Reduction of Volatile Organic Compound Emission. I. Synthesis and Characterization of Alkoxy-Modified Silsesquioxane

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ABSTRACT: The preparation and characterization of a class of alkoxy-modified silsesquioxane (AMS) compounds containing less than 5 wt % of latent alcohol is described. The AMS derived from octyl triethoxysilane (OTES) behaves as a shielding agent in silica-filled rubbers while significantly reducing the volatile organic compounds that are released during the manufacture of rubber articles. Analysis of AMS by high pressure liquid chromatography and ^{29}Si NMR shows that it has a plethora of structures present that can best be described as a highly condensed opened oligomeric, branched arrangement of silsesquioxanes units. This structure is moisture stable, hydrocarbon soluble, and reactive with silica at compounding temperatures. The AMS has been prepared by acid- or base-catalyzed hydrolysis and condensation in alcohol solution to form a product that often separates from the lower density reaction mixture. The kinetics of the AMS formation was examined and showed two separate rate processes occurring. The co-AMS prepared from OTES and 3-mercaptopropyl trimethoxysilane yielded an effective shielding agent and coupling agent when used in silica-filled vulcanizates. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 79–90, 2010

Key words: VOC; silane; silica; rubber; silsesquioxane

INTRODUCTION

When producing elastomeric compositions, it is desirable that reinforcing fillers, such as silica and/or carbon black, be well dispersed throughout the rubber to improve various physical properties, such as the compound Mooney viscosity, cured modulus, and hysteresis (tan δ). Tires produced from vulcanized elastomers exhibiting these improved properties have reduced rolling resistance that resulted in improved fuel economy, increased snow, ice, and wet traction. Mixing silica into rubber stocks, however, is difficult because the polar silanol groups on the surface of the silica particles tend to self-associate and reagglomerate after compounding, thereby leading to poor silica dispersion and a high compound viscosity.[1,2] Such a strong and highly developed silica filler network produces a rigid uncured compound that is difficult to process during extrusion, molding, and subsequent tire build processes.

To alleviate this problem, various silica coupling agents such as *bis*-(triethoxysilyl propyl) polysulfides [e.g., tetrasulfide (TESPT) and disulfide (TESPD)][3–7] and combinations of octyl triethoxysilane (OTES) and 3-mercaptopropyl trialkoxy silanes (MPS)[8] have been used to improve silica dispersion and processing. These coupling agents have alkoxy silane groups that are reactive with the silica surface and sulfur containing functionality, which react with unsaturation in the polymer. A concern of using the aforementioned silanes is the release of the by-product alcohol, a volatile organic compound (VOC), into the environment from the alkoxysilane-silica reaction. The release of alcohol is of particular concern at high processing temperatures. At lower processing temperatures, the rubber stock retains a considerable amount of unreacted alkoxysilyl groups that are then available to further react with the silica and moisture during storage, extrusion, tire building, and/or curing. Such delayed alcohol formation can result in blisters, tread porosity, undesirable increases in the compound viscosity, and shorter shelf-life.[9] These factors force a lower tread extrusion speed, a decrease in production and a concomitant increase in cost. As the present trend in rubber-making technology continues toward the use of higher silica loadings in rubber compounds, the challenge to reduce levels of environmentally released alcohol also increases. Therefore, a need

exists to prevent the evolution of alcohol during compounding, processing, storage, and cure of silica-reinforced rubbers.

This work describes the synthesis and characterization of a class of alkoxy-modified silsesquioxane (AMS) compounds that provide the benefit of traditional alkoxysilane-silica reaction as a silica shielding agent in rubber, but release negligible alcohol during compounding and processing.

EXPERIMENTAL

Materials

The n-OTES was obtained from Dow Corning (Midland, MI). The 3-mercaptopropyl trimethoxysilane and octyl trichloro silane were acquired from Gelest (Morrisville, PA). The thiooctanoyl propyl triethoxysilane (NXT[TM]) was received from Crompton Corp. (Greenwich, CT). The polyhedral oligomeric silsesquioxanes (POSS)[10] were purchased from Hybrid Plastics (Hattiesburg, MS). The silica used was HiSil[®]190 purchased from PPG Industries (Pittsburgh, PA), which had a 200–210 m^2/g surface area. All of these materials were used without further purification.

Characterization

Because of the complex three-dimensional geometry that must be generated in the AMS formation, a variety of analyses were applied, of which, total latent alcohol content, high pressure liquid chromatography (HPLC), and ^{29}Si-NMR were the most useful.

^{29}Si-NMR measurements

Samples were dissolved in deuterated chloroform ($CDCl_3$) and filtered before transferring into a 10 mm NMR tube for measurement. A Varian Mercury Plus 400 NMR Spectrometer System was used. Observation frequency was 79.546 MHz. All samples were referenced to tetramethyl silane (TMS) at 0.0 ppm. Gated decoupling was used to avoid the negative nuclear Overhauser effect. A 30° pulse was used with a delay time of 58 s.

HPLC

Experimental procedure. The analysis of the AMS materials was accomplished by HPLC. The column used was a Zorbax XDB C8 (250 × 3.0 mm) supplied by MAC-MOD. The mobile phase was 75% methanol/25% tetrahydrofuran at a flow rate of 1.0 mL/min. An Alltech evaporative light scattering detector was used for detection with the drift tube at 70°C and nitrogen flow at 1.3 L/min. Sample solutions were prepared in 1/1 mixture of methanol/tetrahydrofuran at a concentration of 5 mg/mL. An injection of 20 μL of this solution was used.

Latent alcohol measurement

The latent alcohol content was determined by treating a sample with a siloxane hydrolysis reagent composed of 0.2N toluenesulfonic acid/0.24N water/15% n-butanol/85% toluene. This reagent quantitatively reacts with the residual [EtOSi] or [MeOSi] freeing the stoichiometric amount of ethanol or methanol, which is then following the previously reported analysis measured using headspace gas chromatography.[9]

Preparations of AMS

The silanes used to prepare the AMSs, their formula weight and theoretical silsesquioxane formed from the total hydrolysis and condensations are listed in Table I. These values were used along with the mole fractions of the silanes charged to determine the approximate yield of the desired AMS. Other silanes, solvents, strong acids, and bases have also been successfully used to give different AMS products and to prevent the phase separation of the product. These preparations will be the subject of subsequent publications.

