

# Temperature Effects of Silane Coupling on Moisture Treated Silica Surface

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**ABSTRACT:** Moisture and temperature effects were investigated on silica/(triethoxysilylpropyl) disulfide (TESPD)/carbon black (CB)/S-SBR compounds with respect to processability, vulcanization characteristics, physical properties, and alcohol residues. The moisture-treated compounds exhibited lower rates of viscous heat generation during mixing, lower discharging temperatures (drop temperatures), lower Mooney viscosities, shorter cure times ( $T_c$ -90), higher torque rises ( $M_H - M_L$ ), less heat build ups (HBU), and equal or less alcohol residues than the control. As the drop temperatures of the compound were increased, decreased temperature differences between mixer sensor (set drop) and real (proven) temperatures, increased the

scorch times ( $T_s$ -2), decreased the cure times ( $T_c$ -90), increased the tensile moduli, and decreased the alcohol residues remaining in the compound. The higher temperature drop compounds (160 and 176°C) exhibited no reversion behavior; however, the lower temperature (120 and 140°C) drop compounds exhibited marching behavior. The treatment of moisture on the silica surface influenced the hydrolysis reaction to the silane and improved coupling on the silica surface. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 623–633, 2005

**Key words:** moisture absorption; silica–silane; alcohol residue; hydrolysis reaction; mechanical properties

## INTRODUCTION

Green tires have been found to exhibit reduced rolling resistance and better traction than carbon black tires.<sup>1,2</sup> However, silica particles, used in a green tire, are known to be more difficult to process and disperse than carbon black (CB) during mixing<sup>3–5</sup> due to their polar and porous character.<sup>6</sup> Due to polar characteristics of silica particles, they are easily agglomerated and hard to disperse in a rubber matrix.<sup>3–5</sup> Bifunctional silanes, such as bis(triethoxysilylpropyl) tetrasulfide (TESPT) and bis(triethoxysilylpropyl)disulfide (TESPD), chemically bind between a silica surface and a rubber matrix. The use of TESPT, in combination with silica, has been patented for practical application in “green tires” by Rauline since 1991.<sup>1,2</sup> Later, TESPD was introduced<sup>7</sup> to improve the processing stability of the tread compounds during mixing because the sulfur–sulfur dissociation energy of TESPD is lower than TESPT,<sup>8–10</sup> and silanes have been used as a dispersing agent<sup>11</sup> to reduce the polarity of the silica particles. Bifunctional silane in silica compounds improves the processability<sup>3,4,12–18</sup> and the mechanical property<sup>17,18</sup> of the compounds. The sulfur level in the silane plays an important role during processing.<sup>19–21</sup>

Recently, a silica–carbon dual–phase filler has been developed<sup>22</sup> to fortify the polymer–filler interaction due to increased surface energy of the carbon domain of the filler via bonding between polymer chains and silanols on the silica domain<sup>23</sup> and also lower filler–filler interaction in tire tread compounds due to reduced filler–filler interaction.

Hydrolysis is an important factor in alkoxy silane coupling on silica surface. An alkoxy group in an alkoxy silane first hydrolyzes, then the hydrolyzed hydroxy group forms a hydrogen bond with a hydroxy group on a silica surface; they then form a covalent bond between a silica surface and a silane via condensation reaction. Finally, the interface between the inorganic silica surface and the organic silane forms a silica–silane bond.<sup>24–27</sup> The presence of catalyst in water significantly increases the degree of silane coupling on silica surface. In the hydrolysis reaction, it has been reported that the primary reaction of silanization is increased in the presence of water and the secondary reaction is increased with increased water level.<sup>28–30</sup> Moisture on the silica surface favors the reaction between the silica and the coupling agent, thus reducing the interparticle reactions<sup>29</sup> and increasing the mechanical properties.<sup>31</sup> Moisture also affects the silane compounds’ processability. Lin et al.<sup>11</sup> reported that, under humid conditions, the TESPT-treated silica-filled compounds showed a higher Mooney viscosity than the silica compounds without TESPT. Schaal et al.<sup>32</sup> observed a higher Mooney peak

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TABLE I  
Materials Used in This Study

	Trade name	Supplier	Code
Rubber	Duradene 753	Firestone	SBR
Filler	ZS 1165MP	Rhodia	ZS (Silica)
	N339	Harwick	CB (Carbon black)
Activator	ZOCO-172	ZOCHEM	ZnO (Zinc oxide)
	Stearic acid	Textile Chemical Co.	StAc
Processing oil, plasticizer	Sundex 790	Sun Company, Inc.	Sun790 (Oil)
Antiozonant, inhibitor	Sunolite 240	Witco	Sun240
Antioxidant/antiozonant	6PPD(I) <sup>a</sup>	Struktol	6PPD
Bonding agent	Struktol SCA 985CB <sup>b</sup>	Struktol	SCA985CB (Silane)
Vulcanizer	Rubbermakers Sulfur	R.E. Carroll Inc.	S (Sulfur)
Accelerator	Santocure NS <sup>c</sup>	Monsanto	TBBS
	Perkacit DPG <sup>d</sup>	Flexsys America L.P.	DPG

<sup>a</sup> *N*-(1,3-dimethyl)*N'*-phenyl-phenyl-*p*-phenylenediamine.

<sup>b</sup> Bis(3-triethoxysilylpropyl)disulfide mixture with carbon black.

<sup>c</sup> *N*-*tert*-butyl-2-benzothiazolesulfenamide.

