

**THE EFFECT OF SILANE LOADING ON PROPERTIES OF A SILICA FILLED
SBR MODEL TREAD COMPOUND**

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Abstract

The effect of silane loading in a silica-filled tread compound was studied to better understand how the silane coupling agent effects tear and abrasion. A series of compounds were prepared in which the silane varied from 0% to 10% by weight of silica loading. The silane was bis(triethoxysilylpropyl)polysulfide (Struktol SCA985). The abrasion resistance was tested on an angle abrader. The tear properties were obtained from molded groove trouser tear specimens. The effect of silane on the tear strength and abrasion resistance was significant. The tear strength decreased and the abrasion resistance increased as a function of silane loading. The molecular structures governing tear and abrasion were studied. DMA analysis and crosslink density (with and without ammonia) were used to try to understand the tear and abrasion results.

Introduction

The advantages of using silica as a reinforcing agent in tire tread compounds are well documented¹. The development of tires possessing long service life, driving safety and fuel economy has been enhanced with the introduction of bifunctional organosilanes which provide a chemical means of linking the silica and rubber together. Properties such as tensile strength, modulus, abrasion resistance and heat build up reduction due to hysteresis can be improved. Furthermore, chemical modification of the silica surface characteristics aids to lower filler-filler network attraction which is beneficial for improved compound processability. Moreover, the use of silica fillers is paramount in achieving the desired combination of wet traction versus rolling resistance in tire tread compounds².

We have been studying the dynamic behavior of a model silica filled solution SBR compound for use in tire treads^{3, 4, 5}. These studies have confirmed that functionalization of the SBR preferentially lowers $\tan \delta$ thus reducing rolling resistance and improving fuel economy. It is thought that additional favorable interactions between the chains (backbone and chain end modified) and the silica are responsible for decreasing hysteretic effects^{4, 6}. Other functionalized solution SBRs providing similar advantages in tire properties have been investigated by other groups as summarized in ref. 7. Both the hysteresis and the Payne effect were lessened due to the lowering of the number of free polymer chain ends by their absorption and reaction with active filler surface.

The influence of the silane coupling agent concentration upon silica/chain interactions will be investigated using various tests for a model silica filled solution SBR compound. Silane coupling agent concentrations will be varied from 0 to 10% by weight of its optimal concentration. The mixing procedure will be the same for all compounds to ensure compound consistency. The testing includes time-domain NMR, tensile, abrasion, crosslink density by swelling with and without ammonia hydroxide, bound rubber with and without ammonia hydroxide, molded groove trouser tear, and dynamic mechanical testing (DMTA) to predict tire performance. Correlations between the different test methods will be also be carried out.

Experimental

Compounds and Mixing Procedure

The five compounds identified in Table 1 were mixed in three stages in accordance to the procedure outlined in Table 2. Detailed ingredient descriptions are provided in the appendix. A silane coupling concentration of 5.2 phr (8% silane coupling agent by weight) (compound D) was considered the optimal concentration assuming a ratio of silica/coupling agent of 12.5. Two levels below this concentration (Compounds B and C) and one above (Compound E) were added in order to probe an expanded range of coupling agent levels. Compound A does not contain any coupling agent.

Ingredient	Compound Identification				
	A	B	C	D	E
Silane Coupling Agent Level	0% by weight	2.6% by weight	5.4% by weight	8.0% by weight	10.6% by weight
STAGE 1					
F-S-SBR	75	75	75	75	75
PB	25	25	25	25	25
Carbon black	15	15	15	15	15
Silica	65	65	65	65	65
Silane Coupling Agent	0	1.7	3.5	5.2	6.9
Aromatic Oil	24	24	24	24	24
Stearic acid	1.5	1.5	1.5	1.5	1.5
Masterbatch 1	205.5	206.8	208.1	209.4	210.7
STAGE 2					
Zinc oxide	1.9	1.9	1.9	1.9	1.9
Wax	2	2	2	2	2
A/O 1	2	2	2	2	2
A/O 2	0.5	0.5	0.5	0.5	0.5
Masterbatch 2	211.9	213.2	214.5	215.8	217.1
STAGE 3					
Sulfur	1.05	1.05	1.05	1.05	1.05
CBS	0.91	0.91	0.91	0.91	0.91
DPG	1.05	1.05	1.05	1.05	1.05
Total Phrs	214.9	216.2	217.5	218.8	220.1

Table 1: Chemical compositions of the five silica based SBR compounds

Mixing took place on a Farrel BR laboratory size mixer. Rotor speed was increased during stages 1 and 2 at the 4.5' and 3.5' marks in order to reach the desired hold temperature. The third stage drop temperature was reached after about 2.5 minutes. The mixed rubber was sheeted out three times on a two roll mill after completion of each stage.

Stage	Rotor speed (rpm)	Temperature (°C)	Ram Pressure (psi)	Hold time (min)	Hold and Drop Temperature (°C)
1	65	65	50	2	160
2	65	65	50	4	140
3	60	50	50	0	110

Table 2: Mixer and mixing conditions during the three stages of compound mixing.

Test Procedures

Room temperature tensile properties were measured using die C dumbbell specimens according to ASTM D412.

Double Strain Sweeps in the tensile mode were carried out on a Metravib +150 Dynamic Mechanical Thermal Analyser (DMTA) at 10Hz and 30°C. Second sweep results are presented.

A Temperature sweep in tensile mode was conducted on a Metravib +150 Dynamic Mechanical Thermal Analyser (DMTA) at 2Hz and 1.5% static strain +/- 0.3% dynamic strain.

Molded groove trouser tear (Type CP modified trouser tear test piece with a constrained path for tear) was performed at room temperature according to ASTM test method D624.

The angle abrasion testing was performed according to ISO 23233 (first edition 2009-02-15) titled “Rubber vulcanized or thermoplastic – Determination of resistance to abrasion using a driven, vertical abrasive disc. This ISO method (ISO 23233) was designed for the LAT 1000 (Groshe) abrader, however, it is applicable to the angle abrader.

The determination of the chemical crosslink density of the five compounds was carried out by performing equilibrium solvent swell measurements followed by use of the modified Flory Rehner equation assuming crosslink fluctuations (i.e. phantom network) and a functionality of four.

$$\ln(1 - v_r) + v_r + \chi v_r^2 = -\frac{\rho}{2M_{c,sw}} V_s v_r^{\frac{1}{3}} \quad (1)$$

In equation 1, V_s is the molar volume of the swelling solvent, v_r is the volume fraction of rubber in the swollen state and χ is the Flory Huggins polymer-solvent interaction parameter. A χ value of 0.413 (in toluene) was used in order to estimate $M_{c,sw}$, the average molecular weight between crosslinks (chemical crosslinks and trapped entanglements together) for the SBR rich compounds⁴. This method assumes the disentanglement of the polymers chains during swelling in the good solvent.

