Hysteresis Temperature Dependence in Filled Rubbers. II. Mechanical Mixing, Filler Microdispersion, and Polymer–Filler Interactions

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ABSTRACT: The effects of mechanical mixing and filler–filler (F–F) and polymer–filler (P–F) interactions on the normalized state of a filler microdispersion $[d(x)]$ and the viscoelastic properties of silica-filled rubbers were studied. The rubbers were prepared with or without the addition of *n*-octyl-triethoxysilane (OTES) to modify F–F interactions or coupling agents such as 3-mercapto-propyl-trimethoxysilane and 3-mercaptopropyl-triethoxysilane (MPTES) to increase P–F interactions. Increased mixing improved $d(x)$ and enhanced the hysteresis temperature dependence (HTD) by giving a higher tan δ value near the compound glass-transition temperature (T_g) but lowered tan δ at elevated temperatures for stocks containing a coupling agent. The changes in P–F and F–F interactions in rubbers with mixing and subsequent thermal treatment were shown to be responsible for the property differences observed among stocks containing different silanes. Attempts were made to quantify the efficiency for improving $d(x)$ with various silanes. The increased P–F interactions in compounds containing MPTES showed better efficiency for improving $d(x)$ and enhancing HTD in comparison with OTES. It was also demonstrated that the change in hysteresis near T_g was mainly governed by the degree of filler networking, whereas elevated-temperature hysteresis was strongly influenced by the P–F interactions in compounds. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1722–1736, 2008

Key words: dispersions; hysteresis; silane; rubber; silicas

INTRODUCTION

Tire manufacturers constantly strive to reduce their products' rolling resistance to help the environment by minimizing the use of fossil fuel to power automobiles. The tighter U.S. corporate average fuel economy standard imposed on the automobile industry[1] has also provided an impetus to obtain tires with better rolling resistance. However, care must be taken so that the improvement in rolling resistance does not reduce opposing performance characteristics such as wet traction. Indeed, for a tire-tread material, tire rolling resistance and wet traction are both dictated by the energy losses from the tire service but encompass different deformation magnitudes and frequencies.[2–5] These energy losses have been predicted by the measurement of 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 to 100°C.[6] Thus, the desired rubber compound should have a lower tan δ value at 50–80°C to reduce rolling resistance and improve fuel economy. At the same time, this rubber compound needs to exhibit higher tan δ values in the range of −20 to 0°C to generate high skid and wet grip. Various approaches have been attempted to make rubbery materials that would have such viscoelastic responses upon deformation, such as the use of rubber filled with different mineral fillers,[7] the use of a polymer blend or a polymer with tailored microstructures that exhibits a broad tapered glass-transition temperature (T_g),[8] the use of functional polymers,[9–14] and the use of silane coupling agents.[15,16] In general, these approaches alter the compound viscoelastic properties to give stronger hysteresis temperature dependence (HTD) upon dynamic deformation to satisfy the performance targets.

The dynamic viscoelastic responses of the rubber compounds can also be greatly influenced by a variety of parameters such as networking from the filler morphology,[6,17,18] modification of the filler surface,[19–21] and polymer–filler (P–F) interaction.[6,11,22–24] These factors, along with the resultant compound properties, are greatly influenced by the mixing procedure and conditions employed to prepare the silica-filled rubbers with the addition of a organosilane coupling agent such as *bis*(3-triethoxysilylpropyl)tetrasulfide (TESPT) or *bis*(3-triethoxysilylpropyl)disulfide (TESPD).[25–36] Recently, the use of the

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TABLE I
Formulations for the Preparation of the Rubbers Used for this Study

Ingredient	phr
Polymer	100
Precipitated silica	65
OTES	0–3.25
MPTMS	0–1.5
MPTES	0–2.84
Process oil (aromatic oil)	16
Wax	1.5
Antioxidant [N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene-diamine]	0.95
Stearic acid	2.0
Sulfur	1.7
Accelerator [N-cyclohexyl-2-benzothiazolesulfenamine]	1.5
Zinc oxide	2.5
Diphenyl guanidine	0.5

mercapto silane system[37] or a silane-containing mercaptan moiety[38] has been shown to offer silica-filled compounds with properties comparable to or better than the properties of those using a TESPT or TESPD. The choice of proper mixing conditions to prepare silica compounds with better overall filler dispersion, including agglomerate dispersion, filler network dispersion (microdispersion), and polymer-phase distribution,[39] along with the desirable properties attained is a critical concern for a tire manufacturer. In particular, the microdispersion is believed to govern the dynamic behaviors of the filled rubber for a given polymer and cure system.[6] This process is even more complicated in the preparation of silica compounds for which a variety of silica shielding or coupling agents can be selected. In this article, variations in the mixing conditions are reported that affect the filler microdispersion and the viscoelastic properties of the compound in the presence of a silica shielding agent or a silica coupling agent. Particular attention is paid to how the degree of mixing changes the P–F and filler–filler (F–F) interactions in the silica compounds containing coupling agents. This will be contrasted to the F–F interactions in compounds containing shielding agents and how the resultant silica microdispersion and compound HTD responses vary.

EXPERIMENTAL

Materials

The silica used was HiSil190 purchased from PPG Industries, Inc. (Pittsburgh, PA), which had a 200–210 m^2/g surface area. The n-octyl-triethoxysilane (OTES) was obtained from Dow Corning (Midland, MI). The 3-mercaptopropyl-trimethoxysilane (MPTMS) and 3-mercaptopropyl-triethoxysilane (MPTES) were acquired

from Gelest, Inc. (Morrisville, PA). All these materials were used without further purification.

Rubber compound preparations

The formulations used for preparing rubber compounds for this study are shown in Table I. The poly(butadiene-co-styrene) polymer was Duradene 715 obtained from Firestone Polymers, LLC*; it was characterized as follows: 47% vinyl, 23.5% styrene, a Mooney viscosity (ML$_{1+4}$)[40] number of 58 measured at 100°C, and a T_g value of −36°C. The amounts of the ingredients used are given with respect to 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 silane that included OTES, MPTMS, and MPTES. The type of silane and its loading to the test compounds are specified in Table II. Table III lists the mixing stages in which the silane was added and the total mixing stages used to prepare the compounds. Water has been shown to have a major role in the reaction between the silane and silica during the compounding.[41,42] This reaction is particularly difficult to control on a laboratory scale because the hydrophilic characteristics of silica can result in 6–10 wt % water absorption. To obtain more consistent and meaningful results, master-batch (MB) mixing was employed to drive off most of the water absorbed onto the silica before any silane addition was performed in later mixing stages. To improve the uniformity among stocks, a large quantity of the rubber prepared from the MB was divided into several stocks for the subsequent mixing with or without the addition of various silanes.

The prepared compounds were designated with a stock number (listed in Table II) followed by a letter (shown in Table III) indicating the mixing stage in which the silane was added and the total mixing stages used to prepare the stock. For example, OTES was added to stocks **2d–2f** at the remill 1 (R1) mixing stage with total mixing stages of 5, 4, and 3, respectively. Similarly, in stocks **3g** and **3h**, MPTMS was added in the remill 2 (R2) and remill 3 (R3) mixing stages, respectively. Both stocks **3g** and **3h** were prepared with a total of five mixing stages that included the MB, R1, R2, R3, and final mixing stages. All stocks were mixed under the conditions described in Table IV. Some of these final stocks that contained curatives were sheeted and then were subsequently cured at 171°C for 15 min.