General procedure

The general procedure used to prepare the AMS was a modification of Dittmar.[11] Typically at ambient temperature, 43.74 g (158.2 mmol) of OTES, 15.17 g (842 mmol) of distilled water, and 15.56 g (157.9 mmol of acid and 544 mmol of water) of concentrated hydrochloric acid were added to

TABLE I
Silanes Used to Prepare AMS

Number	R-Silane	Si-X₃	R-SiX₃ (g/mol)	R-SiO₁.₅ (g/mol)
1	Octyl	Triethoxy	276.49	165.31
2	Octyl	Trichloro	247.67	165.31
3	3-Mercapto propyl	Trimethoxy	196.34	129.23
4	Thiooctanoyl propyl	Triethoxy	364.63	253.44

TABLE II
Preparation of AMS with One Silane

AMS #	Silane # (runs)	Weight (g)	Catalyst (ratio/Si)[a]	Time (h)	Water (g)	Yield (%)	EtOH (wt %)
1a	1	27.64	HCl (2.3)	16	17	93.2	0.25
1b	1 (2)	22.11	NaOH (0.06)	72	10	102	0.26 EtOH and 3.67 MeOH[b]
1c	1	27.53	DBU (0.2)	17	28	88.7	1.69
1d	1 (2)	292.27	HCl (0.4)	72	70	98.2	2.35
1e	1 (11)	501.6	HCl (1.9)	261	–	–	2.8[c]
1f	1 (11)	501.6	HCl (1.9)	261	186	97.4	3.13
1g	1 (10)	326.46	HCl (1.9)	260	58.5	94.6	3.5
1h	2 (2)	49.6	SiCl₃ (3)	39	18.2	99.4	4.39

[a] The catalyst to silane was based on the initial charge. No additional catalyst was added with subsequent silane addition.
[b] This preparation was in methanol as solvent.
[c] Sample isolated by extraction.

120 mL of absolute ethanol and mixed. When the solution was allowed to stand, it became cloudy and phase separation began in about 5 min. Within 3 h, two clear solutions were formed, which did not increase in the ensuing hour. Separation gave 35.6 mL of product as the lower layer, which was reduced to 24.9 mL after drying. Analysis for latent alcohol showed only 2.29% ethanol.

The parameters used to prepare the AMSs can be seen in Tables II and III. The AMSs listed in Table II derived from silane **1** or **2** are designated as **AMS1** followed by a lower case letter suffix that was chosen to increase with the latent ethanol present in the AMSs. In the case of *co*-AMS listed in Table III, both silane numbers were used as a suffix with an additional parenthetical mole percent composition of the minor component added adjacent to the second trialkoxysilane number. For example, **AMS1, 3 (8)** denotes an 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.

The aforementioned procedure has been used successfully with 0.2–1*M* solution of the desired organo trialkoxy silane in absolute ethanol or methanol with added concentrated hydrochloric acid (<2 mol/mol of silane) and water (>1.5 mol/mol of silane). The total water includes both the contribution of the added water and that provided by the addition of the hydrochloric acid. The initially clear mixture separates into two layers at temperatures up to 50°C within 1 h to 3 days. Reaction rate and phase separation was dependent on the solvent used, the percent water present, concentration of the silane, and most strongly on the organo group attached to the silane.

Other variations in the choice of the aforementioned parameters such as work up, catalyst, and *co*-silane are briefly listed later.

Method A: Extraction

Where total recovery of the AMS was sought, the soluble AMS was isolated by decanting the top aqueous layer and extracting with hexane or

TABLE III
Preparation of *co*-AMS in EtOH

AMS #	Silane #s (runs)	Weight (g)	HCl acid/Si[a]	Second R-SiX₃ (mol %)	Time (h)	Water (g)	Yield (%)	EtOH (wt %)
1, 3 (8)	2, 3 (1)	23.09	3	8.0	3	21.2	88.8	4.39
1, 3 (11)	1, 3 (2)	102.68	1.5	10.9	140	40	89.7	4.31
1, 3 (42)	1, 3 (2)	90.81	3.5	41.9	34	218	91.4	1.45
1, 4 (9)	1, 4 (2)	87.17	2.0	9.1	35	48	95.6	4.05
1, 4 (10)	1, 4 (1)	75.29	1.4	10.1	17	100	103.4	3.38
1, 4 (11)	1, 4 (5)	308.86	1.9	10.5	67	300	100.2	2.19
1, 4 (33)	1, 4 (5)	27.76	1.9	33.4	17	48	85.1	4.01
1, 4 (43)	1, 4 (3)	119.69	1.9	42.6	51	200	96.3	2.44

[a] The HCl to silane was based on the initial charge. No additional catalyst was added with subsequent silane addition.

TABLE IV
^{29}Si-NMR Analysis of AMS

| Sample # | Latent EtOH (wt %) | Percent of ^{29}Si-NMR in 5 ppm range centered at | | | | | | Method |
		−49.5	−54.5	−59.5	−64.5	−69.5	−79.5	
POSS	0.002	0.2	0.7	4.8	5.9	88.3	0.1	–
AMS 1b	0.26	3.8	31.6	37.8	21.2	5.3	0	A
AMS 1g	3.5	3.1	27.4	32.4	30.8	5.9	0.3	B-1
AMS 1e	2.8	1.1	34.7	30	26.9	7.2	0.2	B-1
AMS 1h	4.4	1.4	26.2	36	27.6	8.8	0	B-2
AMS 1a	0.25	1.3	18.8	20.5	23	36.2	0.2	B-3
AMS 1c	1.69	0.3	9.5	13.4	46	30.7	0.2	B-3
AMS 1, 4 (9)	4.1	0.6	28.8	25.3	35.6	7.5	2.1	B-1
AMS 1, 4 (33)	4	0.2	23.9	24.4	37.6	13.8	0	B-1
AMS 1, 3 (8)	∼ 4	1.9	23.1	39.6	27	8.4	0	B-2

cyclohexane. The hydrocarbon extract was isolated by rotary evaporation and could be combined with the original lower layer. The two fractions were found to be indistinguishable by NMR and HPLC. This was used to prepare **AMS1b**.

Method B-1: Continuous AMS production

A separatory funnel may be used to remove the higher density AMS from the reaction mixture. The concentrated product in the lower phase may then be vacuum dried to remove traces of alcohol, water, and acid. Sequential multiple additions of silane to the residual alcohol and catalyst solution has been repeated up to 11 times with no loss in reactivity. In fact, an increase in the rate and yield of product separation was seen, when the addition of silane was made before total conversion of the preceding reaction occurred. Method A can be used to isolate the residual product that has not separated at the end of the chosen reaction time. The extracted AMS has a slightly reduced latent alcohol, but a similar HPLC analysis as the phase separated product; see **AMS1e** and **AMS1f** in Table II.

Method B-2: Using octyl trichlorosilane

Another variation involves the use of octyl trichlorosilane (silane **2**), either alone or in combination with another trialkoxysilane. No hydrochloric acid addition was required and if a sequential reaction was done with the supernatant, the increased acid generated from the hydrolysis of silane **2** causes an acceleration of the rate of product formation. In this case, 3 equiv of additional water per equivalent of trichlorosilane was added to insure complete hydrolysis. The products obtained by this procedure **AMS1d** and **AMS1, 3 (8)** have typical AMS characteristics.

Method B-3: Use of basic catalysts—Sodium hydroxide to prepare AMS 1a

The AMS has also been prepared by the use of basic catalysts. However, when greater than a stoichiometric amount of sodium hydroxide (2.5 equiv) was used, an alcohol insoluble sodium salt was formed. Isolation required neutralization with aqueous acid and extraction. A summary of integration ranges from the ^{29}Si-NMR can be seen in Table IV, which showed that a slightly different product was formed, when compared with the other acid-catalyzed samples. The latent ethanol level was 0.25%.