This crosslink density by solvent swelling was repeated placing a beaker of ammonia hydroxide in the bottom of a desiccator and placing the samples on the shelf above it during the 24hr swelling period.

The bound rubber determination for each of the five compounds was conducted. The green compound was swelled in toluene for 48 hours at 70°C. It was then dried at 50°C overnight. This test was then repeated placing a beaker of ammonia hydroxide in the bottom of a desiccator and placing the samples on the shelf above it during the 48 hour swelling period at 70°C.

A Bruker model mini-spec time domain NMR apparatus was employed to measure spin echo relaxation data for the unvulcanized and vulcanized compounds. A resonance frequency of 20 MHz and test temperature of 363K were used. The standard Hahn-Echo pulse sequence (90°/t/180°/t(acquisition up to 200ms)) was employed using 32 scans and a recycle delay of 0.5s. Each compound was tested in triplicate and the resulting curve fitting data were averaged.

A linear combination of exponential decay functions will be used to model the decrease in magnetization ($M(t)$) of the rubber compounds:

$$\frac{M(t)}{M_0} = A \exp\left(\frac{-t}{T_{21}}\right) + B \exp\left(\frac{-t}{T_{22}}\right) + C \quad (2)$$

The decay times of the rigid (chemical crosslinks and physical entanglements) and mobile (dangling chain ends) phases are given by T_{21} and T_{22} respectively. The amplitude values of A , B and C reflect the relative amount of proton magnetization of the rigid, dangling chain end and highly mobile sol fractions. Curve fitting software (Jump software) was used for equation verification and subsequent calculations and analyses in order to provide confidence in the NMR parameters. Needless to say, the curve fitting analysis is not without error and can lead to misinterpretation^{8,9,10}.

The number average molar mass between crosslinked chains ($M_{c,NMR}$) is directly proportional to the fast decay component of the relaxation:

$$M_{c,NMR} \propto T_{21} \quad (3)$$

This same relationship can be applied to estimate the number average molar mass between physical chain entanglements (M_e) for the gum and unvulcanized compound. In the usual case of tetrafunctional crosslinking in rubber systems, a chemical crosslink density (ν_c) may be calculated by using $\nu_c = \rho/2M_c$ where ρ is the density of the elastomer.

Results and Discussion

A summary of the mechanical properties of the five compounds is presented in Figures 1 and 2. Without silane coupling, the stress strain curve displays lower moduli and the

highest elongation to break due to the lack of compatibility between the silica surface and the polymer chains. Upon its progressive addition, mechanical properties improve as witnessed by an increase in both higher strain moduli and the tensile strength. A general decrease in elongation to break is noted. The modulus at 300% elongation, which is commonly used to measure the extent of silica/chain coupling effects, demonstrates an excellent correlation with increasing silane coupling concentration. Tensile strength on the other hand, shows less of a correlation and less of a change of value. The 5.4% and 8% by weight stress strain curves are demonstrating quite similar mechanical behavior while the 10.6% by weight curve suggests an improvement over the properties of the optimized formulation. This series of stress strain curves provide evidence that chemical coupling has taken place between the polymer unsaturation and the silica surface.

The double strain sweep plots of Fig. 3 provide a combination of the Payne (elastomer-filler interactions) and Mullin's (stress softening) effects. In the region of particular interest from 0.01 to 0.1 dynamic strain, the general trend is a decrease in $\tan \delta$ signifying that rolling resistance is enhanced upon addition of the coupling agent. In other words, less of the filler-polymer network is destroyed under the action of dynamic strain. Compound E, which represents 10.6% by weight silane coupling agent, is displaying the lowest $\tan \delta$ in the dynamic strain region of interest for tire rolling resistance. This particular finding corroborates with the mechanical property test results. Chemical coupling by the silane coupling is responsible for the improvement in properties along with a reduction in filler-filler interactions.

Results from the temperature sweep, as plotted in Fig. 4, show an interesting trend below 27°C. At low temperatures (namely -27 – 10°C) it is observed that the 8% by weight silane coupling level has the highest tangent delta values. The 10.6% by weight silane level has values below the 5.6% by weight silane level over this temperature range. The other silane levels behave as expected by showing an increase in tangent delta values as coupling level increases.

Figure 5 shows the tear strength results measured on each of the five compounds using molded groove trouser tear specimens. It is noticed that the 8% by weight silane coupling level has the lowest tear strength and the 0% by weight level has the highest.

A double strain sweep was conducted on separate trouser tear specimens. Because tear strength is related to the loss mechanism, tangent delta should give a good correlation. Using this knowledge it is observed that the tangent delta values obtained in the strain sweep correlate very well with the tear strength data (Fig. 6).

The results from the angle abrader show that as the silane coupling agent increases, the abrasion resistance increases (Fig. 7). The graph shows the weight loss of the abrasion sample decreasing, which indicates the abrasion resistance is increasing.

While the results from the tear strength and abrasion resistance seem to be opposite each other, a correlation graph was constructed to view how similar the trends in the data are (Fig. 8). This graph shows that these two properties are directly correlated to each other.

Using the excellent correlation between tensile strength and abrasion resistance, it was decided to try to find a prediction equation for abrasion resistance. After multiple attempts, it was found that the tensile strength paired with the tangent delta value at 3% strain (from the strain sweep in tension) gives the best prediction ($R^2 = 0.9993$) (eq. 4 and Fig. 9).

$$\text{Weight Loss} = A * \text{tensile strength} + B * \text{tan delta at 3\% strain} + C \quad (4)$$

Equilibrium volume swell coupled with the Flory-Rehner analysis by eq. 1 provided chemical crosslink data (chemical crosslinks + trapped chain entanglements) for the five vulcanized compounds. The equilibrium volume swell was repeated and a beaker of ammonia hydroxide was placed in a desiccator with the swelling samples to give an ammonia atmosphere. The crosslink density results came out lower in the samples exposed to the ammonia atmosphere as expected (Fig. 10).

The percent bound rubber of the green compound was obtained following the method listed in Rubber Chemistry and Technology¹³. The procedure was repeated and a beaker of ammonia hydroxide was placed in a desiccator with the swelling samples to give an ammonia atmosphere. The bound rubber results came out higher in the samples exposed to the ammonia atmosphere (Fig. 11). The explanation for this is still being studied.

The unvulcanized and vulcanized NMR relaxation curves have been plotted in the previous paper⁵. The unvulcanized curves in the acquisition region of approximately 0.3 to 20 ms (which is sensitive to the chemical crosslinking and dangling chain end behavior) appear to display more variation while the vulcanized ones superimpose onto one curve as a function of silane coupling agent concentration.