TABLE II
Summary of the Stocks

Feature stock	Si(OR)$_3$ concentration (mmol/kg of silica)	Silane loading (phr)		
		OTES (R=C$_2$H$_5$)	MPTMS (R=CH$_3$)	MPTES (R=C$_2$H$_5$)
1	0			
2	181	3.25		
3	116		1.5	
4	181			2.84
5	16			0.25
6	32			0.5
7	64			1
8	91			1.42
9	363			5.68
10	16	0.29		
11	32	0.57		
12	64	1.14		
13	91	1.63		
14	362	6.50		

Test conditions

Dynamic mechanical viscoelastic property measurements

The dynamic viscoelastic properties of cured stocks were obtained from temperature and strain sweep experiments with Dynamic Analyzers Rheometrics Inc., Piscataway, NJ (models RDA-700 and RDA-II). Rheological data such as the storage modulus (G') and loss modulus (G''), strain, shear rate, viscosity, and torque were measured. Temperature sweep experiments were conducted with a frequency of 5 Hz and with various levels of deformation ranging from 0.25 to 2%. Test specimens used for dynamic temperature sweep tests were rectangular slabs with dimensions of 27 × 12.5 × 2 mm^3 (length × width × thickness). The sample geometry used for the strain sweep test was cylindrical with a 9.5-mm diameter and a 15.6-mm length. A frequency of 0.5 Hz was used for the strain sweep with the strain sweeping from 0.25 to 14.75%. The strain sweep on unvulcanized rubber stocks containing no curatives was performed with an RPA 2000 (Alpha Technologies). The strain sweep was conducted at 50°C with a frequency of 0.1 Hz by the variation of the strain from 0.25 to 1000%. The thermal annealing experiment was conducted at 171°C for 15 min to mimic curing conditions. The annealed rubbers were then cooled in the RPA 2000 rheometer with blown air to reach 40°C within 2 min. After the sample was held in the RPA 2000 rheometer at 40°C for 30 min, the strain sweeps were measured. Similar tests were also undertaken on the corresponding cured stocks.

Bound rubber content measurement and determination

The bound rubber content was determined with Bernnan's procedure.[43] These data were used to determine the percentage of polymer bound to filler particles and thus to quantify the degree of P–F interaction in the filled rubbers. The detailed procedure to measure bound rubber was described in a previous publication.[12]

Latent alcohol measurements

A quantitative determination of the amount of alcohol that could be released by complete hydrolysis of the residual alkoxy silane was measured. The released alcohol (latent alcohol) measurements were made in stocks as a function of mixing stages and thermal treatments. The detailed procedure to measure the latent alcohol in rubbers was described in a previous publication.[42]

Mooney viscosity measurements

Mooney viscosity measurements were conducted according to procedures described in ASTM D 1646-89.[40] The test was performed with a small rotor at 130°C (MS$_{1+4}$) for the filled rubbers and with a large rotor at 100°C (ML$_{1+4}$) for the unfilled rubbers. The

TABLE III
Identification Codes for Stocks Prepared with Various Mixing Conditions

Code	Mixing stage with silane added	Total mixing stages
a	NA	5
b	NA	4
c	NA	3
d	R1	5
e	R1	4
f	R1	3
g	R2	5
h	R3	5

NA = not applicable.

TABLE IV
Mixing Procedures Employed for the Preparation of the Rubber Stocks

Stage 1: MB	
Agitation speed	60 rpm
Initial temperature	100°C
Mixing at 0 s	Charged polymers
Mixing at 30 s	Charged filler, process oil, wax, antioxidant, and stearic acid
Mixing at 5 min	Drop
Target drop temperature	155°C
Stage 2: R1	
Agitation speed	60 rpm
Initial temperature	100°C
Mixing at 0 s	Charged MB
Mixing at 30 s	Charged silane if applicable
Target drop temperature	145°C
Stage 3: R2	
Agitation speed	60 rpm
Initial temperature	70°C
Mixing at 0 s	Charged R1 stocks
Mixing at 30 s	Charged silane if applicable
Target drop temperature	145°C
Stage 4: R3	
Agitation speed	60 rpm
Initiation temperature	70°C
Mixing at 0 s	Charged the R2 stock
Mixing at 30 s	Charged silane if applicable
Target drop temperature	145°C
Stage 5: Final batch	
Agitation speed	45 rpm
Initiation temperature	60°C
Mixing at 0 s	Charged the appropriate remill stock
Mixing at 15 s	Charged the curatives
Target drop temperature	104°C

sample was preheated at the test temperature for 1 min before the rotor started, and then the Mooney viscosity was recorded as the torque after the rotor had rotated for 4 min at 2 rpm (average shear rate ≈ 1.6 s^{-1}); the measurement is reported as the Mooney viscosity number.

RESULTS AND DISCUSSION

Effect of the mixing history on the microdispersion and viscoelastic properties of silica-filled rubbers

Viscoelastic properties such as the HTD and filler microdispersion were examined as a function of the mixing and thermal history. The filler microdispersion is usually quantified by the degree of filler networking or Payne effect data ($\Delta G'$, which is the difference in G' measured at low and high strains).[44–46] The extent of mixing was qualitatively determined by the number of mixing stages used to prepare the stocks. The number of mixing stages was chosen as a way to track the differences in treatment conditions and is commonly used to follow the amount of mixing that a tire plant needs to obtain desirable compound properties. In light of this study, a refinement of this procedure of following the cumulative mix energy could well give further insight into this process. However, the following treatment allows for

a simple way to follow the mixes. The HTD as measured by tan δ is plotted in Figure 1(a–c) (for stocks prepared with various mixing stages that are described in Tables II and III). Figure 1(a) shows the HTD of stocks **1a–1c**, which were prepared without any silane added. The HTD of stocks **2d–2f**, which were prepared with the addition of the silica shielding agent OTES, can be seen in Figure 1(b), whereas those of stocks **3d–3f**, which were prepared with the addition of the coupling agent MPTMS, are shown in Figure 1(c). In the cases of stocks **1a–1c** [Fig. 1(a)] and **2d–2f** [Fig. 1(b)], the degree of P–F interaction was limited,[12,15,42,47] and no substantial differences in the HTD mixing dependence were observed. However, when MPTMS was added to stocks **3d–3f** [Fig. 1(c)], a stronger HTD mixing dependence was found for stocks prepared with increased mixing. This was seen in the low-temperature (−60 to −10°C) region close to the polymer T_g, at which the tan δ values increased to a constant value with the two subsequent increases in mixing.

The higher low-temperature tan δ values in filled rubber have long been attributed to a larger contribution from the polymer T_g.[6] Alternatively, it has been argued that higher bound rubber in filled stocks increases P–F interactions and decreases the low-temperature tan δ value.[6,16,48–50] Comparing Fig-
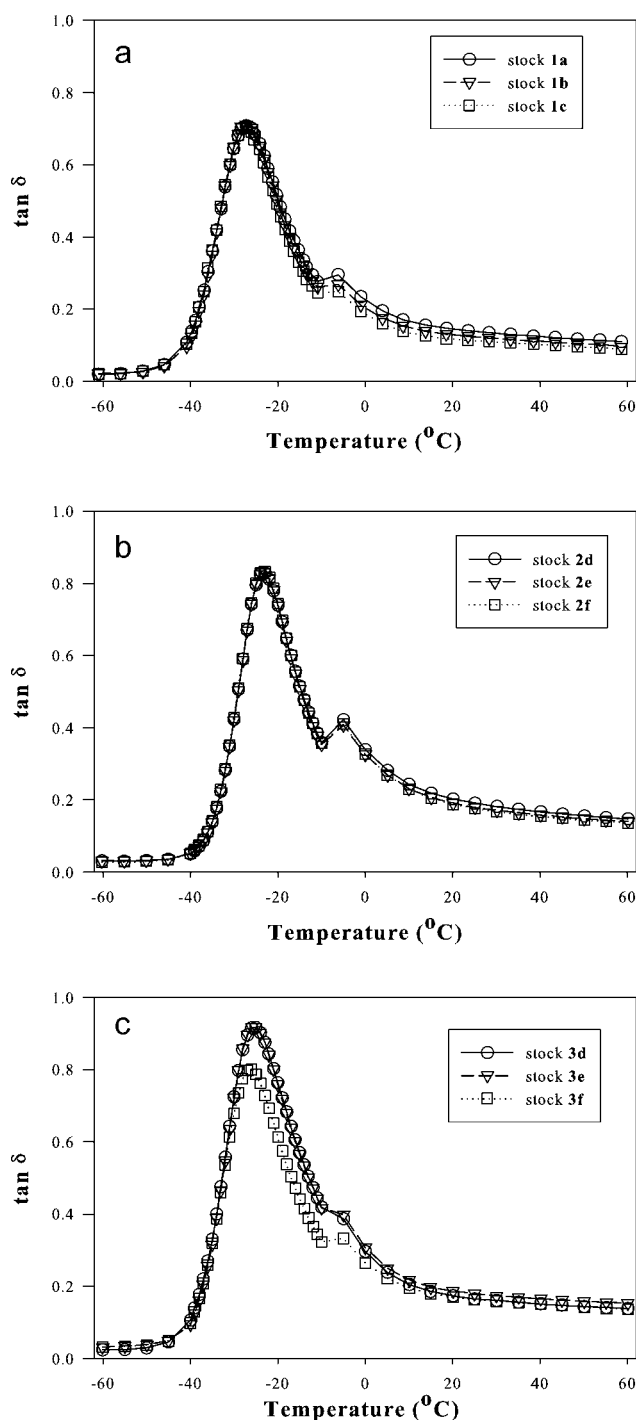
Figure 1 (a) HTD for stocks with different mixing histories: (○) stock **1a**, 5 mixing stages; (▽) stock **1b**, 4 mixing stages; and (□) stock **1c**, 3 mixing stages. A change in strain (from 0.25 to 2%) was made at −10°C. (b) HTD for stocks containing OTES with different mixing histories: (○) stock **2d**, 5 mixing stages; (▽) stock **2e**, 4 mixing stages; and (□) stock **2f**, 3 mixing stages. A change in strain (from 0.25 to 2%) was made at −10°C. (c) HTD for stocks containing MPTMS with different mixing histories: (○) stock **3d**, 5 mixing stages; (▽) stock **3e**, 4 mixing stages; and (□) stock **3f**, 3 mixing stages. A change in strain (from 0.25 to 2%) was made at −10°C.