<sup>d</sup> Diphenylguanidine.

when comparing predried silica and "as is" silica for moisture content 5 ~ 7%, filled compound. They<sup>32</sup> proposed that the role of the water molecule was to "screen" interparticle interactions of silica particles and that drying of the water from the silica surface led to an increase of the intensity of the interparticle interactions resulting in poor processability. They explained that water molecules adsorbed on the silica surface partially "shield" the interparticle interactions. Other reasons were decreased interaction between the silica particle and the coupling agent due to the low level of water in the dried silica and/or a partial curing of sulfur groups in the silane during the heat treatment. Depending on the water level surrounding the silica surface, the pH level of the silica surface varies. Goerl et al.<sup>29</sup> showed that the moisture level affects the silica-TESPT bond formation by investigating evolved alcohol contents. They showed the rate of ethanol evolution was increased as the moisture content was increased with moisture levels ranging from 2.6 to 9.0%.

There has been no research on large amounts of water molecules adsorbed on a silica surface to improve the silane hydrolysis reaction and to improve the physical properties of the compounds.

This paper concentrates on the effects of a large amount of water molecules and processing temperature on silica-TESPD/CB/SBR compounds with respect to processability, rheology, vulcanization, and physical properties. Alcohol content, which is related to the degree of hydrolysis reaction, remaining in each compound was investigated.

## EXPERIMENTAL

### Materials

The silanes used in this study were the TESPd with CB carrier trade name SCA985CB (50% Carbon Black), which is a product of Struktol.

The elastomer used was S-SBR (SBR), which is a Firestone product with the brand name of Duradene 753 (35% styrene).

The silica used was Rhodia ZS 1165 MP (ZS), which was precipitated amorphous silica with BET area 145–180 (m<sup>2</sup>/g), supplied by Rhodia. Distilled water (H<sub>2</sub>O) was treated on silica particles at 20 phr. The moisture level of the untreated silica was 4.9 wt %, which was 2 phr. The carbon black used was N339, which is a furnace amorphous black, supplied by Harwick.

Various additives, including activators (ZnO, stearic acid), processing aid (Sunolite240), plasticizer (Sundex 790), antiozonant (6PPD), curing agent (Sulfur), and accelerators (TBBS, DPG), were used for the tire tread compound. The information on the materials used in the study is summarized in Table I.

### Mixing

A Banbury internal mixer (BR 1600) was used for masterbatch (MB) mixing of rubber and additives. All of the materials with the same ingredients were added in masterbatch 1 (MB1) and dropped at a set temperature (set drop temperature) of 120, 140, 160, and 176°C, respectively. During second pass mixing, sulfur and other accelerators were added into compounds. The fill factor, RAM pressure, and rotor speed were fixed at 70%, 30 psi, and 77 rpm, respectively. The mixing formulations and procedures are included in Table II.

### Mooney viscosity measurement

Mooney viscosities were measured as a function of apparent shear rate at 2 rpm and ML(1 + 4) at 100°C as of ASTM D1646. The rotor diameter of the shearing disc rheometer was 38.1 mm and the thickness of the rotor was 5.5 mm. A Mooney Viscometer 2000 (MV

**TABLE II**  
**Mixing Formulations and Procedure on SBR Compounds 2.1 Formulation**

1st Pass (Masterbatch MB1)					
Material	AN (Control) (120°C)	AO (120°C)	AP (140°C)	AQ (160°C)	AR (176°C)
SBR	100.0	100.0	100.0	100.0	100.0
CB	40.0	40.0	40.0	40.0	40.0
ZS	38.0	38.0	38.0	38.0	38.0
Oil	20.0	20.0	20.0	20.0	20.0
H <sub>2</sub> O	2.0	22.0	22.0	22.0	22.0
ZnO	3.0	3.0	3.0	3.0	3.0
StAc	1.5	1.5	1.5	1.5	1.5
Sun240	1.0	1.0	1.0	1.0	1.0
Sun790	23.0	23.0	23.0	23.0	23.0
6PPD	2.0	2.0	2.0	2.0	2.0
SCA985CB	6.4	6.4	6.4	6.4	6.4
2nd Pass (MB2)					
Material	AN (Control)	AO (120°C)	AP (140°C)	AQ (160°C)	AR (176°C)
MB2 AI	236.9	0.0	0.0	0.0	0.0
MB2 AJ	0.0	239.9	0.0	0.0	0.0
MB2 AK	0.0	0.0	239.9	0.0	0.0
MB2 AL	0.0	0.0	0.0	239.9	0.0
MB2 AM	0.0	0.0	0.0	0.0	239.9
S	1.4	1.4	1.4	1.4	1.4
TBBS	1.7	1.7	1.7	1.7	1.7
DPG	0.2	0.2	0.2	0.2	0.2

### 2.2 Mixing Procedure

Master batch mixing (MB1): 100 rpm and 30 psi

1. Add rubber.
2. Mix for 30 s.
3. Add rest additives.
4. Mix for 120 s and sweep.
5. Sweep at every min. Drop at 120°C(AN, AO), 140°C(AP), 160°C(AQ), and 176°C(AR).

\* 2 pass mixing (MB2): 77 rpm and 30 psi

1. Add 1/2 MB1.
2. Mix for 30 s.
3. Add cures and 1/2 MB1.
4. Mix for 2 min or 93°C (200°F) and dump.

2000) manufactured from Alpha Technology was used for measuring Mooney viscosity. The shear rate at the outer radius of the shearing disc is expressed as follows:<sup>33,34</sup>

$$\gamma(R) = \frac{R\Omega}{H} \quad (1)$$

where  $R$  is the radius of rotating disc,  $\Omega$  is the rotor rotation rate, and  $H$  is the distance between the disc surface and the stationary housing.