A table of the calculated NMR bi-exponential curve fitting parameters is given for the unvulcanized and vulcanized compounds in Table 3. The progressive insertion of the coupling agent acts to lower the overall rigidity of the network chains (increased mobility due to lubrication) by increasing the mobility of the free chain ends. For further analysis, refer to the previous paper⁵.

	A	B	C	D	E
Unvulcanized					
A	82.6	82.4	82.0	80.5	80.3
T ₂₁	2.54	2.50	2.56	2.72	2.63
B	17.4	17.6	18.0	19.5	19.7
T ₂₂	26	25	26	26	25
Vulcanized					
A	83.6	83.8	84.4	83.9	83.9
T ₂₁	2.20	2.14	2.11	2.20	2.17
B	16.4	16.2	15.6	16.1	16.1
T ₂₂	27	27	26	28	28

Table 3: Summarized NMR bi-exponential curve fitting parameters for the unvulcanized and vulcanized compounds. A and B amplitudes have been normalized to 100%.

Perhaps the most surprising result is that no significant difference between all four curve fitting parameters is observed from the vulcanized compounds A to E (see also Fig. 12). At first sight, this observation suggests a relatively constant crosslink density in the five compounds. Additional chain restrictions caused by the linking of the silane coupling agent with the unsaturation in the polymers, which were expected to be seen by a lowering of T_{21} , were not observed. However, amplitude values of A and B do become more constant for the five compounds upon vulcanization suggesting that the silane coupling agent has changed into a less mobile chemical form compared to the unvulcanized state. To say the least, this is still weak and indirect evidence extracted from the NMR curves to support the chemical coupling reaction.

Using both the crosslink density by swelling and NMR results, if it is assumed that the combined chemical crosslink and trapped chain entanglement density is constant through the five compounds (since the NMR T_{21} values were constant), then it is likely that the additional silane coupling to the polymer unsaturation is responsible for the perceived increase in total chemical crosslink density. In this case, assuming that it is possible to decouple the chemical crosslinks (+ trapped chain entanglements) from the additional filler-chain reactions, one can estimate that,

$$\frac{1}{M_{c,sw}} \approx \frac{1}{M_c} + \frac{1}{M_{chain-filler}} \quad (5)$$

where M_c represents only the chemical crosslink and trapped chain entanglements molecular weights.

Reported values of M_e for SBR containing 23.5% styrene vary from 3-3.2 kg/mol²⁰ while for *cis*-poly(butadiene), the measured value is 2.3 kg/mol²⁴. Given a 75/25 blend of SBR/PB in the tread compound, inverse linear additivity will be assumed in the entanglement density values in the compound and an averaged value of 2.8 kg/mol will be used to represent the average molecular weight between entanglements. Given the values of T_{21} for the vulcanized compounds in table 3 along with the relationship of eq. 3, an estimated value of $M_{c,NMR}$ for the vulcanized compounds is 2.16 kg/mol. Assuming that this derived value of M_c by NMR pertains only to the linear combination of chemical crosslinks, trapped entanglements and free chain entanglements, it is possible to write:

$$\frac{1}{M_{c,NMR}} \approx \frac{1}{M_c} + \frac{1}{M_e} \quad (6)$$

It can be readily seen that combining equations 5 and 6 provides a means to estimate the magnitude of $M_{chain-filler}$. These values are plotted in Figure 13 as a function of silane coupling agent level. The magnitude of $M_{chain-filler}$ decreases in a regular and linear fashion with the addition of silane coupling agent. This can be attributed to its reaction with the rubber unsaturation during vulcanization. The value of $M_{chain-filler}$ for no coupling agent can be related to the interactions taking place between the polymer chains with the silica surface. In addition, an improvement in chain-filler interaction appears beyond the

optimal level of silane coupling agent (8% by weight). This observation agrees with the tensile, abrasion and strain sweep results.

More work is required to understand the filler-rubber interactions, in particular in the challenging case of silica and SBR. Future work needs done to understand the bound rubber results that were observed. Further studies on these topics will be presented in subsequent investigations.

Conclusions

Two distinct families of NMR relaxation curves for the five model compounds were observed depending on whether the system was vulcanized. Biexponential fitting of the relaxation provided the best confidence in the curve fitting parameters. The magnitude of the rigid lattice slowly decreases upon addition of the silane coupling agent in the unvulcanized state. Vulcanization causes an increase in the rigid lattice amplitude and a decrease in the short decay time due primarily to the crosslinking reactions. No noticeable trend in the NMR curve fitting parameters was detected as a function of coupling agent level in the vulcanized samples. However, the progressive increase in silane coupling concentration brought about a linear increase in modulus at 300% elongation, a lower $\tan \delta$ (and rolling resistance) and a decrease in perceived crosslink density as measured by equilibrium volume swell. It is assumed that the crosslink density increase is due to the silane coupling reaction and that the NMR short decay results suggest a constant total chemical crosslink density. Combining these two observations together allowed the measurement of an average molar mass of interaction between the chains and the silica filler. A 33% increase over the optimal silane coupling agent concentration was beneficial for rolling resistance enhancement. A discussion is included about improving the experimental method and future investigations.

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Appendix

Ingredient	Trade name	Description	Supplier
F-S-SBR	Sprintan SLR-4602	Tin coupled F-S-SBR, 37.5phr TDAE, high vinyl (67% of BD), 25% S	Styron
PB	Budene 1207	cis 1-4 Poly(butadiene) (97% cis 1-4 content)	Goodyear
Carbon black	N234	Carbon Black	Sid Richard
Silica	Ultrasil 7000 GR	Silica	Evonik
Silane coupling agent	Si266	Bis(triethoxysilylpropyl)polysulfide	Strukol SCA985
Aromatic oil	Aromatic Oil	Sundex 790	Sunoco (Holly Refinery)
Stearic Acid	stearic acid	Fatty acid	Harwick
Zinc Oxide	zinc oxide	Cure activator	Harwick
Wax	Okerin wax 7240	microcrystalline wax	Astor Wax
A/O 1	Santoflex 6PPD	6PPD	Harwick
A/O 2	Wingstay 100	diphenyl p-phenylene diamine	Goodyear Chemical
Sulfur	Sulfur	Cross-linker	Harwick
CBS	Santocure CBS	Accelerator	Harwick
DPG	Perkacit DPG-grs	Accelerator	Harwick