ure 1(a–c) shows that higher low-temperature tan δ values were found for the system with higher degrees of P–F interaction and less developed filler network in stocks containing MPTMS. Higher low-temperature tan δ was also reported in silica compounds containing a coupling agent such as *bis*(3-triethoxysilyl propyl) tetrasulfide, Dynasilane 3201,[51] or MPTMS.[15] The higher P–F interactions and less developed filler network in stocks containing MPTMS are confirmed by their higher bound rubber content and lower $\Delta G'$ data as a function of increasing mixing, which are shown in Tables V and VI, respectively. A higher P–F interaction in stock **3** was developed by the reaction between a mercapto silane and rubber, which resulted in a higher bound rubber content.[52]

Interestingly, the low-temperature tan δ values of stock **2** (containing OTES) in Figure 1(b) are higher than those of stock **1** (containing no silane) in Figure 1(a), even though a slightly lower bound rubber content and lower $\Delta G'$ were found in stock **2**. It appears that the low-temperature tan δ values close to the compound T_g are greatly affected by the degree of filler networking, regardless of the extent of P–F interactions in rubbers. Therefore, in addition to the contribution from polymer T_g, the low-temperature tan δ value appears to be strongly influenced by the filler network developed in the filled rubbers. This is consistent with the data reported for a silica-filled compound containing a silica covering agent[51] and in previous findings.[15] Thus, it is not surprising to find that the low-temperature tan δ values and HTD of stocks **1** and **2** were independent of mixing because no mixing dependence on the bound rubber content and filler networking ($\Delta G'$) from these stocks was found. In contrast, changes in HTD and low-

TABLE V
Bound Rubber Content Data

Feature stock	Agent used	Bound rubber (%)				
		MB	R1	R2	R3	Final
1a	None	26	29	31	32	33
1b	None	26	29	30	—	32
1c	None	26	29	—	—	32
2d	OTES	21	26	28	30	29
2e	OTES	21	26	29	—	29
2f	OTES	21	26	—	—	28
2g	OTES	22	29	32	33	33
2h	OTES	22	28	31	36	34
3d	MPTMS	26	54	61	61	70
3e	MPTMS	26	54	59	—	68
3f	MPTMS	26	54	—	—	61
3g	MPTMS	26	27	56	59	57
3h	MPTMS	26	30	33	54	53
4d	MPTES	22	69	74	73	73
4g	MPTES	22	28	67	70	68
4h	MPTES	22	28	31	67	67
8g	MPTES	—	—	—	—	62
9g	MPTES	—	—	—	—	75

TABLE VI
$\Delta G'$ Measured from the Cured Stocks

Feature stock	Agent used	$\Delta G'$ (MPa)
1a	None	10.3
1b	None	10.2
1c	None	11.0
2d	OTES	5.80
2e	OTES	5.40
2f	OTES	4.97
3d	MPTMS	1.86
3e	MPTMS	3.06
3f	MPTMS	5.76

temperature tan δ with mixing were found only in a compound with stronger P–F interactions induced by the presence of a coupling agent (stocks **3d–3f**). The higher low-temperature tan δ values found in stocks **3d–3f** may be attributed to the less developed filler network because of flocculation suppressed by the presence of stronger P–F interactions during the curing process. Filler flocculation suppression and P–F interaction are detailed in the following section.

Filler microdispersion mixing dependence

To further investigate the filler networking effect on the HTD, the degree of filler networking from flocculation was examined as a function of thermal annealing and mixing.[15,47,53] It has been reported that $\Delta G'$ measured from the final product is strongly dependent on the degree of the filler flocculation that occurs during the rubber preparation stages.[47] The mechanisms and factors affecting the filler flocculation have been largely discussed in detail in various publications.[12,47,53–55] The $\Delta G'$ values from the stocks treated with and without thermal annealing at 171°C for 15 min were measured. For this, stocks containing no curatives in the fashion previously reported[47] were measured to reduce the effect that vulcanization has on the measurements.

To compare the filler microdispersion mixing dependence in rubbers, a normalized microdispersion [$d(x)$], expressed as a percentage, was defined as the normalized $\Delta G'$ difference in stocks prepared with different mixing histories or with different silane utilization. Specifically, the normalized microdispersion $d_1(x)$ was defined according to eq. (1) as a function of an arbitrary mixing parameter x, where x is the number of accumulated mixing stages:

$$d_1(x) = \frac{\Delta G'_{MB} - \Delta G'_x}{\Delta G'_{MB}} \times 100 \qquad (1)$$

$\Delta G'_{MB}$ and $\Delta G'_x$ represent $\Delta G'$ values obtained from the stock prepared with a reference mixing history MB (first mixing stage) and x number of total mixes, respectively. Now, $d_1(x)$ represents the normalized

change in the microdispersion in a filled rubber before and after mechanical treatments. Depending on the system chosen, a different reference may be used for the sake of better comparison, as shown later in this article. The $d_1(x)$ data for stocks **1**, **2**, and **3** before and after thermal annealing are shown in Figure 2(a,b), respectively.

Filler networking and $d_1(x)$ in the filled rubbers before thermal annealing

In Figure 2(a), the $d_1(x)$ values obtained from stocks prepared without thermal annealing (**1a–1c**, **2d–2f**, and **3d–3f**) are plotted against x experienced by the stock. For example, $x = 2$ stands for a stock that experienced MB and R1 mixing stages, whereas $x = 3$ indicates MB, R1, and R2 mixing stages for a stock, and $x = 4$ indicates MB, R1, R2, and R3 mixing stages for a stock. The results in Figure 2(a) show that $d_1(x)$ of all stocks increased with mixing, indicating that more mixing reduces the overall F–F contacts and favors more P–F contacts. When either
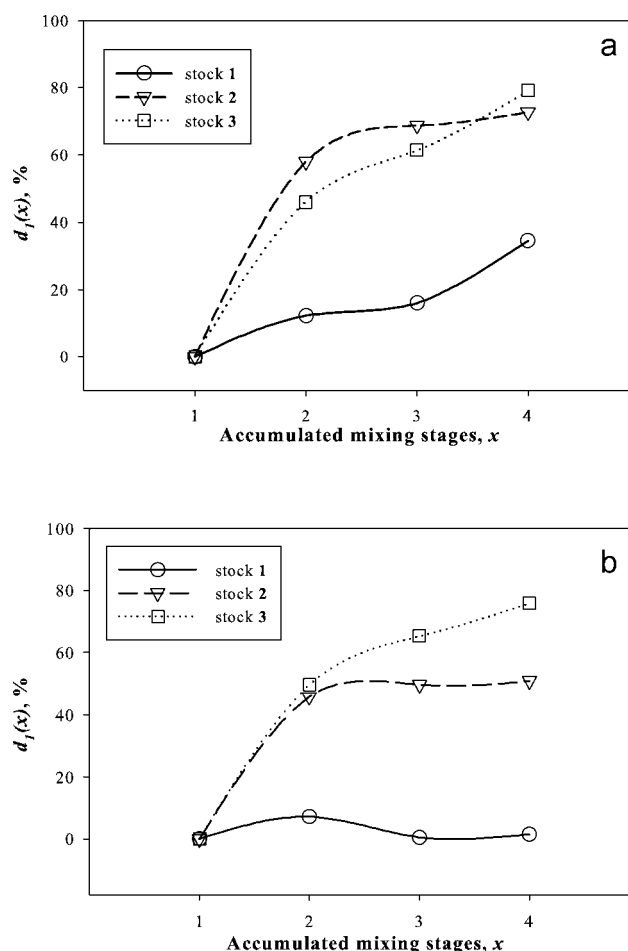

Figure 2 Effects of mixing on $d_1(x)$ (a) before thermal annealing and (b) after thermal annealing at 171°C for 15 min for stocks containing different silanes: (◯) stock **1**, no silane added; (▽) stock **2**, OTES; and (□) stock **3**, MPTMS.