Reducing the level of sodium hydroxide to 0.06 equiv gave less of the insoluble sodium salt, but required 72 h for the phase separation to appear. The analysis indicated that an almost identical product to that obtained from the use of the excess base resulted.

DBU to prepare AMS 1c

The use of 0.25 equivalents of DBU (1, 8-diazabicyclo [5.4.0] undec-7-ene) as a catalyst to prepare AMS 1c gave an apparently gelled product, which became liquid after extraction with cyclohexane and hydrochloric acid. The yield was 90% after vacuum drying. ^{1}H-NMR analysis showed a similar peak distribution to the product obtained using the sodium hydroxide catalyst shown earlier. A latent 1.68% ethanol was measured.

Kinetics of AMS formation

The kinetics of the AMS formation at 23, 40, and 49.9°C was studied by running the condensation in a 1 L Imhoff sedimentation cone graduated from 0 to 1 mL (in 0.1 mL subdivisions); 1–10 mL (in 0.5 mL subdivisions) and 10–40 mL (in 1 mL subdivisions). At elevated temperatures, the alcoholic silane

TABLE V
Kinetic Runs for AMS 1

Run #	Solvent	[OTES] (mol/L)	[HCl] (mol/L)	[Water] (mol/L)
A	EtOH	0.79	0.77	13.62
B	EtOH	0.40	0.40	13.99
C	EtOH	0.40	0.40	6.41
D	MeOH	0.40	0.40	6.39
E	EtOH	0.40	0.80	3.72
F	EtOH	0.80	0.40	7.00

and the aqueous acid solutions were heated for 30 min in an oven at 5°C below the reaction temperature before mixing in the Imhoff cone held in a thermostatically controlled water bath. The kinetic data for the formation of AMS 1 by varying the reaction parameters is listed in Table V.

Because of the slight solubility of the reaction solvent in the AMS, the volumes of the product measured in the cone were normalized to the final volume measured at long reaction time. The final time has been chosen as the volume of product that did not increase after 1 h of standing after the last volume reading was made. The final volume of the crude product measured was always greater than expected because of the solubility of some of the various aqueous alcohol compositions used in the AMS. However, assuming that this final volume represented 100% of the moles of OTES charged, the conversion to reactants and products could be calculated. This generally amounted to about 10 wt % reduction in the separated product to give the final weight of AMS produced (the density of the AMS is 1.01 g/mL). When plots of [OTES] was made, the final [AMS] = 100% was used so that it could be subtracted from the initial [OTES].

TABLE VI
Formulation Used for Preparing the Rubber Compounds

Ingredient	Phr[a]
Natural rubber	0
SBR[b]	100
Carbon black	0
Precipitated silica	65
Process oil	20 (aromatic)
Wax	1.7
Antioxidant[c]	0.95
Stearic acid	2.0
Silica-dispersing agent (Silane, AMS)	Various
Sulfur	2.8
Accelerator 1[d]	1.17
Accelerator 2[e]	0.39
Zinc oxide	1.94

[a] Parts per 100 parts of rubber, by weight.
[b] Solution SBR (23.5% styrene, T_g −36°C, ML$_4$ 58).
[c] N-(1,3 dimethylbutyl)-N′-phenyl-p-phenylene-diamine.
[d] N-Cyclohexyl-2-benzothiazolesulfenamine (CBS).
[e] Diphenyl guanidine (DPG).

TABLE VII
**Silica-Dispersing Agent used for Preparing the Rubber Compounds**

Feature stock	Agent type	Agent phr
1	0	
2	OTES	6.67
3	**AMS1g**	4.1

Rubber compound preparations

The formulation used for preparing rubber compounds for this study is shown in Table VI. The poly(butadiene-co-styrene) polymer was DURADENE™ 715, obtained from Firestone Polymers, LLC,* which was characterized as 47% vinyl, 23.5% styrene, with a Mooney viscosity (ML$_4$)[12] of 58 measured at 100°C, and a midpoint T_g of −36°C. The amounts of the ingredients used are given based on a total of 100 parts of the rubber or combination of rubbers used. This is commonly expressed as parts per hundred of rubber (phr). Rubber compounds were prepared with or without the addition of a silica-dispersing agent that include OTES or AMS. The type of silica-dispersing agent and its loading to the test compounds are specified in Tables VI and VII. Table VIII lists the mixing procedure to prepare the rubber compounds.

RESULTS AND DISCUSSION

The AMS generated from a single trialkoxysilane and the co-AMS formed from two different trialkoxysilanes can be most simply depicted by the Formula a.

$$\left(R^1SiO_{3/2}\right)_w\left(R^2SiO_{3/2}\right)_x\left(R^1SiO\left(OR^3\right)\right)_y\left(R^2SiO\left(OR^3\right)\right)_z$$

(a)
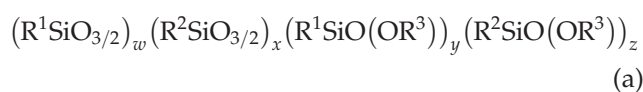
In an AMS compound, either w or x but not both can be zero. In a co-AMS, both w and x are not zero. The mole fraction of the silanes containing R^1 and R^2 can be calculated as the mole fraction of the sum of w and y or the sum of x and z. Suitably, ratios of the R^1 mole fraction (or the R^2 mole fraction) to the sum of the mole fractions w, x, y, and z can range from about 0.01–0.5. The sum of the mole fractions w, x, y, and z is always equal to one, and the sum of y and z is always greater than zero. The R^1 and R^2 groups used can be the same or different and have been limited in this artilce to octyl, 3-mercaptopropyl, and 3-thiooctanoyl propyl (NXT™, which is a blocked mercaptan). Other functionalities have

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*Duradene is a registered trademark of Firestone Polymers, LLC for synthetic rubber.

TABLE VIII
Mixing Procedures Used for Preparing the Rubber Compounds

Master Batch Stage	
Agitation speed	60 rpm
Initial temperature	100°C
Mixing at 0 s	Charging polymers
Mixing at 30 s	Charge 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**) or 165°C (stocks **2** and **3**)
Remill batch stage	
Agitation speed	50 rpm
Initial temperature	90°C
Mixing at 0 s	Charge masterbatch stock
Mixing at 30 s	Charge the other 1/3 of the silica
Target drop temperature (T_d)	146°C (stocks **1**) or 155°C (stocks **2** and **3**)
Final batch stage (if needed)	
Agitation speed	50 rpm
Initial temperature	75°C
Mixing at 0 s	Charge remilled stock
Mixing at 30 s	Charge curing agent and accelerators
Target drop temperature (T_d)	100–105°C

also been prepared and will be discussed in later publications. The R^3 group can be either methyl or ethyl derived, either from the solvent and/or trialkoxysilane used in the synthesis.