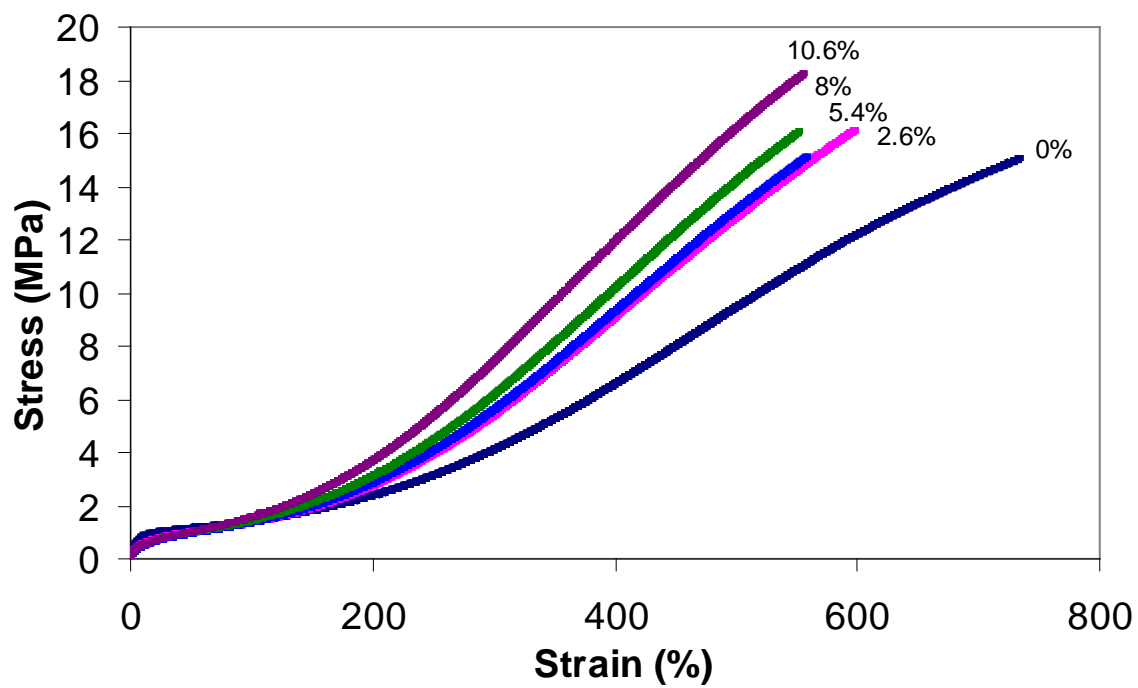


FIG. 1 – Stress-Strain curves of the SBR compounds as function of silane coupling agent concentration (N.B. 8% = 5.2 phr)

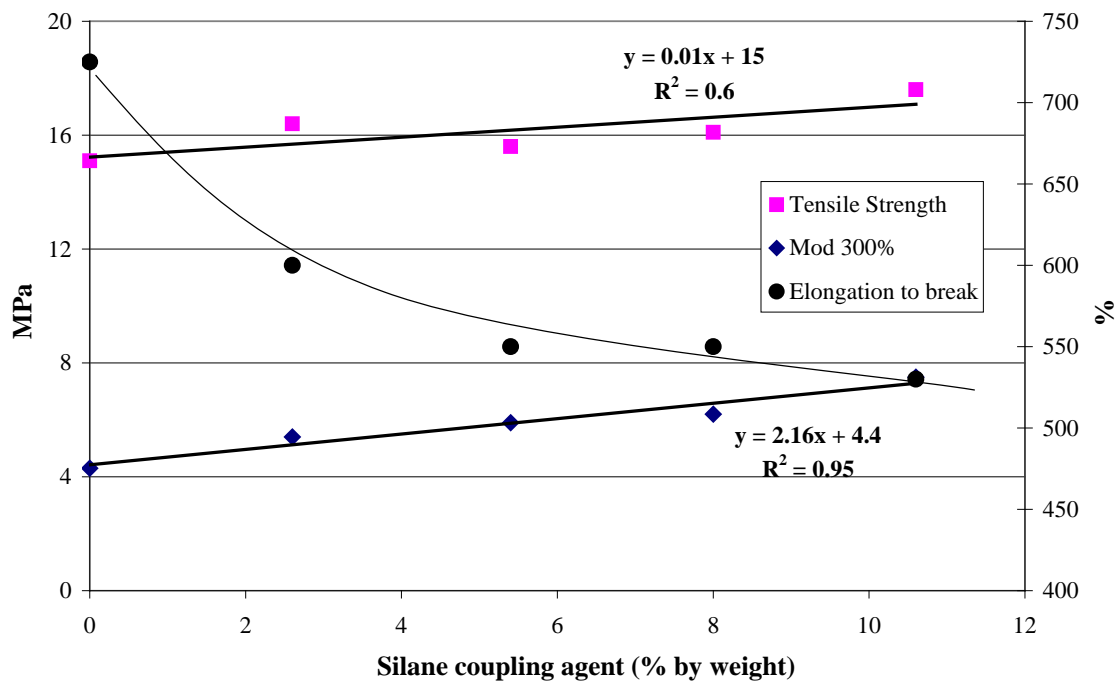


FIG. 2 – Selected mechanical properties plotted against silane coupling agent level.

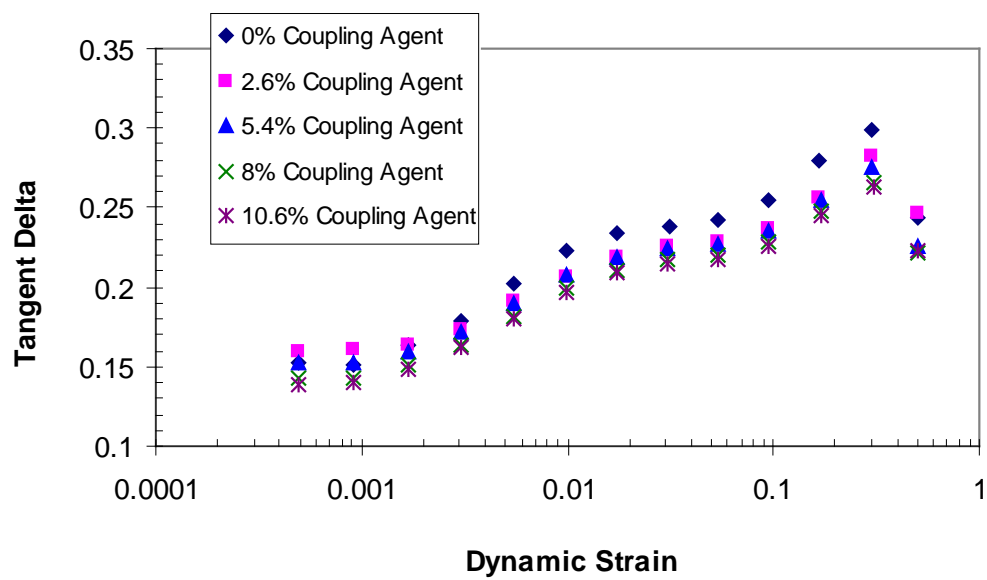


FIG. 3 – Double strain sweep results for rolling resistance performance (30°C).