TABLE VII
Alcohol Data Measured from the Uncured Stocks

| | | | Alcohol (ROH) | | | | | |
| | | | Latent ROH in rubber (wt %) | | Latent ROH in silane (wt %) | | Emitted ROH in silane (wt %) | |
Feature stock	Agent used	Mixing stage x	BT	AT	BT	AT	BT	AT
1a	None	5	0	0	0	0	0	0
1b	None	4	0	0	0	0	0	0
1c	None	3	0	0	0	0	0	0
2d	OTES	5	0.317	0.180	39.14	22.22	60.86	77.78
2e	OTES	4	0.382	0.203	47.16	25.06	52.84	74.94
2f	OTES	3	0.448	0.246	55.31	30.37	44.69	69.63
3d	MPTMS	5	0.080	0.090	21.68	24.39	78.32	75.61
3e	MPTMS	4	0.094	0.086	25.47	23.31	74.53	76.69
3f	MPTMS	3	0.121	0.088	32.79	23.85	67.21	76.15

AT, after thermal annealing; BT, before thermal annealing.

OTES in stock **2** or MPTMS in stock **3** was added in the R1 stage ($x = 2$), $d_1(x)$ of the stocks were greatly enhanced compared to those of stock **1**. Apparently, the higher $d_1(x)$ values observed in stocks **2** and **3** were a result of a lower degree of filler networking caused by both reduced F–F interactions due to silica hydrophobation in stocks **2** and **3** and the introduction of more P–F interactions in stock **3**.[15] The silica hydrophobation was achieved by the condensation reaction (silanization) of the silanol group on silica with the alkoxy group in silane.[42,56,57] The degree of silanization in stocks **2** and **3** can be estimated by the measurement of the latent alcohol content in these stocks. These results in Table VII show that higher degrees of silanization occurred with increasing mixing.

The silanization reaction with MPTMS leveled off after mixing for four stages ($x \geq 4$) and was close to the level obtained after curing. The compound Mooney viscosities (MS_{1+4}) of these two stocks (**3d** and **3e**) shown in Figure 3 are similar. The bound rubber contents of these stocks also were comparable. Apparently, additional mechanical and thermal treatments of these MPTMS-containing stocks do not increase the reaction extent between MPTMS and the rubber over that obtained with $x \geq 4$. It has been reported that the radical addition of methyl mercaptan to a rubber latex proceeds almost quantitatively at 50°C.[58,59] This efficient addition of a mercapto functionality has also been reported when the mixing temperature was over 150°C.[42] Thus, it may be concluded that little free mercaptan from the MPTMS-containing stocks **3d** and **3e** would be expected to be able to endure mixing and be present during vulcanization. Such a low residual level of mercapto functionality should have a minimum effect on the cure and would be insignificant in comparison with stocks containing a polysulfane[32,60,61] such as TESPT or TESPD. It is well known that all

efforts to maintain the multiple sulfur linkages in the polysulfane must be made to prevent premature addition to the rubber before the cure.[56,57,60,62] Such an approach then allows the polysulfane to participate in the curing reaction. Also, lower compound viscosities were found in those containing OTES in comparison with those with MPTMS, regardless of the degree of mixing, as shown in Figure 3.

Filler networking and $d_1(x)$ in the filled rubbers after thermal annealing

The degree of the filler networking and $d_1(x)$ in stocks **1**, **2**, and **3**, discussed previously, were also examined after they were thermally annealed. It is widely understood that when a filled stock is annealed at an elevated temperature, it promotes filler flocculation resulting in higher $\Delta G'$ values.[15,47,53] This is reflected in the loss of $d_1(x)$ in stocks **1** and **2** after annealing. It has been reported that vulcanization has a limited effect on filler flocculation.[47] To determine the main factors contributing to the development of the filler networking, stocks containing no
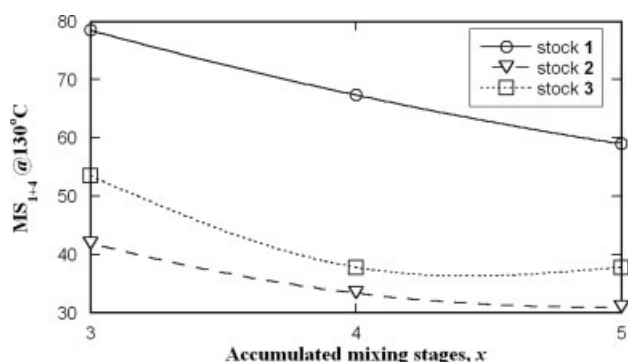

Figure 3 Compound Mooney viscosity data for stocks containing different silanes: (○) stock **1**, no silane added; (▽) stock **2**, OTES; and (□) stock **3**, MPTMS.
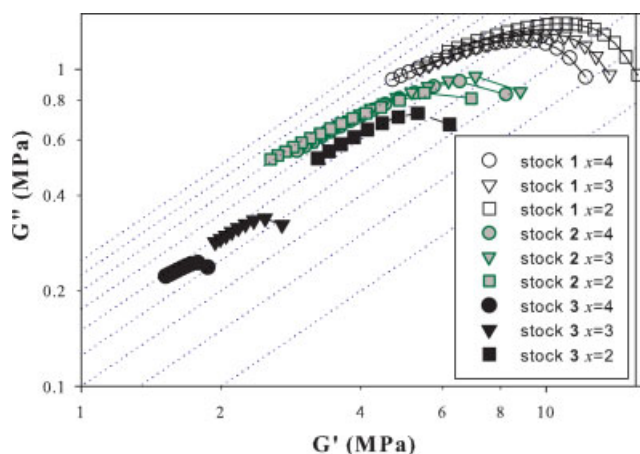
Figure 4 Gplot measured at 50°C as a function of the mixing history for stock **1** (open symbols; no silane added), stock **2** (gray solid symbols; with OTES added), and stock **3** (black solid symbols; with MPTMS added). The number of accumulated mixing stages (x) experienced by a stock was as follows: circles for $x = 4$, inverse triangles for $x = 3$, and squares for $x = 2$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

curatives were used so that increased G' after annealing could be attributed only to increased filler networking without concerns of an increase from polymer networking or filler retardation caused by cure. Thus, it is assumed that the measured $\Delta G'$ values in these thermally annealed uncured stocks can represent only the maximum amount of filler reagglomeration that can occur during curing.

The annealed results in Figure 2(b), where $d_1(x)$ for $x \geq 2$ [$d_1(x \geq 2)$] is measured for stock **1**, show no significant improvements with increased mixing. With stock **2**, there still is a substantial increase in $d_1(x)$ from MB ($x = 1$) to R1 ($x = 2$) due to the addition of OTES, but further mixing does not seem to significantly increase $d_1(x)$. The benefits of increased mixing in stocks **1** and **2** [observed in Fig. 2(a)] before heating were either eliminated or reduced by one third once the stocks were annealed. On the contrary, additional mixing improved $d_1(x \geq 2)$ measured on stock **3**, which contained MPTMS as the coupling agent. The increase in bound rubber, listed in Table VI, also was shown to be dependent on the P–F interactions and $d_1(x)$. Therefore, it seems that the presence of a coupling agent effectively reduced filler flocculation upon heating and preserved the higher $d_1(x)$ value obtained with increased mixing.