### Cure rheometer test

An oscillating disc cure rheometer (Model Rheotec) manufactured from Tech Pro Inc. was used to measure vulcanization and reversion resistance property of the compounds in a pressurized rotational rheometer

with a biconical rotor following ASTM D 2084 at 160°C. The oscillation frequency was 100 cycles/min (1.66 Hz) with amplitude of 3°. Minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), torque rise ( $M_H - M_L$ ), scorch time ( $T_s-2$ ), cure time ( $T_c-90$ ), and reversion resistance time ( $T-2$ ) were measured.

### Tensile test

An Instron tensile tester (Model 4201) with data acquisition system was used to obtain tensile test data on dumbbell specimens and the average of three specimens was obtained following the ASTM D 412-87 method. This instrument meets ASTM E4 standards and measures mechanical properties of materials. The modulus (Pa) of each compound was measured at 300% elongation. The thickness and the width of the specimens averaged 2.2 and 6.3 mm, respectively.

### Heat build up (HBU) and blowout (BO) test

HBU and BO test were carried out using the "Firestone Flexometer"<sup>33</sup> according to ASTM D 623. This is a testing apparatus for applying a uniform circulatory oscillating action under compression. The test specimen is located between the fixed upper part and the moving bottom part. The bottom part is circulatory oscillating at a constant speed of 787 rpm. The amplitude of the lower moving part was 7.6 mm. The pressure applied was 0.8 MPa on the HBU and 1.7 MPa on the BO sample. The test specimen was in the shape of a frustum of a rectangular pyramid with the following dimensions: base, 54.0 × 28.6 mm; top, 50.8 × 25.4 mm; and altitude, 38.1 mm. For the HBU test, inside temperature of the specimen was measured after 45 min running. After the BO test, the dimension of the center part of the sample length was measured and the deformation ratio (%) was determined.

### Viscoelastic property ( $\tan\delta$ ) measurement

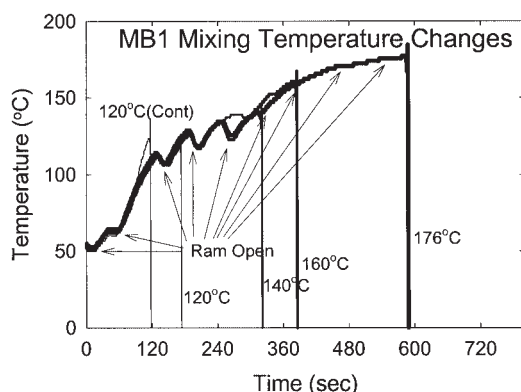
Vulcanized specimens were characterized using a Mechanical Energy Resolver (MER-1100B) manufactured by Instrumentors, Inc. This instrument measures oscillatory input of axial compression and tension response of the cylindrical specimen. Oscillatory signal response depending on the material was measured and recorded as elastic and viscous properties as follows:<sup>34,35</sup>

$$\tan\delta = G''/G' \quad (3.1)$$

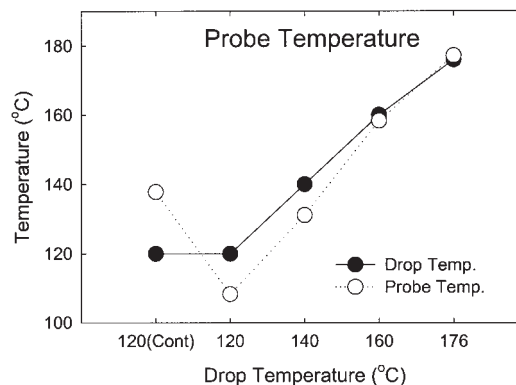
$$G'(\omega) = G^* \cos\delta \quad (3.2)$$

$$G''(\omega) = G^* \sin\delta \quad (3.3)$$

$$\eta'(\omega) = \frac{G''}{\omega} = \frac{G^*}{\omega} \sin\delta \quad (3.4)$$



**Figure 1** Temperature changes during an internal mixer processing of various drop temperature compounds [control (120°C), 120°C, 140°C, 160°C, and 176°C].



**Figure 2** Probe and set drop temperatures of master batch compounds after an internal mixer processing.

where  $\omega$  represents oscillation frequency;  $G^*$ , the complex modulus;  $\delta$ , the phase angle;  $G'(\omega)$ , the storage modulus;  $G''(\omega)$ , the loss modulus; and  $\eta'(\omega)$ , the dynamic viscosity.

The diameter and the length of the cylindrical specimens averaged 17.5 and 25.5, respectively.

### Alcohol contents

Quantitative determination of ethanol was used as a measure of the concentration of ethoxy silane (EtOSi) left unreacted in the uncured stocks. The (EtOSi) in the stock was found 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 residual (EtOSi) freeing the stoichiometric amount of ethanol that is then measured by a headspace/gas chromatographic technique. Alcohol residues remaining in the compounds were analyzed by Bridgestone–Firestone R & D, Inc.

## RESULTS AND DISCUSSION

### Internal mixer processing

Figure 1 represents the heat generation during internal mixer processing at different drop temperatures. The rate of temperature rise of the control compound was higher than that of the moisture-treated compounds, i.e., the addition of moisture reduced the rate of temperature rise during mixing. As the drop temperature increased, the mixing time increased. The temperature rise between 160 and 176°C was longer than for other compounds.

It seems that the vaporization energy of water maintains the stock temperature rise at a low rate and prevents the compounds from overheating.