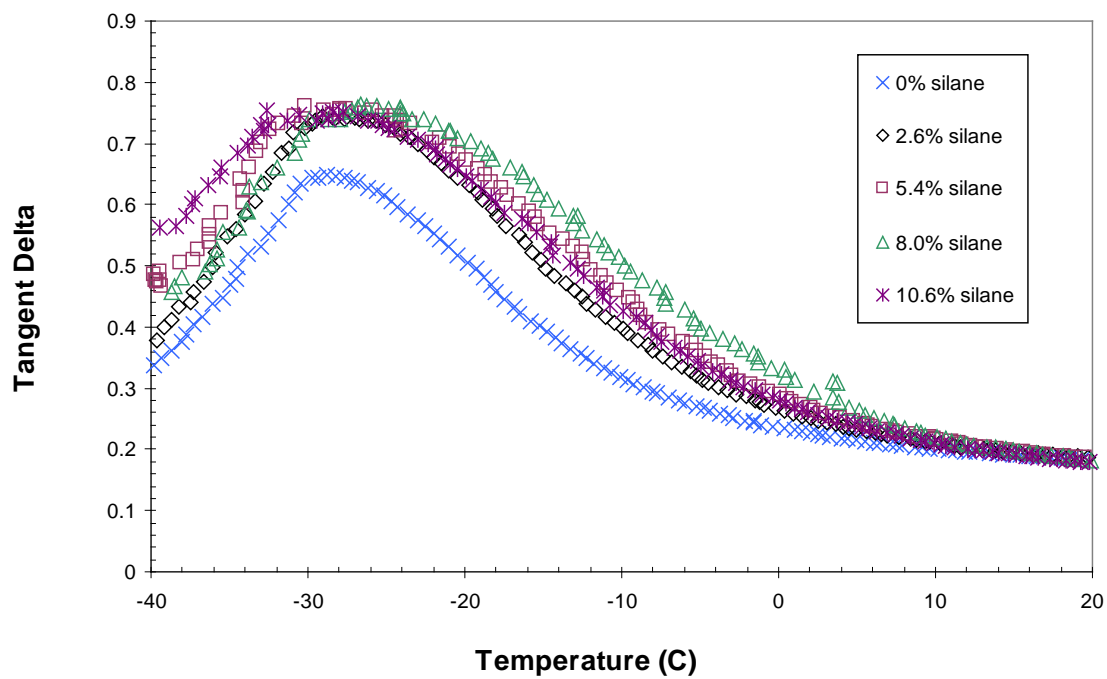


FIG. 4 – Tangent Delta results from DMA temperature sweep for ice and wet traction performance (-10°C and 0°C, respectively).

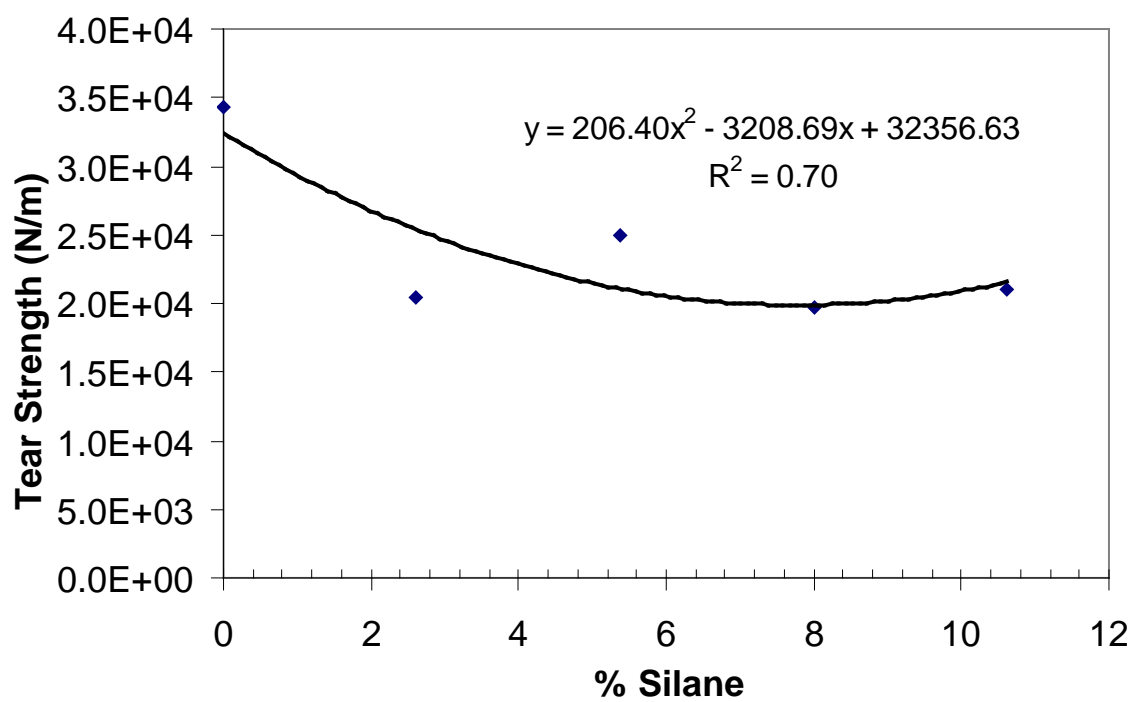


FIG. 5 – Tear strength results plotted against silane coupling agent level.