Elevated-temperature hysteresis mixing dependence

The elevated-temperature viscoelastic properties of cured stocks are presented in Figure 4 by Gplots obtained from strain sweep measurements at 50°C,

in which G'' is plotted against G'.[63] The parallel iso-hysteresis lines are included in these Gplots to allow a comparison of viscoelastic quantities such as G', G'' and tan δ on the same diagram. Each isohysteresis line represents a set of G' and G'' values that lead to constant hysteresis values as the line's intercept and hysteresis increase toward the upper left corner. For this measurement, the deformation was under a constant strain condition, and G'' was directly proportional to the energy loss upon deformation.[3] Thus, it is convenient to compare the energy loss among stocks at a corresponding reinforcement level (G'). For stocks **1** and **2**, increased mixing only slightly reduces the energy losses at corresponding reinforcement levels; this is similar to results reported for a carbon black filled compound.[63] The energy losses in stocks prepared with MPTMS are lower than those in the stocks prepared without a coupling agent. Energy losses are also reduced upon increased mixing of stock **3**, for which improved $d_1(x)$ and higher P–F interactions (Table V) were found. It has been shown that high-temperature (far above the compound T_g) hysteresis is mainly governed by the P–F interactions.[15] Thus, the development of greater P–F interactions in a compound through increased mixing not only enhances the low-temperature (−60 to −10°C) hysteresis values but also reduces those in the higher temperature region (≥50°C). This may benefit a tread compound used in a tire that has lower tire rolling resistance and higher wet traction.[2,3,5] Figure 4 shows that the properties were improved with the presence of P–F interactions, so that even when they were prepared with reduced mixing, they were better than those obtained in the absence of a coupling agent with extensive mixing.

Effect of the silane mixing residence time (τ) on $d_1(x)$ and hysteresis

The improved properties described in the previous section could be explained in two ways: either increased mixing in a compound containing a coupling agent or greater P–F surface contact created by mixing. To elucidate this effect, stocks **2**, **3**, and **4** with suffixes of **d**, **g**, and **h** were prepared with the same number of mixing stages ($x = 5$) but with the silane being added at different stages in the mixing process. Table II summarizes the silane type and concentration used for each stock prepared. The code used for the mixing stage at which silane was introduced is shown in Table III. For example, MPTES was added to stock **4d** in R1, to stock **4g** in R2, and to stock **4h** in R3. Thus, although all the stocks experienced the same total of five mixing stages, τ increased as follows: **4d** > **4g** > **4h**.

Figure 5(a) shows $d_1(x)$ measured before thermal annealing on curative-free stocks **2d**, **2g**, and **2h**. The
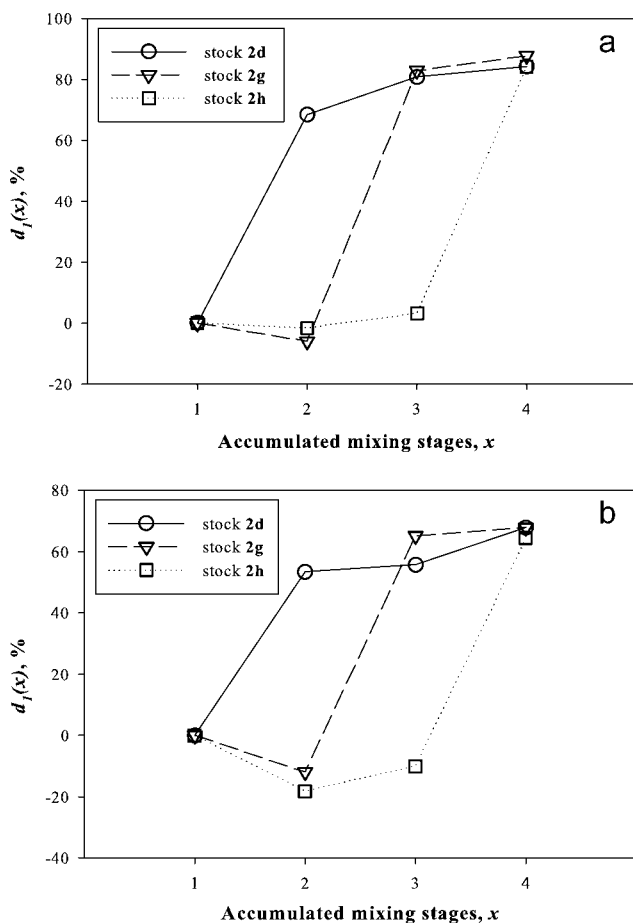
Figure 5 (a) Effects of τ on $d_1(x)$ (a) before thermal annealing and (b) after thermal annealing at 171°C for 15 min for stocks containing OTES added in (○) R1 (stock **2d**), (▽) R2 (stock **2g**), and (□) R3 (stock **2h**).

values of $d_1(x)$ measured for these stocks after OTES was added were found to be very similar regardless of τ. For example, $d_1(x > 2)$ of **2g** is about the same as that of **2d**. Increasing mixing to R3 increases $d_1(x)$ by only 3% for both stocks **2d** and **2g** and gives the same $d_1(x)$ value as that of stock **2h**, to which OTES was added in R3. Thus, the effect of reducing F–F interactions to improve $d_1(x)$ by the addition of OTES dominates $d_1(x)$ obtained over the mechanical mixing. The same stocks after thermal annealing [Fig. 5(b)] showed the same tight $d_1(x)$ clustering, except for an approximately 20% reduction in the $d_1(x)$ values measured before annealing. This demonstrated that the $d_1(x)$ reduction upon annealing reflected in Figure 2(b) was almost totally free of mixing time.

When P–F interaction is induced into a system through the use of MPTES, $d_1(x)$ is higher for the stocks to which the MPTES was added in an earlier mixing stage. These results are shown in Figure 6(a,b) for stocks **4d**, **4g**, and **4h**, to which MPTES was added in the R1, R2, and R3 mixing stages,

respectively. This occurs regardless of thermal histories imposed on the samples before MPTES was added. This shows that the effect of mechanical mixing, which increases P–F surface contact, can be accentuated by the presence of a coupling agent that induces more P–F interactions. As a result, an improved $d_1(x)$ value is obtained through increased τ to give greater P–F interactions. Stocks **3d**, **3g**, and **3h**, to which an MPTMS coupling agent was used at one third of the molar loading of MPTES used in stock **4**, showed results [see Fig. 7(a,b)] similar to those of stocks containing MPTES. The lack of an increase in $d_1(x)$ upon the annealing of these stocks containing the reduced level of MPTMS suggests that this coupling agent reacted with the silica filler more completely at the elevated mixing temperature than the stocks containing MPTES. This is apparent when Figure 5(a,b) is contrasted with Figure 6(a,b). This effect can also be seen in the almost linear increase in $d_1(x)$ caused by increased mixing and MPTMS as opposed to the curved response obtained with MPTES. Some of the small differences in results
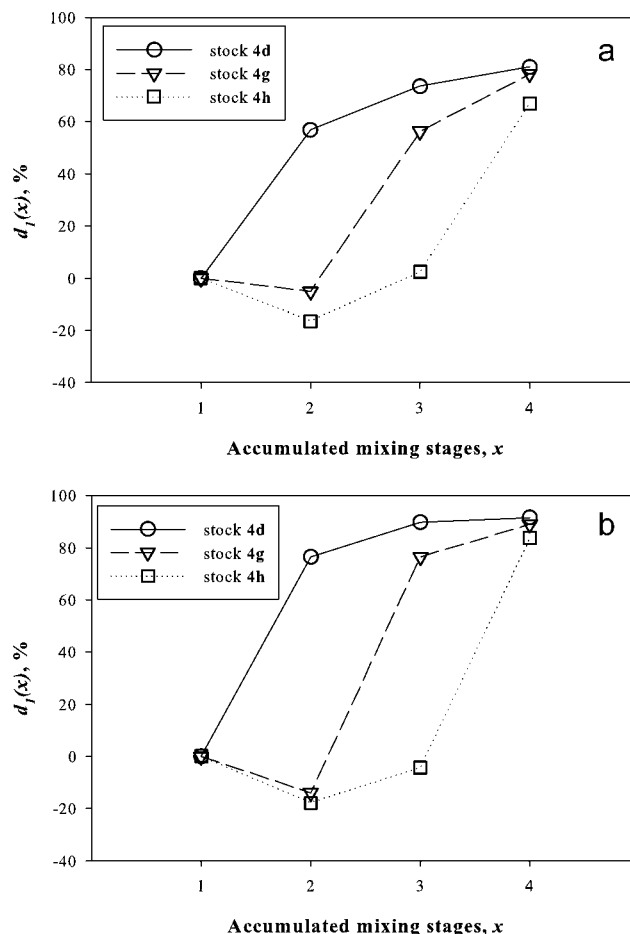