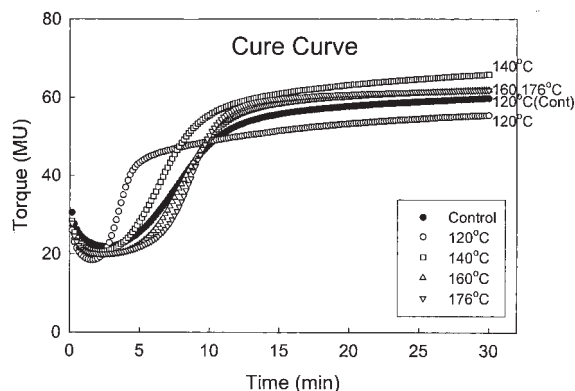


Figure 3 Cure curves of various drop temperature compounds measured at 160°C for 30 min.

Probe temperature

Figure 2 shows the probe temperature of the compounds after master batch mixing. Moisture-treated compounds (22 phr moisture) exhibited lower temperature than the control (2 phr moisture). The probe temperature of the control compound was higher than the drop temperature; however, that of the moisture-treated compounds was lower than the drop temperature. In moisture-treated compounds, as the drop temperature increased, the temperature differences from the probe became close.

Cure rheometer test

Figure 3 shows the vulcanization curve of each compound at 160°C for 30 min. All compounds did not exhibit reversion behavior ( $T_2$ ), rather they exhibited slightly marching behavior. The moisture-added compounds exhibited lower torque ( $M_L$ ) than the control (see Fig. 3). The control compound exhibited higher low torque ( $M_L$ ) and lower high torque ( $M_H$ ) than other compounds except for the 120°C one. As the drop temperature increased, the scorch time ( $T_{s-2}$ ) increased;

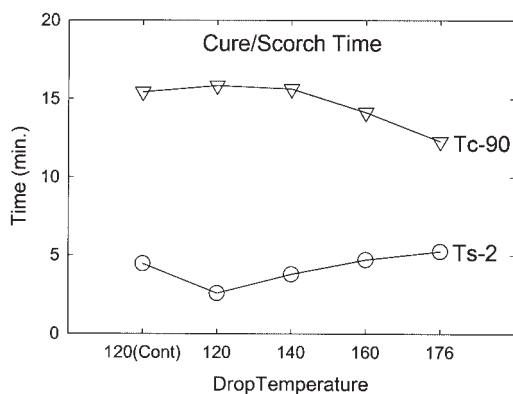


Figure 4 Scorch time ( $T_{s-2}$ ) and cure time ( $T_{c-90}$ ) of various drop temperature compounds measured at 160°C.

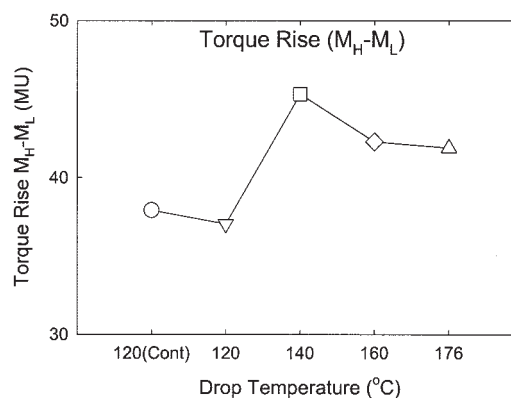


Figure 5 Torque rise ( $M_H - M_L$ ) of various drop temperature compounds measured at 160°C.

however, the cure time ( $T_{c-90}$ ) decreased as shown in Figure 4. Moisture-treated compounds showed higher torque rise ( $M_H - M_L$ ) than the control. Among them the 140°C drop compound showed the highest torque rise as shown in Figure 5.

The moisture-exposed compounds exhibit reduced cure time as the moisture exposure time increases.<sup>36,37</sup> In this experiment, as the drop temperature increases, the cure time  $T_{c-90}$  decreases. This is due to the reduced level of moisture and alcohol residue in the compound by elevated drop temperature during mixing. The addition of moisture changes the cure curve characteristics and increases the degree of crosslinking in the compounds. The moisture level and dump temperature should be considered as important factors in the silane-silica compounds.

Mooney rheometer viscosity

Figure 6 represents moisture effects on Mooney viscosity at 0.2 rad/s and 100°C. The addition of moisture lowered the viscosity of the SBR compounds, which

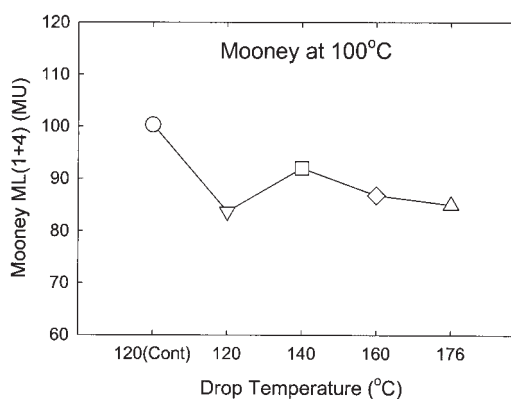
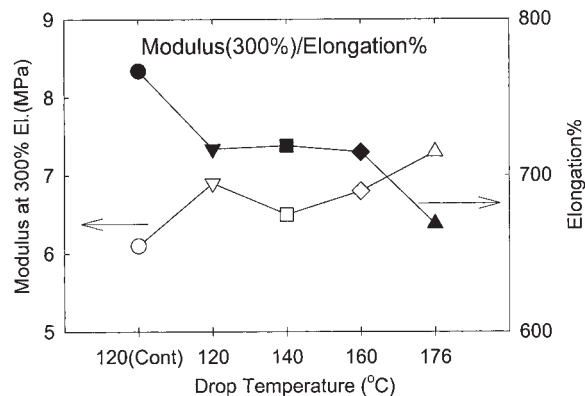


Figure 6 Mooney [ML(1 + 4)] viscosity of various drop temperature compounds measured at 100°C.