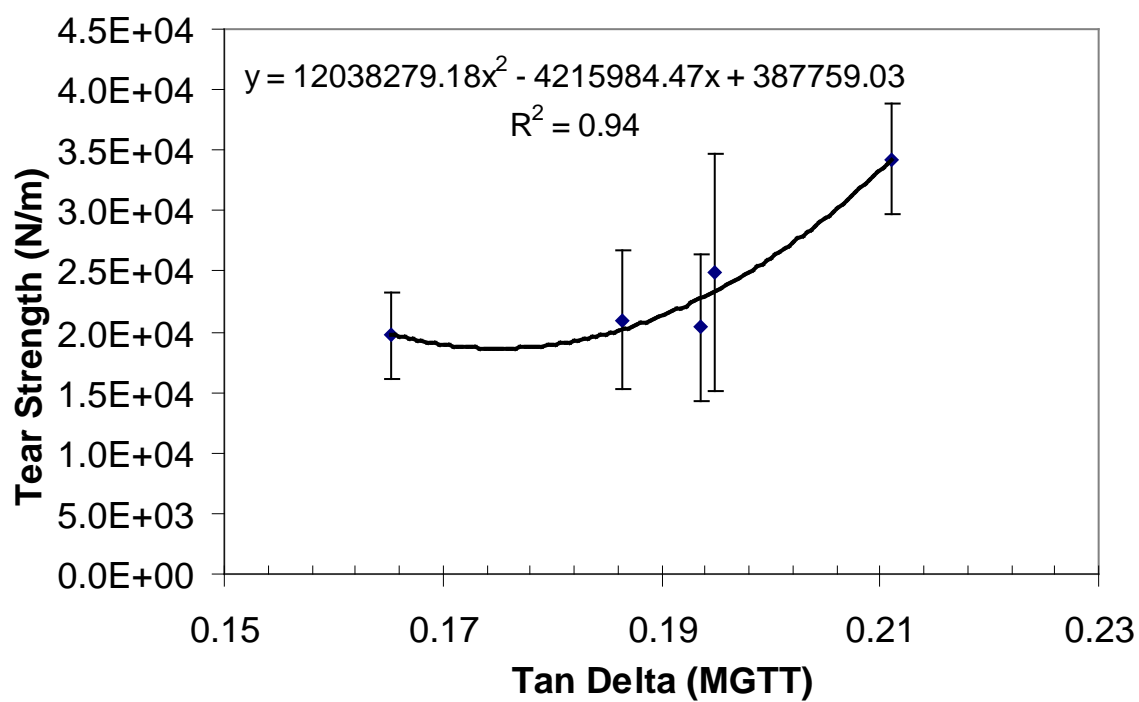


FIG. 6 – Tear strength results correlated with the tangent delta results from the strain sweep conducted on a trouser tear specimen.

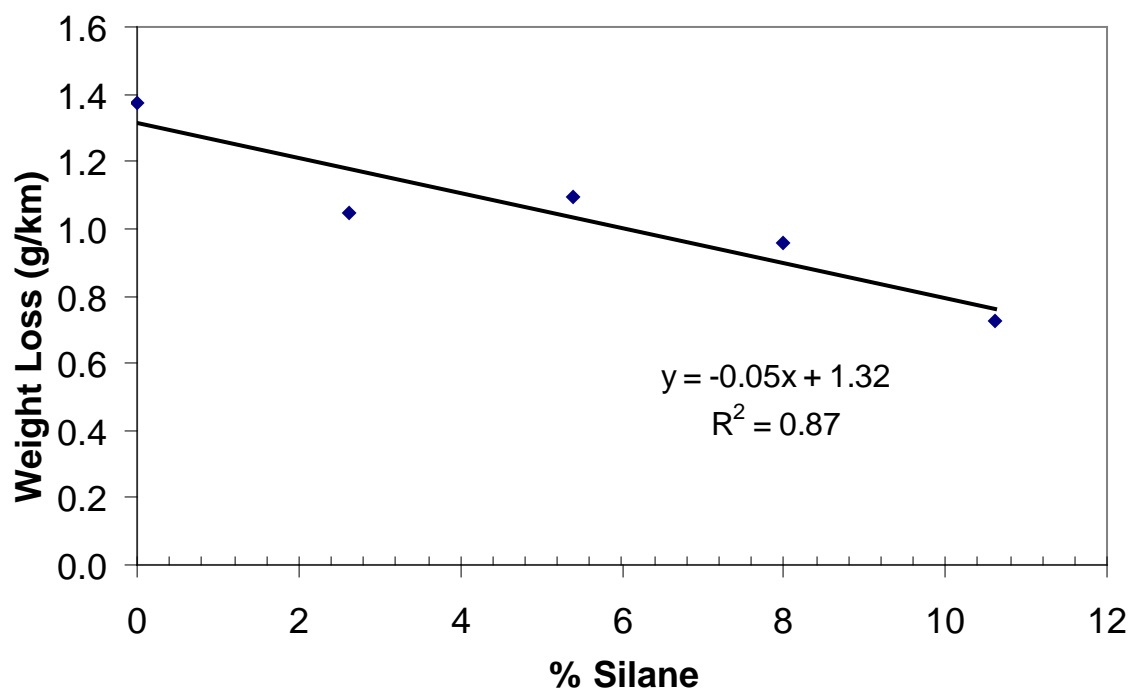


FIG. 7 – Abrasion results plotted against silane coupling agent level.

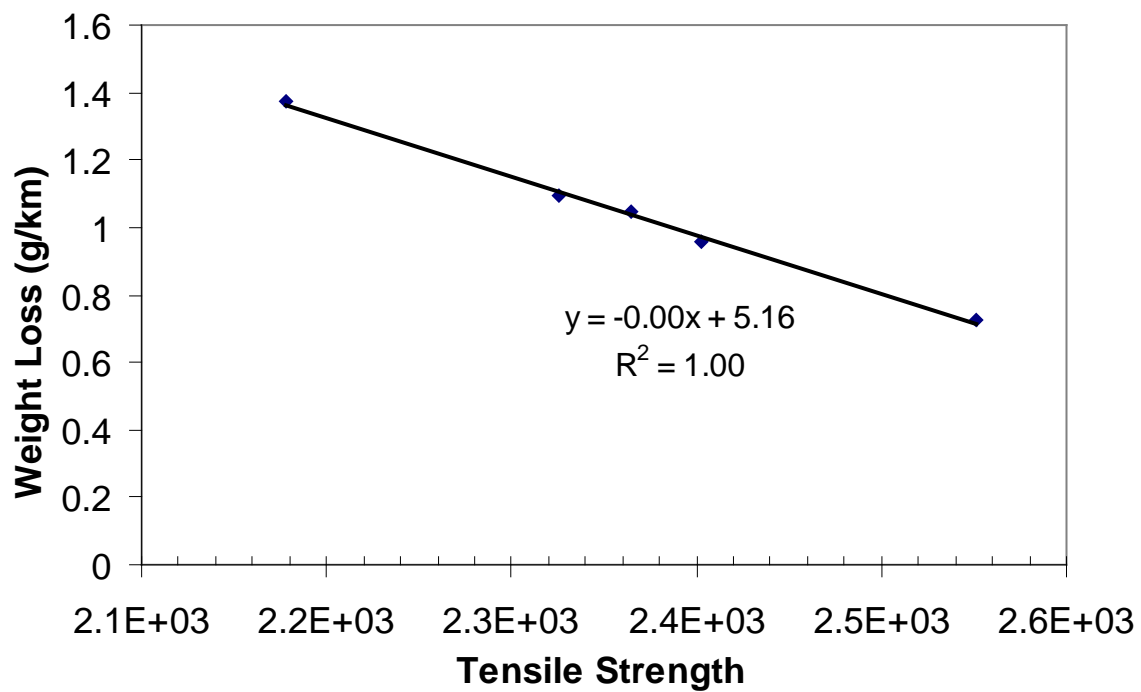


FIG. 8 – Tensile strength results correlated against abrasion resistance results (weight loss during abrasion testing).