Figure 6 (a) Effects of τ on $d_1(x)$ (a) before thermal annealing and (b) after thermal annealing at 171°C for 15 min for stocks containing MPTES added in (○) R1 (stock **4d**), (▽) R2 (stock **4g**), and (□) R3 (stock **4h**).
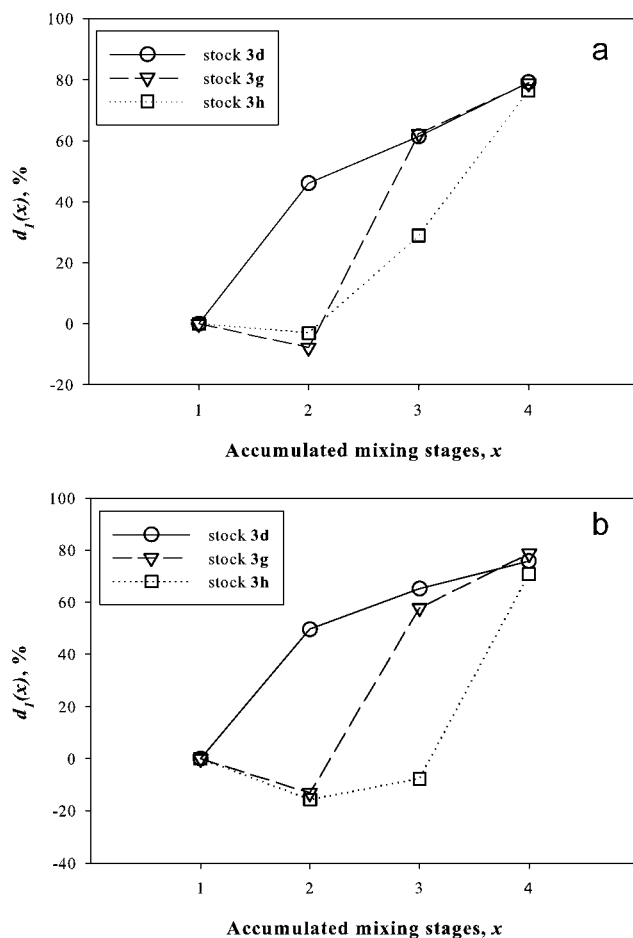
Figure 7 (a) Effect of τ on $d_1(x)$ (a) before thermal annealing and (b) after thermal annealing at 171°C for 15 min for stocks containing MPTMS added in (○) R1 (stock **3d**), (▽) R2 (stock **3g**), and (□) R3 (stock **3h**).

as a function of τ, as shown in Figure 8(b). In the low-temperature region (−60 to −10°C), the increased tan δ values are found in the stocks to
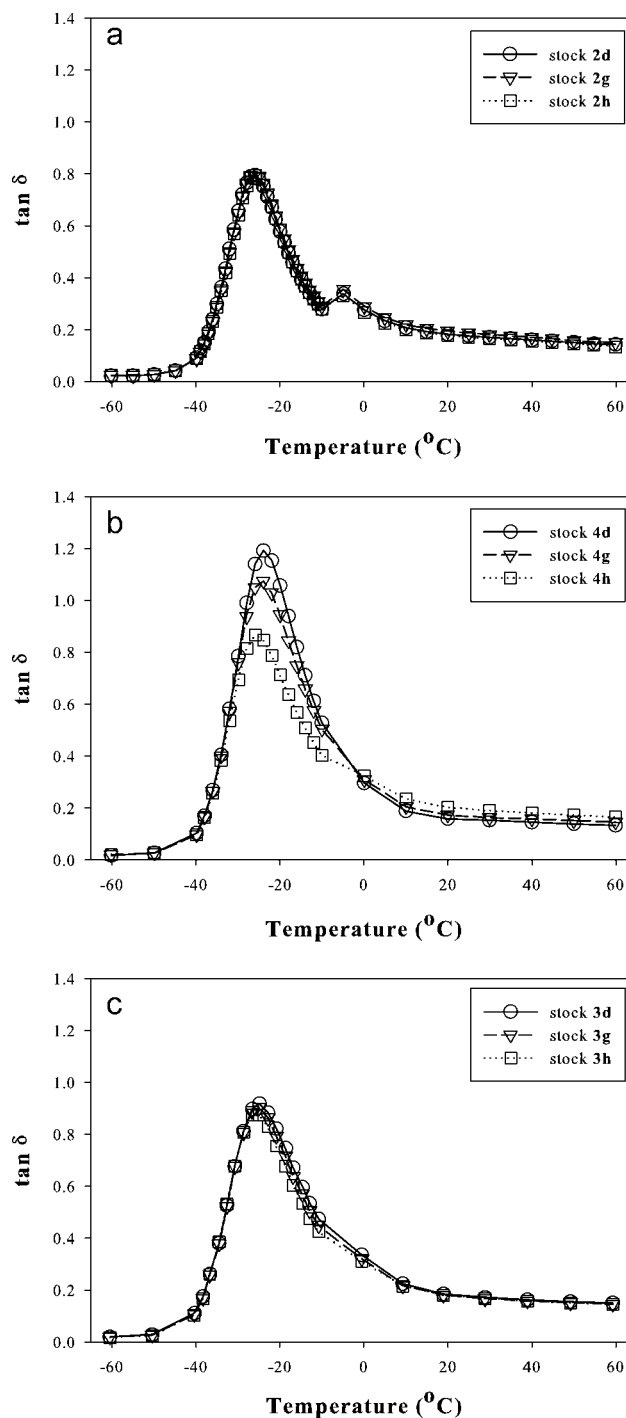

are attributed to overmixing and the limitations of the measurement equipment.

The results obtained with the two coupling agents show that the mixing time has a dramatic influence on the response from the different alkoxy silane functionalities. Small differences can most reasonably be attributed to the reactivity difference of MPTES and MPTMS. It has been reported that an approximately 6–10-fold increase in reactivity with silica has been seen when methoxy silane has been compared to ethoxy silane.[64] Such reactivity differences appear to explain the observed enhancement of MPTMS at a shorter mixing time (R1) compared to the level obtained with MPTES.

The HTD for the previously discussed stocks are plotted in Figure 8(a–c). There are no differences in HTD as a function of τ for the stocks containing OTES (stocks **2d**, **2g**, and **2h**) shown in Figure 8(a). This is similar to the results from the plot of $d_1(x)$ and mixing described previously in Figure 5(a,b). In the case of stocks containing MPTES (**4d**, **4g**, and **4h**), there are readily detectable differences in HTD

Figure 8 (a) HTD as a function of τ for stocks containing OTES added in (○) R1 (stock **2d**), (▽) R2 (stock **2g**), and (□) R3 (stock **2h**). A change in strain (from 0.25 to 2%) was made at −10°C. (b) HTD as a function of τ for stocks containing MPTES added in (○) R1 (stock **4d**), (▽) R2 (stock **4g**), and (□) R3 (stock **4h**). A change in strain (from 0.25 to 2%) was made at −10°C. (c) HTD as a function of τ for stocks containing MPTMS added in (○) R1 (stock **3d**), (▽) R2 (stock **3g**), and (□) R3 (stock **3h**). A change in strain (from 0.25 to 2%) was made at −10°C.

which the coupling agent MPTES was added in the early stages (tan δ: **4d** > **4g** > **4h**). This coincides with the improved $d_1(x)$ value being found in stock **4d** [Fig. 6(a,b)] and is in agreement with the observation that higher $d_1(x)$ leads to higher low-temperature hysteresis, as discussed in the preceding section. The stronger HTD observed in MPTES stocks with longer τ also resulted in lower high-temperature (≥50°C) tan δ values with **4d** < **4g** < **4h**. Bound rubber results also show increasing values for the MPTES stocks to which the coupling agent was added in earlier stages of mixing (see Table V). This agrees with the results reported previously when P–F interactions increased as more coupling agent was added to a compound.[15,47] When the MPTMS coupling agent was used for preparing stocks **3d**, **3g**, and **3h**, no significant differences could be found in their HTD as a function of τ [Fig. 8(c)]. This is similar to their $d_1(x)$ mixing dependence described in the previous section. No quantitative relationship can be established because the molar alkoxy silane concentrations in stock **3** are 64% lower than those in stock **4** and because of the higher reactivity with silica of methoxy in MPTMS over that of ethoxy in MPTES.[64] However, it appears that the HTD differences result from the silane concentration, degree of the alkoxy silane reaction, and mixing time. Work on the HTD as a function of the alkoxy silane concentration in compounds containing MPTES or MPTMS will be addressed in a future publication.