Synthesis of AMS

The reaction to prepare AMS has been found to be dependent on the type of solvent used and the concentration of the silane, catalyst, and water. These factors also control the structure and solubility of the AMS in the reaction mixture, such that the majority of the product can be isolated by decantation. If desired, the residual AMS in the reaction solvent can be extracted with water and hexanes. The product can then be dried in vacuum to remove residual alcohol and water. The resulting product is a viscous liquid. The conditions used to prepare specific AMS compounds are described in Tables II and III.

The formation of AMS can be initially observed as a cloudy solution, which phase separates with increasing time. AMS in the lower phase can be removed from the reaction mixture as it is produced until conversion is complete. Additional amounts of the alkyl trialkoxysilane or alkyl trichlorosilane reactants may be added with water to continuously yield product.

The co-reacting of any pair of alkyl trialkoxysilane or alkyl trichlorosilane under controlled hydrolysis-condensation can provide co-AMS with different

types and concentrations of substituents. For use in rubber compounds, it is desirable to produce a co-AMS compound containing a sulfur atom that can bind to an elastomer. Therefore, a suitable co-AMS compound was prepared by the hydrolysis and cross-condensation of an alkyl trialkoxysilane with a mercapto propyl trialkoxysilane or with a blocked mercapto propyl trialkoxysilane to introduce either the unblocked or blocked mercapto propyl functionality, respectively, into the AMS.

Silane **4** was used as a suitable blocked mercapto-silanes.[13] A deblocking agent can be added at any point during the compounding process, but preferably after the silica-AMS reaction has occurred, so that the sulfur atom of the MPS can bond rapidly with the rubber. Often deblocking is desired during the curing stage, and thus the deblocking agent is added in the final mixing stage. The deblocking agent can be added with the sulfur cure package as it often can function as a cure accelerator, especially in combination with a zinc salt. Examples of known deblocking agents have been described.[14,15]

Kinetics of AMS formation

The volume of separated AMS versus reaction time was measured. The rate of formation of **AMS1** was followed by running the hydrolysis and condensation reaction at selected temperatures in a 1 L Imhoff sedimentation cone as described in the experimental section. A typical plot of reaction time versus [AMS] that was obtained for mixture **F** can be seen in Figure 1. The linear least squares (LSQ) straight line that was fitted to the reaction was used as a measure of the initial rate (*r*1). Although the increase in the percent water in the solvent was necessitated by the setup of these runs, the change in solubility of the AMS produced was not significant enough to prevent comparisons of the rate data. The
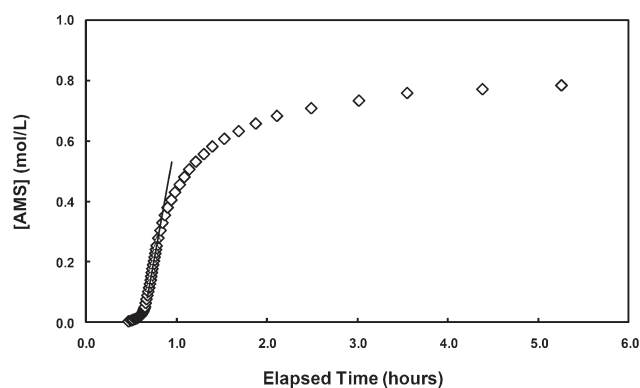
Figure 1 Formation of **AMS-1** at 23°C versus time where the composition was F in Table V. The symbols indicate: All data as open diamonds with the first 3–30% of reaction shown as open triangles. The triangles were fitted with the LSQ line and the slope represents the rate *r*1.
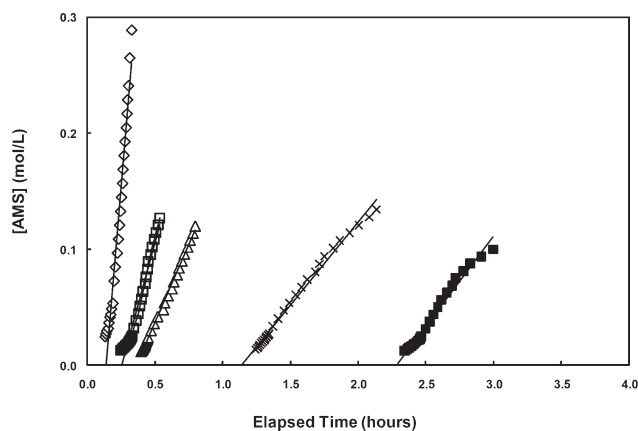
Figure 2 Initial formation of **AMS-1** at 23°C where the composition listed in Table V is as denoted by the symbols: A as open diamonds, B as open triangles, C as solid squares, D as open squares, and E as X. The line shows the LSQ fit of the first 3–30% of the AMS formation.

conversion for this rate was from about 3% to almost 30% of the product formed. In Figure 2, just this initial reaction is shown for mixtures **A–E**. Four of the preparations were made in ethanol solution and the fifth run was made in methanol. They all showed the steady increase in [AMS] in mol/L as the concentrations of the [OTES], [HCl], and [water] increased. The value of $r1$ from the LSQ are shown in Figure 2 and summarized in Table IX.

These preliminary results showed that the initial rate of reaction for the intermediate and high level of water (runs **B–D**) was about the same at a [OTES] = 0.4 mol/L. Even though the OTES to acid ratio was constant, a doubling of these reagents (runs **A** and **B**) gave about a four times increase in the reaction rate. More strikingly was the 10-fold increases in the rates that were seen by doubling the [OTES] (runs **C** and **F**). Exchanging the ethanol with methanol (run **C** and **D**) showed about a twofold increase in the initial rate. The reduction of the [water] to 3.7 mol/L, even with a doubling of the [HCl] reduced the rate by 57% in going from **C** to **E**.

Extrapolation of the $r1$ line to the zero [AMS] formation intercept showed a variety of onset times for the data plotted in Figure 2 and are tabulated in Table IX. A ninefold increase in the onset time was

seen by a 50% reduction of [water] in going from **A** to **C**. Even at the same high water level, a twofold increase of onset time was seen by a 50% reduction in both the [OTES] and [HCl] in runs **A** and **B**. Other interesting changes were also seen, when runs **C** and **D** were compared.

At higher levels of conversion of OTES to AMS, the plot of the logarithm of the reciprocal of the [OTES], Figure 3 gave a good LSQ fit to approximately the last 50% of the reaction. For this, the [OTES] was calculated as the difference between the measured [AMS] and the original charge of [OTES]. Not only Figure 3 shows a good fit for the final reaction ($r2$), but it also gives a good fit as did Figure 1 or 2 up to the first 30% of the reaction ($r1a$). The value of $r1$ from the first part of Figure 3 had a different numerical value than $r1$ obtained from either Figure 1 or 2 because of the difference in the way the data was plotted in Figures 1 and 3. However, either can be used for subsequent analysis with equal success. The slopes from these plots are summarized as rates of reaction in Table IX, where the initial rate measured from Figure 1 has been designated as $r1$ and its similar rate from Figure 3 as $r1a$. The final rate process has been designated as $r2$. Thus, it appears that the rate determining reaction defined by the conditions used to generate Figures 1–3 consists of a series of consecutive and sequential reactions, which could not be readily approximated. A pseudo–first-order rate involving siloxanes and a large excess of water can be assumed, but a series of second-order acid-catalyzed hydrolysis of the trialkoxysilane and further hydrolysis and condensation of the intermediate produced must be occurring. These multiple reactions make the separations of the myriad of individual rates difficult when the only-measured quantity was the formation of AMS. This is most apparent because the rate involves at least two equilibrium reactions involving water and alcohol with two of the alkoxy siloxane groups, followed by the third sequential hydrolysis of the last individual alkoxy siloxane group remaining on the initial OTES molecule.