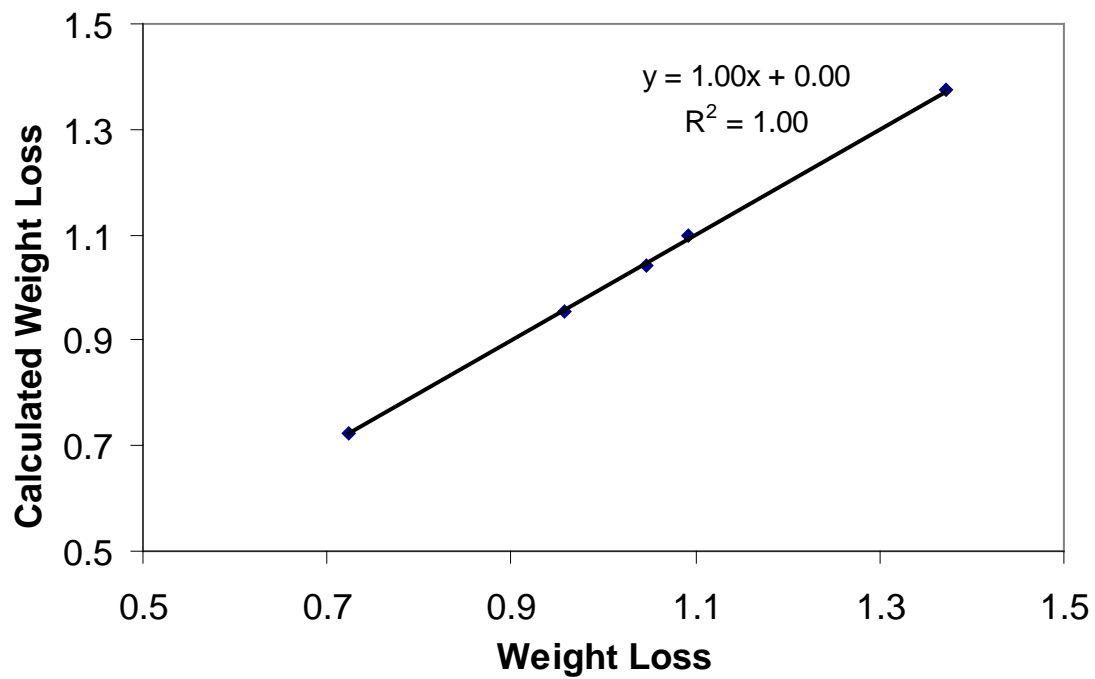


FIG. 9 – Calculated weight loss using Equation 4 plotted against the abrasion resistance results.

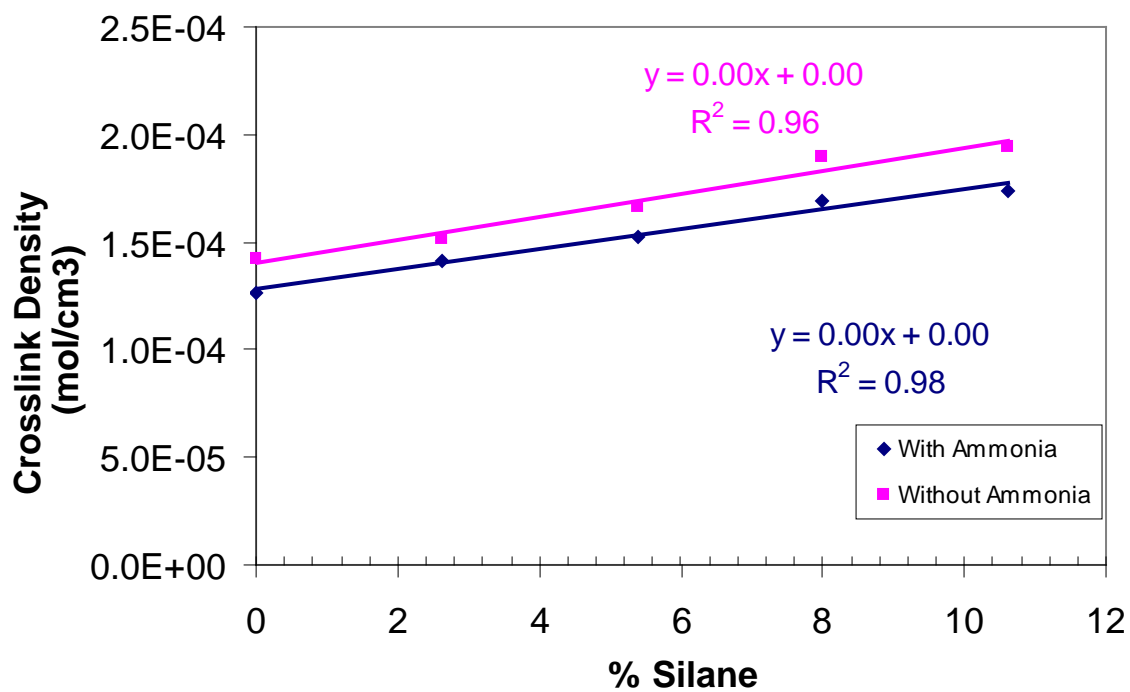


FIG. 10 – Chemical crosslink density by volume swell with and without an ammonia atmosphere during the swelling period.