The high-temperature viscoelastic properties are summarized in the form of Gplots in Figure 9 for G' and G'' measured at 50°C in a strain sweep experiment for stocks **2**, **3**, and **4** with suffixes of **d**, **g**, and **h**. Lower energy losses (G'') were found for
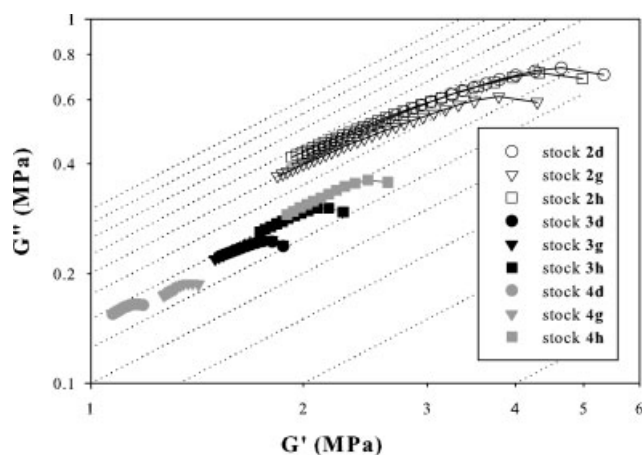

Figure 9 Gplot measured at 50°C as a function of τ for various stocks (open symbols for stock **2** containing OTES, solid gray symbols for stock **3** containing MPTMS, and solid black symbols for stock **4** containing MPTES; circles for stocks with suffix **d**, inverse triangles for stocks with suffix **g**, and squares for stocks with suffix **h**).

stocks where MPTMS or MPTES was added in early stages of mixing. Thus, the benefits of increasing τ to enhance the low-temperature tan δ and of reducing the high-temperature tan δ were found only in stocks with the presence of stronger P–F interactions.

Quantification of the P–F and F–F interactions and their effects on the compound $d(x)$ and hysteresis

The F–F and P–F interactions have been shown to greatly affect the compound $d(x)$ and hysteresis. The efficiency and mechanism of these two interactions for affecting the compound viscoelastic properties are very different yet act in a complementary fashion. To quantify the efficiencies of F–F and P–F interactions and to clarify their differences to improve the compound $d(x)$ and hysteresis, various amounts of OTES or MPTES were added in the R2 mixing stage to prepare stocks **4g** to **14g**.

The viscoelastic properties from compounds containing OTES and MPTES were compared on the basis of the concentration of the triethoxy silane functional group that reacted with silica. The triethoxysilyl concentration (mmol/kg of silica) was calculated and listed in Table II from the following equation:

$$\text{Triethoxysilyl concentration} = \frac{1000X_S}{65M_S} \quad (2)$$

where X_S represent the silane loading (phr) and M_S is the silane molecular weight.

The normalized filler microdispersion [$d_2(x)$] for a given stock defined in eq. (1) can now be given by eq. (3):

$$d_2(x) = \frac{\Delta G'_{\text{no silane}} - \Delta G'_y}{\Delta G'_{\text{no silane}}} \times 100 \quad (3)$$

where $\Delta G'_{\text{no silane}}$ is $\Delta G'$ measured on a stock containing no silane and $\Delta G'_y$ is $\Delta G'$ measured from a stock containing the silane of interest. Note that $d_2(x)$ now represents the change in the microdispersion in a filled rubber before and after treatment by a silane. The $d_2(x)$ data presented were calculated from $\Delta G'_{x=R3}$, which is $\Delta G'$ measured from R3 stocks.

Figure 10(a) shows that before thermal annealing, $d_2(x)$ increased as the silane loading (either OTES or MPTES) was increased. Initially, the $d_2(x)$ improvement seems similar for both the OTES and MPTES stocks at silane loadings less than 150 mmol/kg of silica. At higher silane loadings (>150 mmol/kg of silica), OTES stocks have higher $d_2(x)$ values than MPTES stocks. However, after the stocks were thermally annealed, $d_2(x)$ of MPTES stocks was higher than that of OTES stocks for most of the measured silane loadings [Fig. 10(b)]. $d_2(x)$ leveled off as the
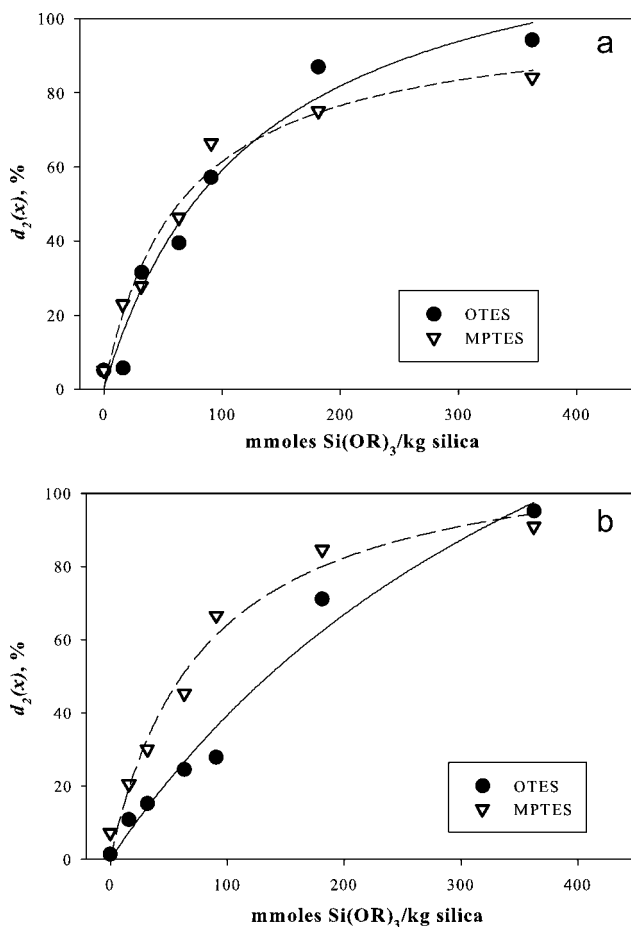
Figure 10 Effects of the silane loading [triethoxysilyl concentration (mmol/kg of silica)] on $d_2(x)$ (a) before thermal annealing and (b) after thermal annealing at 171°C for 15 min for stocks containing different silanes: (●) stocks containing OTES and (▽) stocks containing MPTES.

silane loading approached a maximum for both OTES and MPTES stocks. It appears that the coupling agent MPTES, at similar triethoxy silane concentrations, has a greater efficiency in promoting $d_2(x)$ than OTES does after the heating. The better $d_2(x)$ values for heated MPTES stocks can be attributed to the lower degree of filler flocculation resulting from heating. The combined effect of decreased F–F interactions and increased P–F interactions in MPTES stocks provides a better means to retard the filler flocculation upon heating. When this is compared to stocks containing OTES, for which F–F reduction is the only major mechanism to increase $d_2(x)$, it must be concluded that the P–F interactions derived by mixing with a coupling agent are essential to improve $d_2(x)$.

Figure 11 shows the results for stocks prepared with triethoxy silane added at a concentration of 180 mmol/kg of silica with either OTES (stock **2g**) or MPTES (stock **4g**). The increased bound rubber levels in stock **4g** compared to stock **2g** appear to be related to the previously stated observation that **4g** has a higher low-temperature (−60 to −10°C) hysteresis and lower high-temperature (≥50°C) hysteresis. This is consistent with previous results shown in Figures 8(a–c) and 9. The improved P–F interaction can also be seen in the values of bound rubber reported in Table V along with higher $d_2(x)$ shown in Figure 10(b) for stock **4g** compared to stock **2g**.

Further information on how the P–F interaction or filler networking individually affects the compound properties still needs additional clarification. For this, the viscoelastic properties for stocks containing OTES or MPTES need to be compared at a similar filler $d_2(x)$ value but with various degrees of P–F interaction. Thus, stocks containing either OTES or MPTES with a similar normalized state of the filler microdispersion were chosen from the results in Figure 10(b). In one case, a stock with 180 mmol of OTES/kg of silica (stock **2g**) was compared to that containing 90 mmol of MPTES/kg of silica (stock **8g**). The $d_2(x)$ values of these two samples were chosen to be about 72%. The HTDs of these two stocks are shown in Figure 12, in which similar low-temperature hysteresis spectra (−60 to −10°C) for the two are found even though different silane levels are used in these two stocks. The presence of stronger P–F interactions in stock **8g** (bound rubber content of 62%) gives a compound with lower high-temperature tan δ compared to stock **2g** (bound rubber content of 33%). This suggests that the P–F interaction apparently has a greater influence on high-temperature tan δ than filler networking.