Attempted kinetic equations are shown in eqs. (1)–(5) for the formation of linear oligomeric

TABLE IX
### Kinetic and Latent Alcohol Results for AMS-1 at 23°C

Run #	$r1$ (M/h)	$r2$ (1/h)	Onset (min)	$r1a$ (M/h)	ROH (wt %)
A	1.84	1.44	10.4	1.78	1.45
B	0.27	0.42	21.8	0.34	1.39
C	0.13	0.026	127.4	0.17	1.74
D	0.49	0.39	16.7	0.68	4.95
E	0.14	0.092	68.4	0.19	4.55
F	1.65	0.286	37.5	1.06	2.87
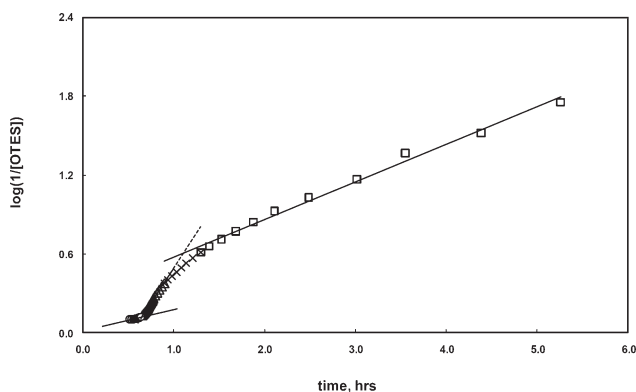
Figure 3 Loss of [OTES] at 23°C versus time where the composition was F in Table V. The symbols indicate the beginning of the reaction as circles: *r1a* as triangles with a fitted LSQ line, transition between *r1a* and *r2* as X, and *r2* as squares with the fitted high conversion LSQ line.

products. For all of these equations, the presence of the catalyst has not been shown to simplify the presentation. Individual equilibrium reaction rates k_1–k_4 are associated with these equations to give the oligomer with a monoalkoxy silane repeat unit shown. Further hydrolysis of this soluble oligomer would involve the intramolecular condensation of the monoalkoxy silanes, such that they soon produce an insoluble AMS in the alcohol solvent as shown by the reaction rate k_5.

Other equations can be written involving the reaction of the silanol directly with the alkoxysilane similar to eqs. (2) and (4). Also, the formation of the AMS in eq. (5) could include multiple hydrolysis and condensation steps before the final product becomes insoluble. However, lacking good evidence for these steps and intermediates, only the minimal number of equations has been presented here. Each reaction has a different rate k_1, k_2, k_3, k_4, and k_5 to generate the specific hydrolysis and condensed intermediates. All but k_5 are in equilibrium while in solution and have the corresponding reverse constants of k_{-1}, k_{-2}, k_{-3}, and k_{-4}.

$$(1)$$

$$(2)$$

$$(3)$$

$$(4)$$

$$(5)$$
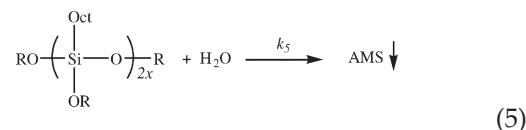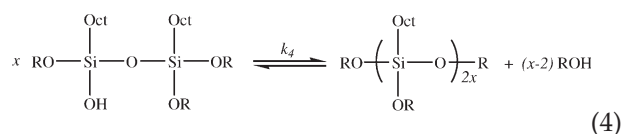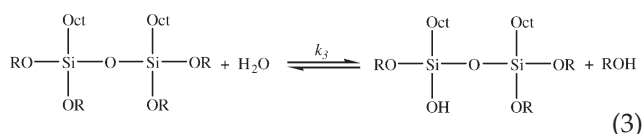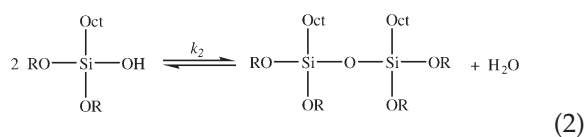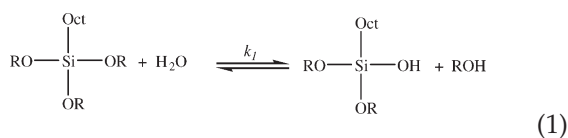
This combination of reactions must produce the break points seen in the plots of Figures 1 and 3. The onset time for the reaction is controlled by the first 4 equations, until a high concentration of the oligomeric product [eq. (5)] is formed and phase separate from the mixture. The onset time results from eqs. (1) to (4) where the change in polarity of the solvent and concentration of the reagents control the rate of formation of the intermediates that are needed for eq. (5) and the phase separation of the AMS. These are shown in Figures 2 and 3 and are summarized in Table IX. The remainder of the hydrolysis proceeds at a slower rate as the concentration of reagents was decreased. Only run **A** with [OTES] = 0.8 mol/L and [water] = 14 mol/L maintained the initial rate of reaction over the entire time. In contrast, run **E** gave an indication of the role of the [water] during the number of possible kinetic steps that are operable with this reaction. Thus, both first-order and/or second-order reactions occur for all stages of the reaction, which appear to be controlled by competing and consecutive second-order condensation of the intermediates to give the AMS. Further expansion of this complex series of reactions are beyond the scope of this article.

Arrhenius plots

The kinetic results obtained so far have shown a wide range of rates being measured for the two processes observed. To further elucidate the chemistry involved in this complex hydrolysis and condensation of trialkoxy silanes, a moderately rapid
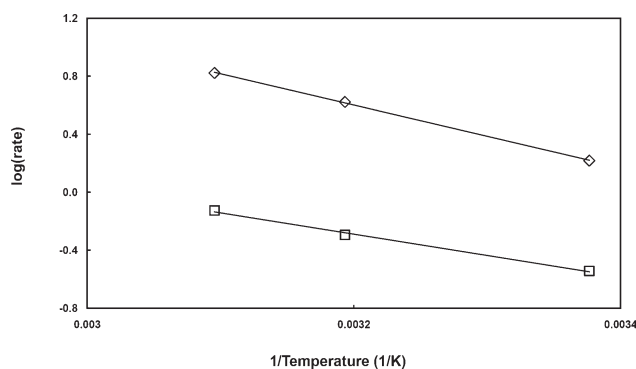
Figure 4 Arrhenius plots of *r1* and *r2* for composition F, where *r1* is diamonds and *r2* is squares.
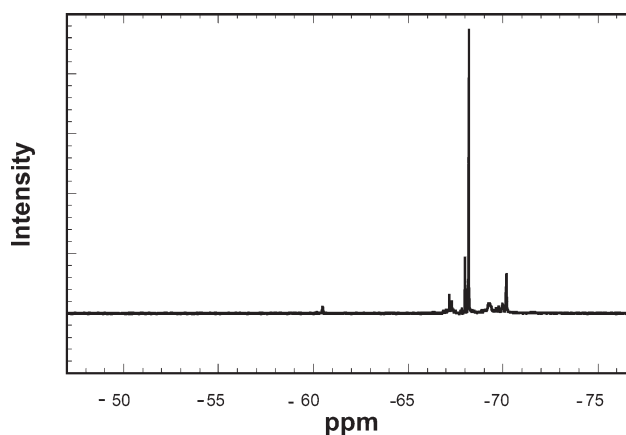
TABLE X
The Latent Ethanol Data in Silica-Filled Rubber Compounds