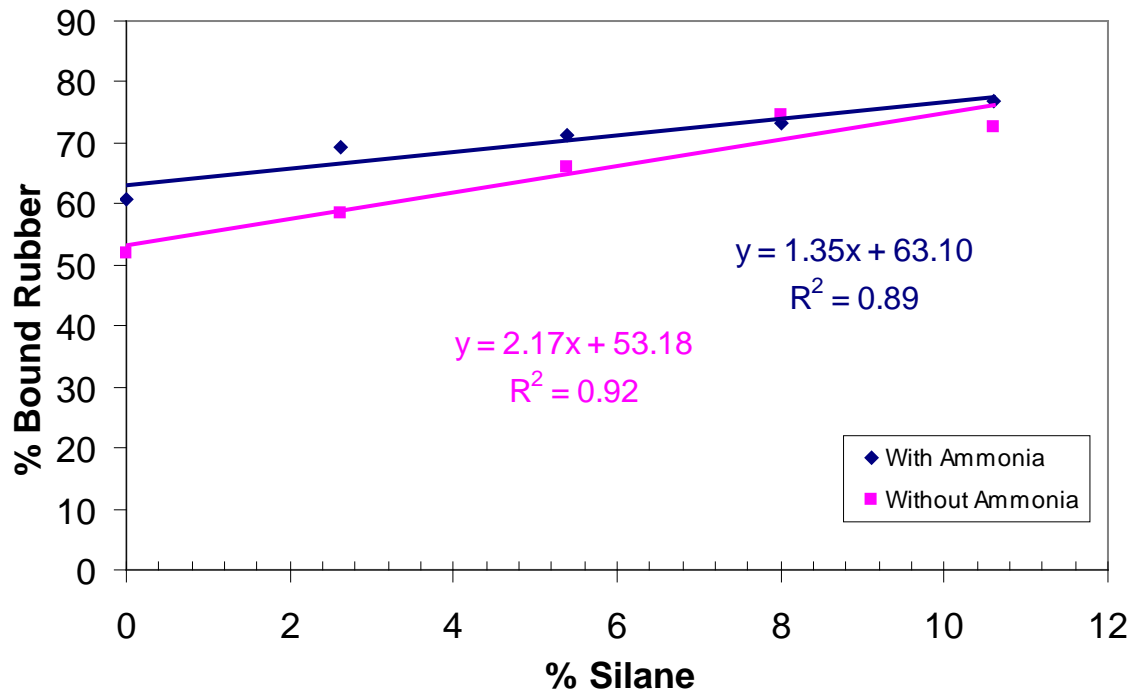


FIG. 11 – Percent bound rubber with and without an ammonia atmosphere during the swelling period.

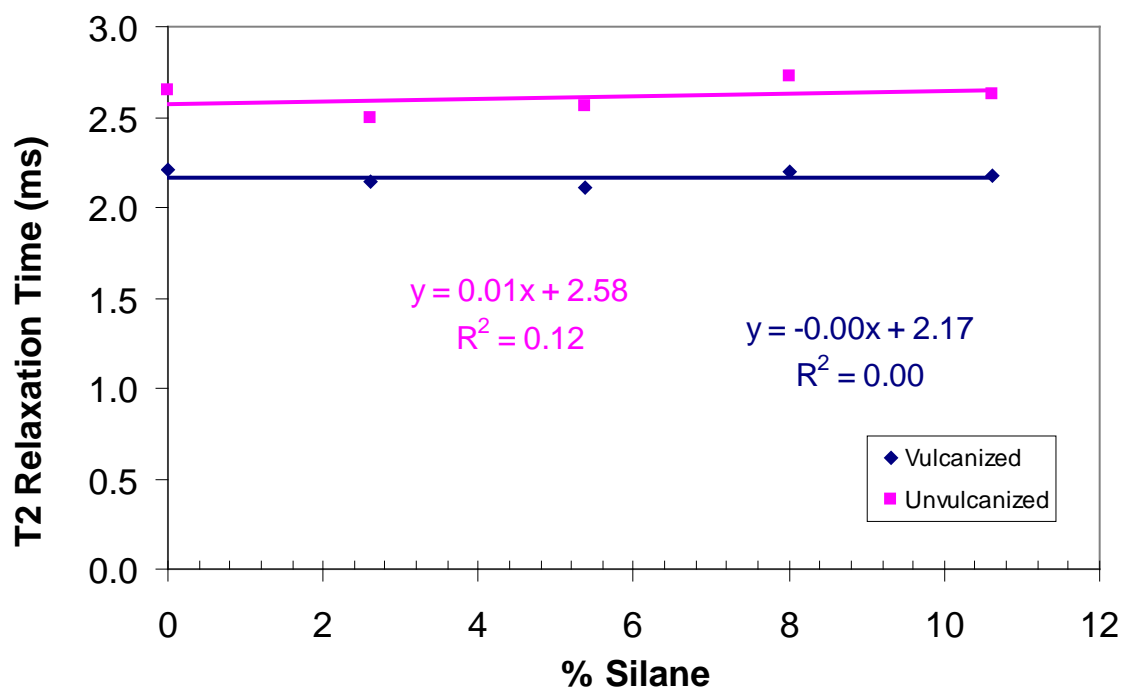


FIG. 12 – The T_{21} bi-exponential curve fitting parameter for the vulcanized and unvulcanized compounds plotted against the silane coupling agent level.

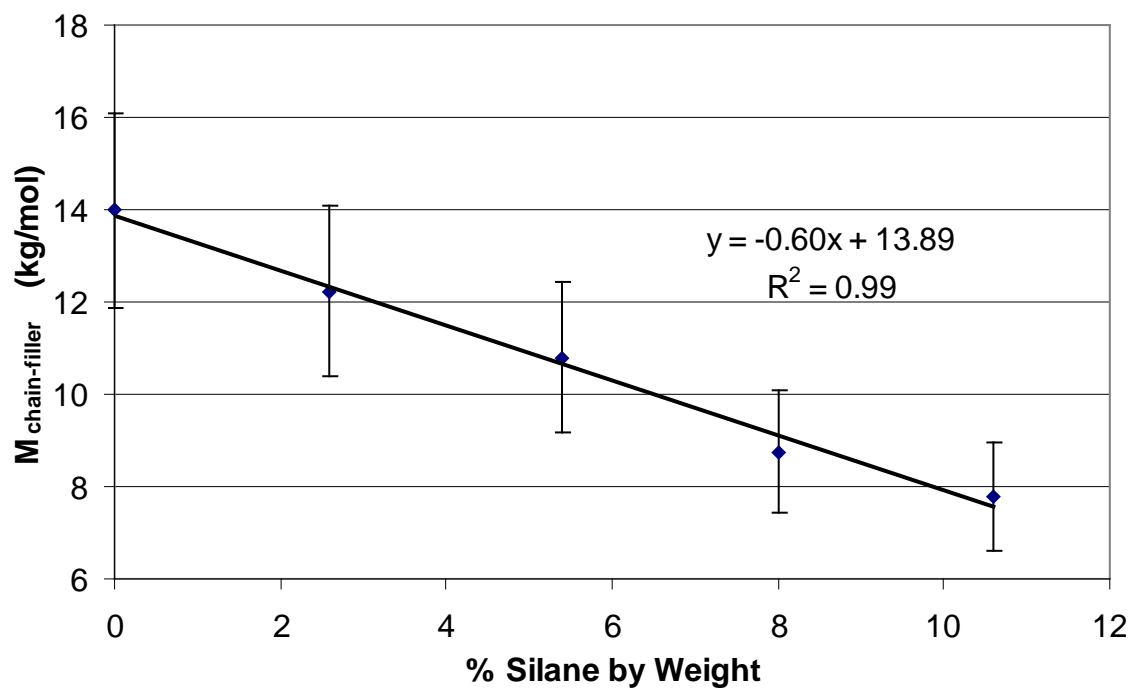


FIG. 13 – Values of the mean molar mass quantifying the interactions between the chains and the fillers (15% estimated total error).