The higher degrees of P–F interactions found in MPTES stocks (**8g**, **4g**, and **9g** with bound rubber contents of 62, 68, and 75%, respectively) may provide additional rubber reinforcement with higher
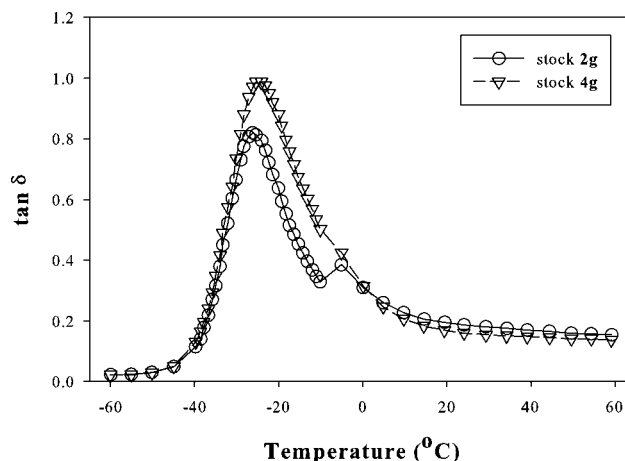

Figure 11 HTD for stocks containing (○) OTES (stock **2g**) and (▽) MPTES (stock **4g**). The silane concentration in both stocks was 180 mmol/kg of silica. A change in strain (from 0.25 to 2%) was made at −10°C.
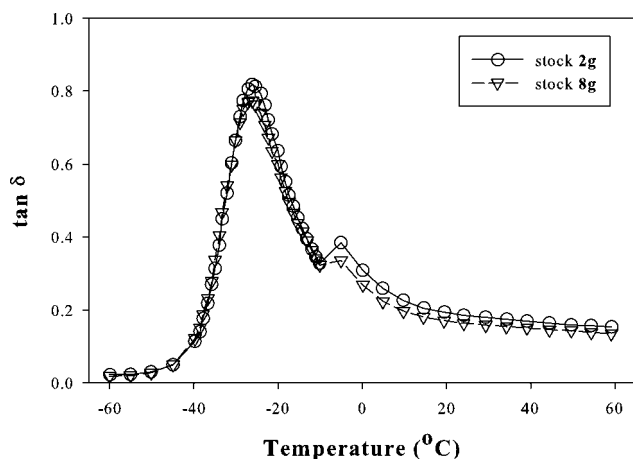
Figure 12 HTD for stocks containing (○) OTES (stock **2g**) and (▽) MPTES (stock **8g**). The silane concentrations for stocks **2g** and **8g** were 180 and 90 mmol/kg of silica, respectively. Stocks **2g** and **8g** had similar values of $d_2(x)$ of about 72%. A change in strain (from 0.25 to 2%) was made at $-10°C$.

G' values but a weaker G' strain dependence, as shown in Figure 13(a). The use of the coupling agent MPTES reduces F–F interaction and filler networking and thus decreases the network contribution at low-strain (1–10%) G'. The increased compound G' at higher strain levels (>10%) with increasing MPTES loading can also be attributed to the enhanced P–F interactions that provide filler clusters with greater resistance to the applied deformation. Similar results were reported previously in silica compounds containing polysulfane coupling agent.[47] As a result, the use of the silica shielding agent OTES (**13g**, **2g**, and **14g**) simply reduces the F–F interactions and thus decreases filler networking and reinforcement levels at all measured strain ranges, as shown in Figure 13(b).

CONCLUSIONS

A systematic study of the mixing affecting the normalized state of a filler microdispersion [$d(x)$] and compound viscoelastic properties of silica-filled rubbers containing various silanes has been conducted. The silica-filled rubbers used for this study were specifically chosen to emphasize the compound viscoelastic properties and their relationships involving F–F and P–F interactions that could be affected by mixing. The F–F interactions in the silica compound were modified with a silica shielding agent, n-octyl triethoxysilane (OTES), whereas the P–F and F–F interactions could be controlled by the addition of a coupling agent such as MPTMS or MPTES. The better $d(x)$ and favorable viscoelastic properties, such as higher $0°C$ tan δ and lower $50°C$ tan δ, are desirable for the rubber compound because of the strong

HTD. A rubber compound with improved $d(x)$ and stronger HTD may provide a tire tread with higher wet traction, lower rolling resistance, and better wear resistance.

In silica-filled compounds, the property improvements not only are attainable through the choice of the proper mixing procedure but also are strongly dependent on the types and functions of the silanes added to the compound. The better $d(x)$ and stronger HTD obtained through mixing in silica compounds require the use of the coupling agent, which provides the permanent links between the rubber and silica. The better $d(x)$ is obtained through the stabilized dispersed filler network during the rubber preparation stages, whereas the presence of strong P–F interactions in rubber gives lower high-temperature (50–100°C) hysteresis. A less developed filler network along with the strong P–F interactions results in a rubber compound with favorable strong
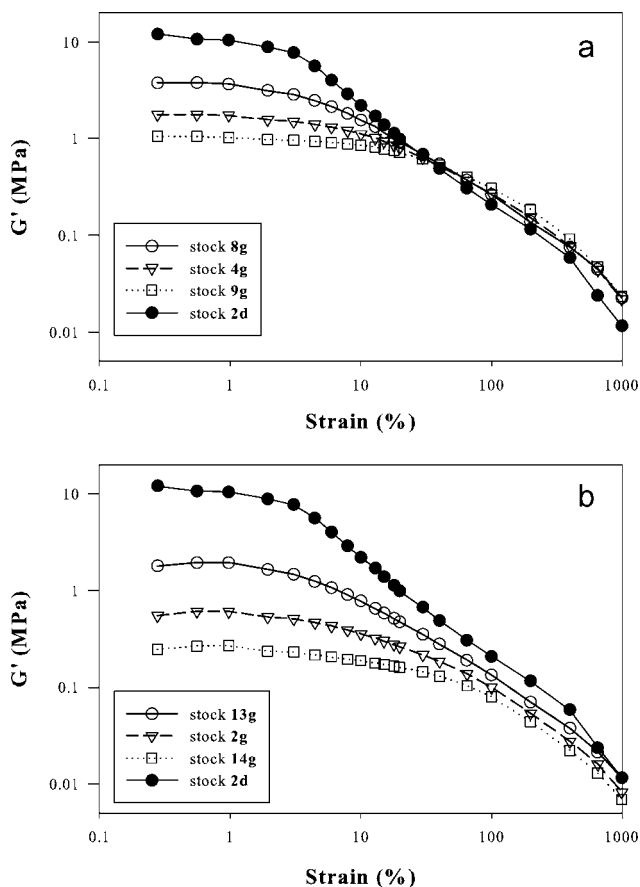

Figure 13 (a) G' strain dependence for stocks containing MPTES [(○) stock **8g**, (▽) stock **4g**, and (□) stock **9g**] and no silane [(●) stock **2d**]. The silane concentrations for stocks **8g**, **4g**, and **9g** were 91, 180, and 36 mmol/kg of silica, respectively. (b) G' strain dependence for stocks containing OTES [(○) stock **13g**, (▽) stock **2g**, and (□) stock **14g**] and no silane [(●) stock **2d**]. The silane concentrations for stocks **13g**, **2g**, and **14g** were 91, 181, and 367 mmol/kg of silica, respectively.

HTD upon dynamic deformation. The efficiency for improving the compound $d(x)$ value with various silanes has also been quantified. Comparing MPTES and OTES used in silica compounds has shown better efficiency for improving $d(x)$ and enhancing HTD for those compounds containing coupling agent MPTES, whereas the processing is improved for those containing OTES. It has also been demonstrated that the change in hysteresis near the compound T_g is mainly governed by the degree of filler networking, whereas elevated-temperature hysteresis is strongly influenced by the P–F interactions in compounds.

Through the experimentation, it appears that a coupling agent is required to reinforce silica-filled compounds. However, a silica shielding agent such as OTES may be used to reduce the compound viscosity and to help with downstream rubber processing and tire building. Proper choices of a combination of silica shielding and coupling agents along with appropriate mixing conditions can provide silica-filled rubbers with better reinforcement, processing, and properties needed for manufacturing tires.

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