Stock	1	2	3
Latent ethanol from formula (%)	0	1.640	0.072
Latent ethanol in green stock (%)	0	0.665	0.012
Ethanol lost during compounding (%)	0	0.977	0.060

formation (mixture **F** in Table V) was run at 23, 40, and 49.9°C. The Arrhenius plot can be seen in Figure 4, from a mixture of [OTES] : [acid] : [water] equal to 0.8 : 0.4 : 7.0 in ethanol. The activation energies for *r*1 and *r*2 of 41.3 and 28.1 kJ/mol were determined. However, 46.2 kJ/mol obtained from the *r*1*a* process was not shown. The onset times measured decreased with increasing temperature as did the latent percent alcohol present in the product of the reaction. In all three cases, the amount of crude AMS collected was identical within experimental error.

Latent alcohol content

The level of alkoxy modification has been successfully measured by quantifying the alcohol released by total hydrolysis of the alkoxysilyl functionality.[9] This allows quantification of the amount of reactive alkoxysilyl group, $x + z$ present in Formula **a**. This structural feature of the AMS containing R^1 and R^2 groups is essential for the use of the AMS as an additive for the reaction with the silica filler. All of the AMSs were prepared such that they always have an "open" structure, which contains the reactive alkoxysilyl group and are never the pure closed caged POSS structures that are known for use as nanoparticle fillers in various applications.[10] The latent alcohol remaining in rubber compounds made with the AMS and/or *co*-AMS and silica filler was determined for samples taken after the rubber compounding is shown in Table X, where the rubber compounds were prepared according to Tables VI–VIII. The amount of alcohol that was released into the environment as VOC for compounding was determined by subtraction. For example, the conventional silica-dispersing agent[8,16] OTES, silane **1** has a latent ethanol content of 49.99 wt %, as calculated or measured by testing. Thus, silane **1** at a 3.30 wt % level in the formulation for a silica-rubber stock can release up to 1.64% ethanol by weight of the stock during compounding, curing, and aging. The maximum potential release has not ever been seen. Even in cured humidity aged samples, latent alcohol contents of 0.01% and lower have been measured. Subtraction of the latent alcohol contents remaining after rubber compounding from the original maximum latent alcohol in the formulation has given the data


Figure 5 The ^{29}Si-NMR of a pure closed caged POSS structure. This POSS is a mixture of closed polyhedral Si_8O_{12} (T_8), $Si_{10}O_{15}$ (T_{10}), and $Si_{12}O_{18}$ (T_{12}) structures.

listed in Table X. These results clearly show the benefit of using AMS in place of the traditional trialkoxy silanes in silica rubber formulations. The use of AMS and/or *co*-AMS in preparing the rubber vulcanizates and their corresponding properties will be detailed in a future publication.[17]

NMR analysis of AMS

The AMS samples were also analyzed by both ^{1}H- and ^{13}C-NMR. Verification of the alkoxy silane content was observed by peaks at 3.53 and 3.80 ppm in the ^{1}H-NMR from the methoxy silane and ethoxy silane, respectively. The ^{13}C-NMR also showed these peaks at 50.30 and 58.24 ppm, respectively. However, by these techniques but because of greater sensitivity, the latent alcohol test described earlier was used for this measurement. The ^{1}H- and ^{13}C-NMR spectra were very useful for determining of the content of the *co*-silane in the *co*-AMS preparation. For the compositional analysis, the CH_2S and CH_2Si peaks were used from ^{1}H-NMR at 2.53 and 0.63
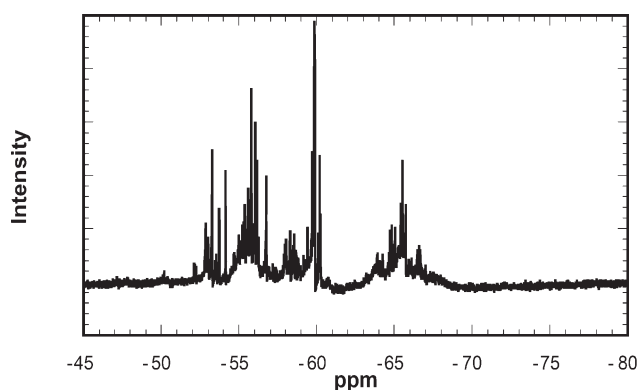
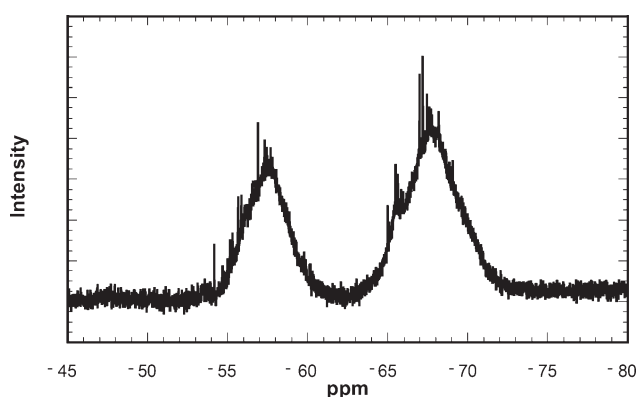**Figure 6** The ^{29}Si-NMR of **AMS1d** with 2.35% latent ethanol prepared by acid hydrolysis.
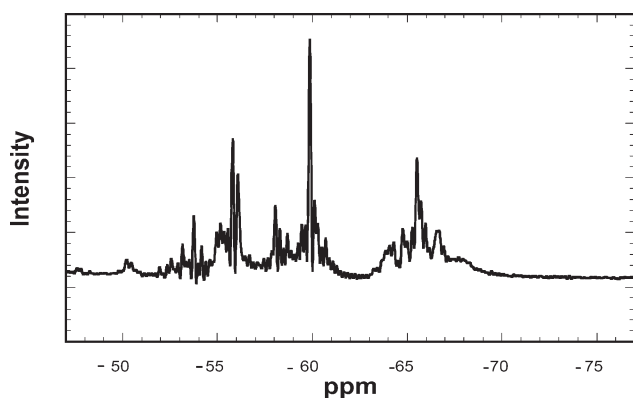
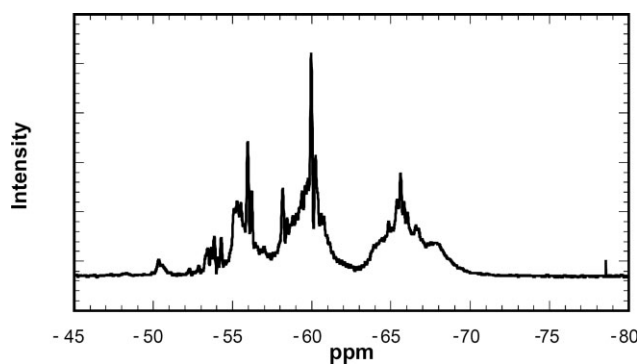**Figure 7** The ^{29}Si-NMR of spectrum of **AMS1g** with 3.5% latent ethanol prepared by acid hydrolysis.