**Figure 7** Modulus (MPa) at 300% elongation and elongation % of various drop temperature compounds.

was in the same order as was observed from the cure rheometer  $M_L$  torque data.

It seems that the excessive moisture coated on silica surface acts as a lubricant in the SBR compounds during mixing.

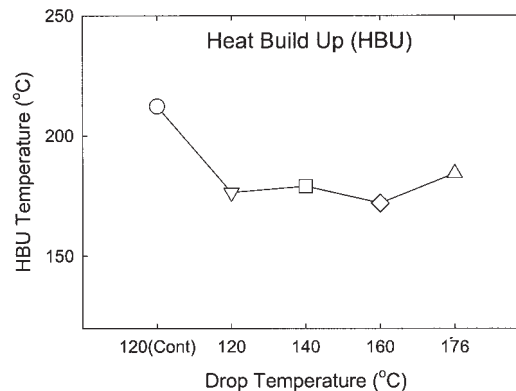
### Tensile test

Figure 7 represents the modulus changes as a function of storage time at 300% elongation measured from the dumb-bell-shaped specimens using the ASTM D 412-87 method.

Moisture-treated compounds exhibited higher elongation modulus than the control. As the drop temperature increased the modulus of moisture-treated compounds (140, 160, and 176°C) increased and the elongation % decreased. Among them, the 176°C drop compound shows the most improved tensile properties. The compound dropped at 120°C showed lower elongation than did the 176°C one. This seemed to be due to too low temperature to hydrolyze the stock during mixing as shown in the probe temperature (see Fig. 2). The actual temperature of the stock was about 110°C even though it was set to drop at 120°C, which seemed too low temperature to activate the hydrolyzation reaction. The moisture remaining in the 120°C compound, however, seemed to contribute to hydrogen bonding in the compound, resulting in a higher elongation modulus close to the 160°C one. The temperature range 120 to 160°C seemed to be the boundary for hydrolyzation of alkoxysilane. At the temperature range from 120 to 140°C, the

**TABLE III**  
Modulus (300%) and Elongation % of Each Compound

	AN (Control)	AO (120°C)	AP (140°C)	AQ (160°C)	AR (176°C)
Modulus at 300% Elongation (MPa)	6.1	6.9	6.5	6.8	7.3
Elongation %	767	717	719	715	669



**Figure 8** Heat build up (HBU) temperature of various drop temperature compounds measured from Firestone Flexometer.

modulus decreased due to decreased moisture level and, from 140 to 176°C, the modulus increased due to increased hydrolyzation. The elongation modulus at 300% and the degree of elongation (%) of each compound are summarized in Table III.

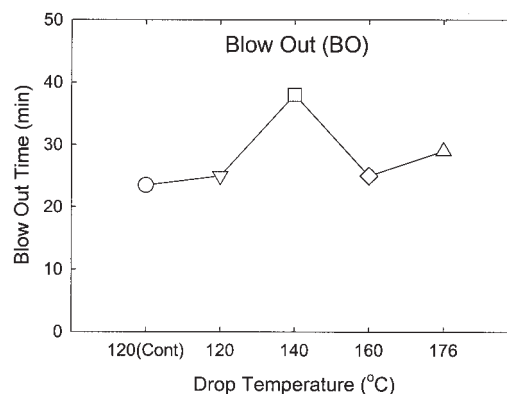
Overall, moisture-treated silica compounds show improved elongation modulus.

### Heat build up (HBU)

Figure 8 represents the HBU of each specimen. Moisture-treated compounds showed lower heat generation (resistance to heat build up) than the control under compressive circular oscillatory shear stress. There were no significant differences among moisture-treated compounds in HBU resistance.

### Blow out (BO) time

Figure 9 shows BO time of each compound. The treatment of moisture on the silica surface exhibited improved BO time for only the 140°C drop compound.



**Figure 9** Blow out (BO) time of various drop temperature compounds measured from Firestone Flexometer.

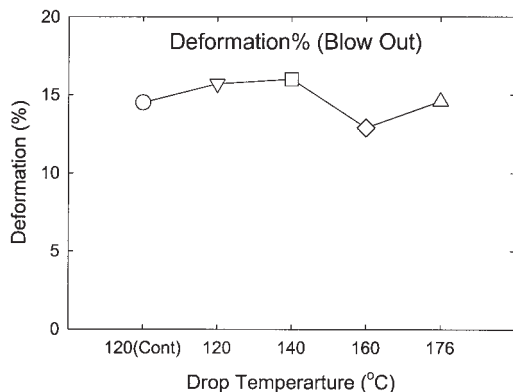


Figure 10 Deformation % of BO specimen measured after Firestone Flexometer test.

The relative degree of deformation compared to the test specimen’s original length is presented in Figure 10. There were no significant differences in deformation (%) between compounds.

Overall, moisture-treated silica compounds show improved BO resistance time.

**Viscoelastic property (tanδ)**

Figure 11 shows viscoelastic properties (tanδ) measured from the MER. The tanδ values measured at 100°C were lower than those of the 23°C ones, a typical trend in this compound. Treatment with moisture showed equal or lower tanδ values for each specimen. This is summarized in Table IV.

This indicates the water molecules effectively hydrolyze the alkoxy groups in silane and then condense with hydroxyl groups on the silica surface, which results in silica-silane covalent bonding network. The treatment with moisture shows equal or improved viscoelastic properties of each specimen.

