wet, and snow traction.

Most importantly, the use of AMS as a shielding and coupling agent in silica-filled rubbers allows significant reduction in the alcohol that can be released from the manufacturing of rubber article by over 95% of the levels currently produced. The reduction in the amount of alcohol that can be released will significantly curtail the total plant VOC emissions, which will soon be the goal of the rubber industry. Thus, the reduction of the alcohol evolved during the production of silica-filled elastomers has a threefold benefit. First, a positive environmental impact was made by reducing VOC evolution. Second, an increase in productivity can be obtained by allowing faster rubber processing. Finally, the elimination of porosity in the cured elastomer results in good quality rubbers and increased productivity.

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