ppm, respectively. The ^{13}C-NMR also showed these peaks at 44.26 and 12.68 ppm, respectively.

The ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra were also run on a sample of *iso*-octyl polyhedral oligomeric silsesquioxane (POSS) and compared with **AMS1d** and **1g** containing 2.35 and 3.5% latent alcohol, respectively. The ^{29}Si-NMR spectra of POSS and selected AMSs are shown in Figures 5–9 and tabulated in Table IV. The HPLC result shown in Figure 10 is consistent with the enormous number of peaks seen in the ^{29}Si-NMR of Figures 6 and 7. Thus, it was concluded that the ^{29}Si-NMR spectra for all of the AMSs prepared from silane **1** consisted of a complex mixture of partially hydrolyzed and condensed OTES with no POSS structure present.

For example, ^{29}Si-NMR of the extracted oligomeric mixture of **AMS1e** with 2.35 wt % latent ethanol, Figure 6 gave an almost identical number and placements of separate resonances as did a phase separated **AMS1g** in Figure 8, which had 3.5 wt % latent ethanol. Each of the over 100 distinguishable peaks seen in these figures are attributed to silicon atoms with a unique structure. A large number of peaks over a broad range of parts per million (ppm) from about −47 to −71 ppm can be seen in the NMR
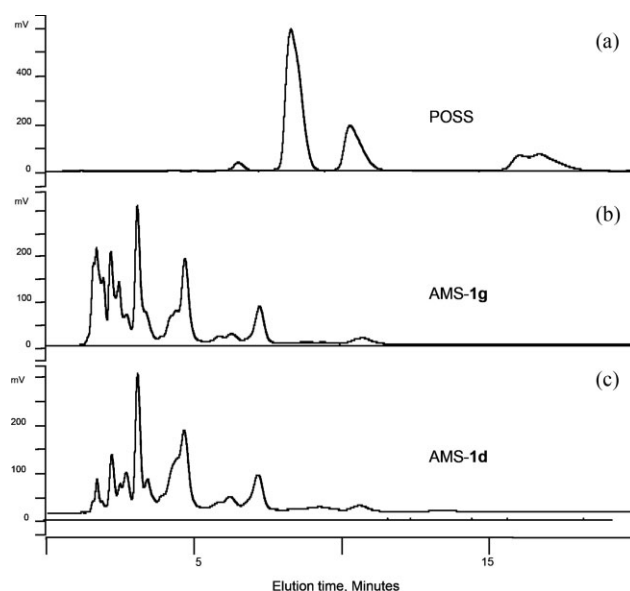
spectrum shown in Figures 8 and 9, which are summarized in Table IV. This is complementary to the HPLC results previously discussed and shown in Figure 10. Both of these techniques support the formation of an open oligomeric silicone oxygen structure in which the latent alcohol, as alkoxysilane, acts as the structure controlling feature.

In comparison, the ^{29}Si-NMR in Figure 5 of a nearly pure closed caged POSS structure shows the major peak at about −67 ppm. In Figure 10, the structure of POSS is a mixture of closed polyhedrals having 95% as Si_8O_{12} (T_8) with the remainder being $Si_{10}O_{15}$ (T_{10}) and $Si_{12}O_{18}$ (T_{12}).[10] The chemical shifts of the octyl-POSS reported[18] are singlets at −66.74 ppm for the T_8 and −68.68 for the T_{10}. The T_{12} has two nonequivalent silicones that should flank the T_{10} peak at about −68.41 and −71.01 ppm. In Table IV, the ^{29}Si-NMR ranges in ppm for various AMS and *co*-AMS products prepared so far show minor peaks in the range of −67 to −77 ppm.

Figure 9 The ^{29}Si-NMR of **AMS1, 4 (8)** prepared by the hydrolysis of silanes **2** and **4** without any added acid.

Figure 8 The ^{29}Si-NMR of spectrum of **AMS1a** with 0.25% latent ethanol prepared by base hydrolysis.

**Figure 10** HPLC of (a) POSS, (b) **AMS1g**, and (c) **AMS1d** with 3.5% and 2.35% latent ethanol, respectively.

The acid-catalyzed AMS preparations give similar number and peak distributions in the ^{29}Si-NMR shown in Figures 6–9 and the summary listed in Table IV. The use of a strong base catalyst with **AMS1a**, in Figure 8, shows the NMR obtained as two broad multipeaked areas that center about −57.5 and −68 ppm. This most probably is a result of a slightly different structure that can be attributed to the use of a basic catalyst.

The most important feature of each of the AMS or *co*-AMS is that the residual reactive alkoxysilyl group is present in such a small amount that only a small amount of alcohol can be liberated by hydrolysis of the product. The majority of the AMS or *co*-AMS described here are suitable for use in rubber compositions in which silica is used as reinforcing filler. In particular, it is thought that the reactive alkoxysilane group(s) attached to the AMS or *co*-AMS can participate in the alkoxysilane-silica reaction to give the initial attachment to the filler. Subsequent processing and cure redistributes the AMS Si—O—Si linkages to form bonds with the silica, increased shielding, and results in improved silica dispersion in the rubber.

Thus, it is apparent that the limited amount of alcohol that can be evolved from the AMS or *co*-AMS should make these compounds very useful for the preparation of silica-filled rubbers because they cannot significantly emit alcohol as a VOC, during compounding and further processing.