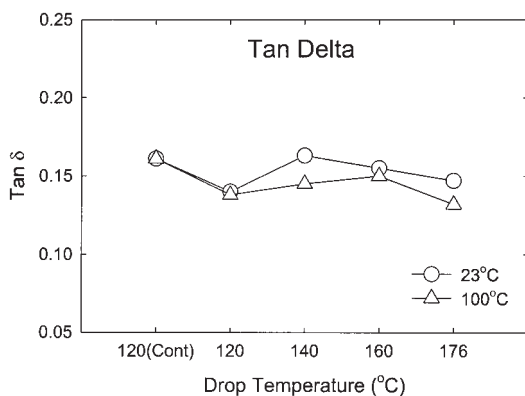


Figure 11 Viscoelastic property (tanδ) of various drop temperature compounds measured from MER.

TABLE IV  
Viscoelastic Properties of Each Compound

Temperature	AN (Control)	AO (120°C)	AP (140°C)	AQ (160°C)	AR (176°C)
23°C	0.161	0.140	0.163	0.155	0.147
100°C	0.159	0.138	0.145	0.150	0.132

**Mixing times and weight loss during mixing**

Figure 12 represents the mixing time and the weight loss of each compound as the set drop temperature increases. Water evaporation during mixing mainly contributed to the loss of MB1 weight. The mixing time and the weight loss of each compound were increased as the set drop temperature increased. While the weight loss among the 140°C, 160°C, and 176°C compounds was not changed significantly, the mixing time of the 176°C dropped compound was significantly longer as shown in Figure 1. The mixing time and the weight loss of each compound is summarized in Table V.

The above results show that the latent heat of moisture plays a significant role in slowing down stock temperature rise. Furthermore, the condensation reaction between the hydroxyl groups on silica surface and the hydroxyl groups of silane occurs effectively. The condensation reaction, which is endothermic ( $\Delta H < 0$ ), consumes the viscous heat generated during mixing, which results in a lower rate of temperature rise during mixing. It also results in longer mixing time to reach the dump temperature.

**Oven aging**

Figure 13 shows a photograph of each compound oven aged at 160°C for 50 min. The high temperature 176°C dropped compound showed less bubbling than the others and this compound showed the most improved tensile properties (see Fig. 7). The specimen of

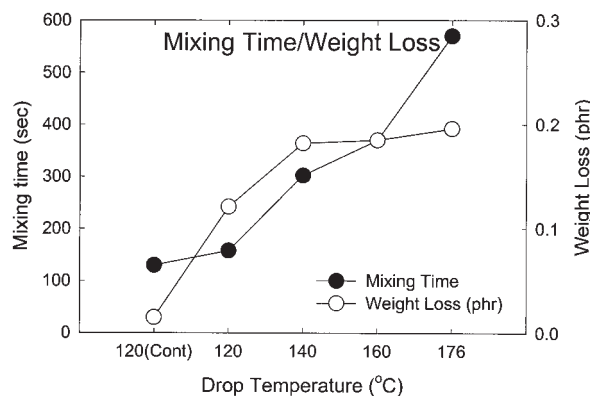


Figure 12 Mixing time and weight loss of various drop temperature compounds.

TABLE V  
Water Loss After MB1 Mixing in SBR Compounds

Batch weight changes	AN (Control)	AO (120°C)	AP (140°C)	AQ (160°C)	AR (176°C)
Before MB1 (g)	1,279	1,387	1,387	1,387	1,387
Loss (g) after MB1	9.9	78.6	118.0	120.0	126.8
Loss (phr) after MB1	0.015	0.121	0.182	0.185	0.196

the 120°C dropped compound showed many small bubbles.

The lesser bubble formation seems to be related to improved mechanical properties of moisture-treated silica compounds as shown in Figures 7 and 9.

#### Alcohol contents

Figure 14 represents the alcohol residue remaining in the compound after mixing. Moisture-treated compounds showed fewer alcohol residues compared to untreated ones (control). As the drop temperature increased, the alcohol content remaining in the compound decreased. The 176°C drop compound showed the lowest level (19%) of alcohol in the compound, which implied completion of 81% of the hydrolysis reaction.

Overall, the high temperature drop compounds show fewer alcohol residues than the control.

#### Background theory of hydrolysis and condensation mechanism

Hydrolysis and condensation mechanisms<sup>38-41</sup> occur between alkoxy silane and water molecules, and hy-

drolyzed silane and hydroxy groups on the silica surface, respectively. The acid catalyzed hydrolysis mechanism is an  $S_N2$ -Si type mechanism,<sup>39,40</sup> in which the incoming nucleophile and outgoing leaving group are further from the  $sp^2$  hybridized silicon atom than the nucleophile and leaving group in an  $sp^3d$  hybridized silicon atom of a pentacoordinate intermediate. This mechanism is a rapid equilibrium protonation of the substrate,<sup>39</sup> and then a bimolecular  $S_N2$ -type displacement of the leaving group by water<sup>39,40</sup> while the base-catalyzed<sup>39,41</sup> mechanism is slow.

Allen<sup>42</sup> showed a hydrolysis and condensation model of trialkoxysilanes derived from the Kay and Assink<sup>43</sup> model. Base catalyzed hydrolysis favors the substitution of the  $-(OSi)_3$  group (bottom right) for the alkoxy group  $[-(OR)_3]$  (top left) and acid catalyzed hydrolysis favors the substitution of a hydroxy  $[-(OH)_3]$  group (top right) for the alkoxy group  $[-(OR)_3]$  (top left) as shown in Figure 15.<sup>42</sup> The rate of the acid hydrolysis is significantly greater than that of the base hydrolysis and is minimally affected by other carbon-bond substituents. Hydrolysis and condensation reactions are affected by the pH level of the solution. The slowest rate of hydrolysis occurs at an

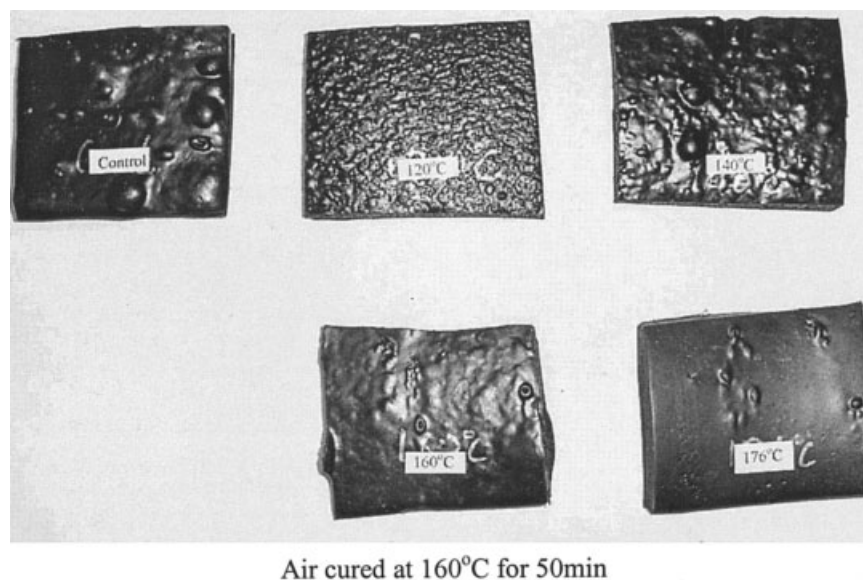
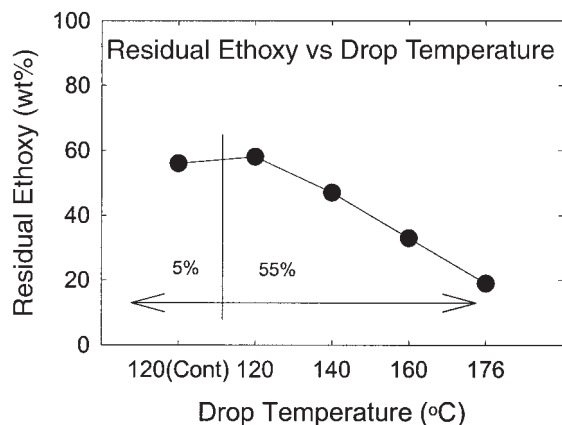


Figure 13 Photograph of air cured compounds at 160°C for 50 min.





**Figure 14** Alcohol % remaining in the various drop temperature compounds.

approximately neutral pH.<sup>44,45</sup> Condensation reaction is also controlled by pH with a minimum at pH 4. Alcohols reverse the hydrolysis reaction, stabilizing the solution for extended periods; thus, removal of alcohol in the compound eliminates the possible reverse reaction in the compound.

The increased level of condensation interferes with the bond formation. The completion of the hydrolysis thus takes longer at room temperature.<sup>44</sup> Moisture affects vulcanization time and mechanical properties of the silane-silica compound.<sup>36,37</sup> This may be due to improved silane coupling on the silica surface.

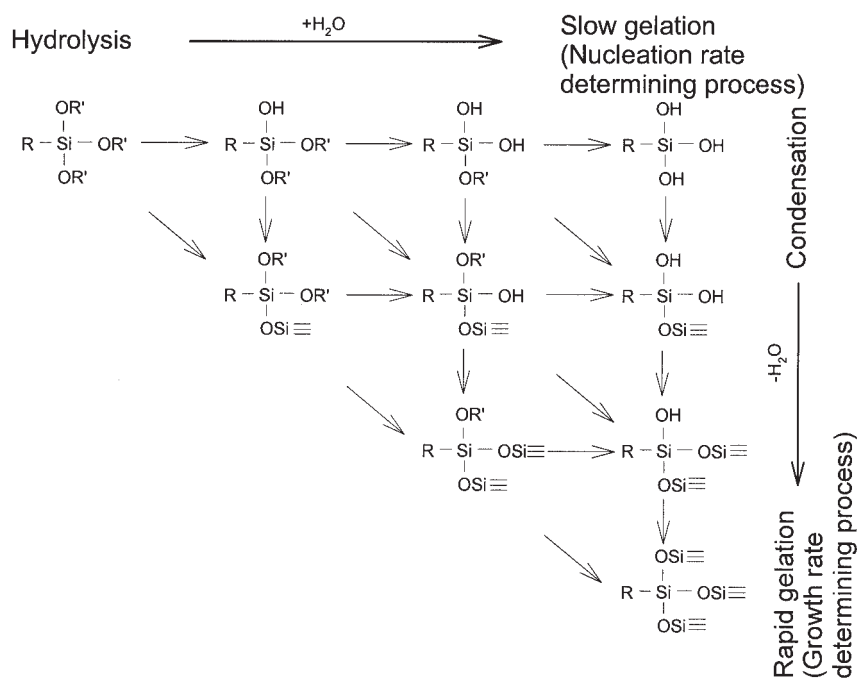
### Proposed mechanism

We propose a mechanism by which a large amount of moisture affects silica-silane coupling.