Structures of AMS

The resulting AMS or *co*-AMS products are mixture of oligomers, and their structures are difficult to completely characterize. The structure of AMS produced consists of a myriad of possible linkages that could be formed during the condensation of the trialkoxysilane. Because of this, no single structure, or even groups of structures can be drawn for AMS. Some of the characteristic structural features present in the AMS have been depicted by Brown[19] and are consistent with the three-dimensional gel free soluble structure that must be formed. Techniques have been used that clearly show these compounds possess certain characteristics, which are essential for use in silica-filled rubbers. The multitude of peaks present in the HPLC of AMSs (Fig. 10) represents individually different compounds with a specific combination of polarity, size, and molecular weight. The NMR spectra, previously discussed, show a greater number of distinguishable sharp peaks, which are probably due to the subtle change in the magnetic environment of the T_n placements in the AMS structure. The comparison of **AMS1d** and **AMS1g,** which were run under identical conditions, can be made and the differences are attributed to
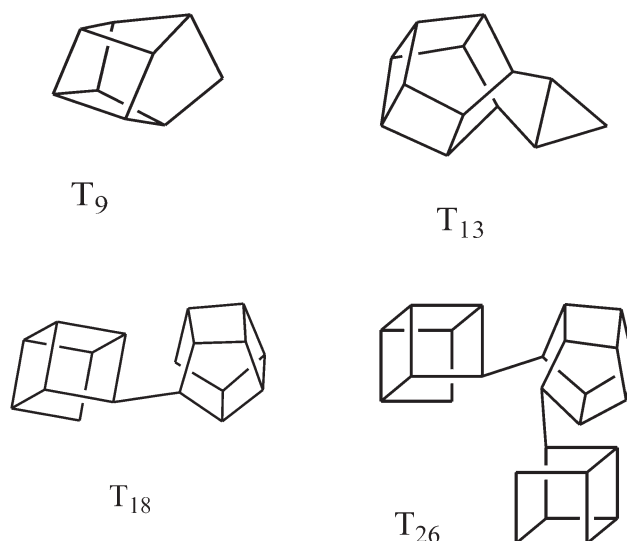
Figure 11 The proposed structures of the AMS.

the latent ethanol content of the AMSs. POSS also seen in Figure 10 emphasizes the absence of the multiple T_n placements in the more polar AMSs. In reverse phase HPLC, the more polar materials elute faster than the less polar substances, if all other features are the same. In this case, the **AMS1g** with 3.5% latent alcohol has a higher proportion of the early eluting peaks in the chromatogram than the **AMS1d**, which has 2.35% latent ethanol in the sample. No similarity in the retention times of chromatogram to that obtained from a known sample of *iso*-octyl POSS can be identified.

Based upon the kinetics, latent alcohol content, ^{29}Si-NMR and HPLC the structures can be proposed for the AMS produced by the synthetic procedure described. As no SiOH structure could be detected, it has been assumed that each unclosed silsesquioxane $SiO_{3/2}$ (T_1) unit must have only an alkoxy silane group attached. The number of isolated SiOR reactive units and arrangement of the attachment of the multiple silsesquioxane (T_n) is a mixture of three-dimensional ring structures with different possible attachments of the SiOR throughout the possible geometric structures.

Fortunately, enough data has been accumulated such that the average number of T_n associated with a minimum of two alkoxy groups attached can be calculated using the following equation.

$$T_n = ((2M_a/x) - 74.12)/M_T \qquad (6)$$

where x is the weight fraction of latent alcohol, M_a is the molecular weight of the alcohol, M_T is the equivalent weight of the base silsesquioxane product (T_n), and 74.12 is the excess molecular weight from the two residual ethoxy groups that have been incorporated. For single alkoxy silane

incorporation, the equation can be modified by division by two. Thus, for example, using octyl triethoxy silane (OTES), which has 49.99% latent ethanol a possible AMS that could be produced with 3.0% latent ethanol would be a mixture of products with an average of 17.74 silicone atoms and two ethoxy groups in the repeat structure. Such a material would have an average molecular weight of 3071 g/mol.

A depiction of just a few of the possible T_n containing alkoxy silane structures are shown in Figure 11, where a RSi-O-SiR unit is represented by a straight line with any R group presence being inferred as being shown as present on the corner of the lines attached. The monoalkoxy groups are shown by the absence of a line from the corner, where only two lines converge. An equation to calculate the number of T_n per alkoxy silane present in AMS from the latent alcohol is as follows,

$$1/T_n = 3.8415 f_{alc} - 0.0025 \qquad (7)$$

where f_{alc} is the weight fraction of ethanol in the AMS.

Proposed representative AMS structures (shown in Fig. 11) that are produced in the reaction mixture, where T_9 and T_{13} contain monoethoxy silane groups and T_{18} and T_{26} are structures with diethoxy silane functionality. The latent alcohol content of T_9 and T_{18} are both 3.02%. Similarly, T_{13} and T_{26} are same and equal to 2.11%.

CONCLUSIONS

The preparation and characterization of a class of AMS compounds has been described, which retains only about 0.5–6 wt % of the latent alcohol. Analysis of the reaction product by HPLC and ^{29}Si-NMR indicated that the AMS has a superabundance of structures present that can only be described as a highly condensed, opened oligomeric, branched arrange-

ment of the silsesquioxanes. This structure is moisture stable and hydrocarbon soluble but still retains enough alkoxysilane functionality so that a silica reactive product is obtained. These characteristics allow for the compounding of improved vulcanizates from silica-filled rubbers.

References

1. Wang, M.-J. Rubber Chem Technol 1998, 71, 520.
2. Mewis, J. Adv Colloid Interface Sci 1976, 37, 132.
3. Rauline, R. U.S. Pat. 5,227,425 (1993).
4. Thurn, F.; Wolff, S. Kautsch Gummi Kunstst 1975, 28, 733.
5. Luginsland, H.-D. Kautsch Gummi Kunstst 2000, 53, 10.
6. Byers, J. T. Rubber World 1998, 218, 38.
7. Evonik Degussa GmbH, Applied Technology Advanced Fillers, Production Information Si 75®, Rellinghauser Straße 1-11 D-45128 Essen Germany.
8. Lin, C.-C.; Hergenrother, W. L. U.S. Pat. 6,433,065 (2002).
9. Lin, C. J.; Hergenrother, W. L.; Hilton, A. S. Rubber Chem Technol 2002, 75, 215.
10. Structures of the isooctyl-POSS cage mixture, sample number MS0805, Hybrid Plastics: Hattisburg, Mississippi.
11. Dittmar, U.; Hendan, B. J.; Florke, U.; Marsmann, H. C. J Organomet Chem 1995, 489, 185.
12. ASTM Standard D1646-89. Annual Book of ASTM Standard, Vol. 09.01; ASTM: Philadelphia, 1990.
13. Cruse, R. W.; Pickwell, R. J. U.S. Pat. 6,127,468 (2000).
14. Hergenrother, W. L.; Rademacher, C. M.; Ulmer, J. D. U.S. Pat. 6,579,949 (2003).
15. Cruse, R. W.; Pickwell, R. J.; Weller, K. J.; Pohl, E. R. U.S. Pat. 6,683,135 (2004).
16. Ladouce, L.; Bomal, Y. In 157th Meeting of Rubber Division of American Chemical Society, Paper No. 33; American Chemical Scoiety: Dallas, Texas, April 4–6, 2000.
17. Lin, C. J.; Hergenrother, W. L.; Hilton, A. S. J Appl Polym Sci, to appear.
18. Rikowski, E.; Marsmann, H. C. Polyhedron 1997, 16, 3357.
19. Brown, J. F. J. J Am Chem Soc 1965, 87, 4317.