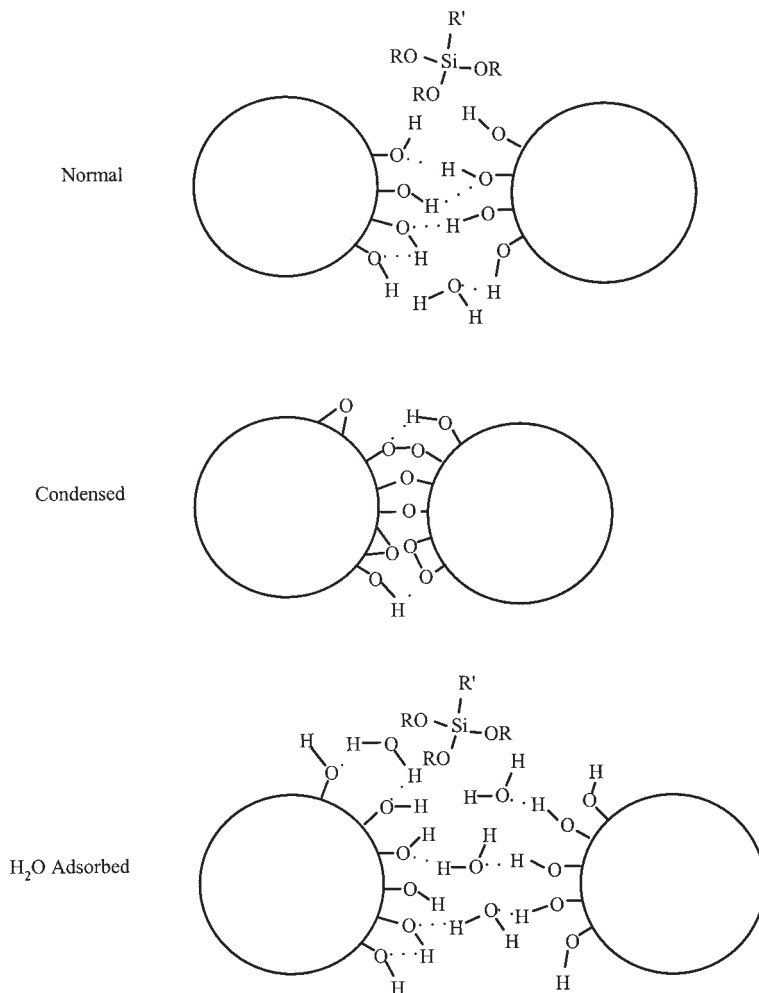
As mentioned in the Introduction, there has been no research on effects of a large amount of moisture in silane-silica compounds even though there are well-established theories as shown in the previous section.<sup>38-43</sup>

To achieve a hydrolysis reaction, enough water molecules should be supplied to an alkoxy silane. In a moisture-starved condition, the hydrolysis reaction would stop somewhere before completion (see Fig. 15), and then the condensation reaction takes over. The fully hydrolyzed silane would finish 100% coupling on a silica surface (bottom right) via a condensation reaction; however, the partially hydrolyzed silane (top middle), due to moisture starvation, would react only with one or two hydroxy groups in the silane, resulting in two or one alkoxy groups remaining in the silane (bottom middle).

We schematically present various silica particles present as normal, condensed, and water molecules in emulsified form in Figure 16. Normal silica particles are agglomerated with hydrogen/polar bonding (top). The aggregated silica particles, due to the self-condensation reaction, are chemically bonded to each other and they are hard to break down during mixing (middle). These types of silica particles were investigated by Schaal et al.<sup>32</sup> Large amounts of moisture adsorbed on silica particles, in our mechanism, have enough water molecules to react with alkoxy groups in a silane molecule (bottom). When an alkoxy silane approaches the silica surface, the water molecules, which are emulsified on the silica surface, react immediately with the alkoxy group (see Fig. 16, bottom). This provides an improved hydrolysis reaction to an ap-



**Figure 15** Hydrolysis and condensation cascade reaction mechanism of trialkoxy silanes.



**Figure 16** Schematic presentation of various silica particles exist as normal, condensed, and  $\text{H}_2\text{O}$  adsorbed forms.

proaching alkoxy silane compared to the moisture-starved conditions (see Fig. 16, top and middle). The excess water molecules also maintain a lower rate of the stock temperature rise (see Fig. 1).

At the beginning of MB1 mixing, the polar bonded silica agglomerates disperse easily by the presence of large amount of polar water molecules because hydrogen bonding is about five times stronger than polar bonding. A large number of water molecule loosen the agglomeration force between silica particles. This facilitates dispersion of silica particles in a rubber matrix. Well-dispersed silica particle compounds produce less HBU and show better mechanical properties as shown in the Results. As the batch temperature increases, the moisture evaporates from the compound.

The steric hindrance theory,<sup>46,47</sup> by which a third alkoxy group in a trialkoxysilane does not hydrolyze (67% hydrolysis) due to steric hindrance, has been accepted in the silane hydrolysis process as a mechanism.<sup>24,25</sup> The unreacted alkoxy groups remaining in a compound later undergo a secondary hydrolysis reac-

tion and produce alcohol in the final stage. However, our excess water molecule treated silica systems have shown additional hydrolyzation of the alkoxy group remaining in a silane (81% hydrolysis) and produce less alcohol in the silane compound and improves mechanical properties. The steric hindrance theory<sup>46,47</sup> has to be reconsidered in the case of the silica system treated with a large quantity of moisture.

## CONCLUSION

Silica compounds (TESPD/silica/CB/S-SBR) treated with a large amount of moisture showed increased mechanical properties and low heat generation during mixing. As the drop temperature increased, the physical properties increased and showed fewer alcohol residues in the compounds.

The degree of crosslinking was increased by the presence of water. A large amount of moisture treatment on the silica surface improved the hydrolysis reaction of the silane by formation of a strong three-dimensional network structure in the TESP/silica/

CB/S-SBR compound. The alcohol residue level in the compounds decreased as the drop temperature increased, which is an indication that the hydrolysis reaction was carried out effectively.

We conclude that addition of a large quantity of moisture on the silica surface improves silane reaction with the silica surface by improved hydrolysis reaction.

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