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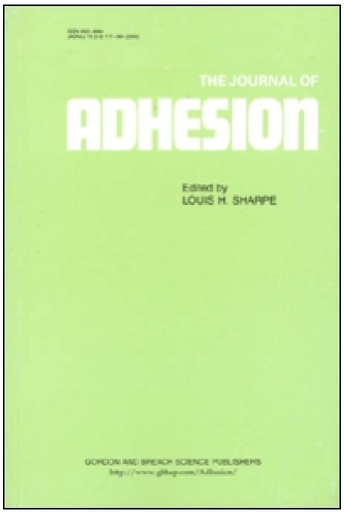

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Effect of Pre-coated *Vs.* Added Coupling Agents on the Vulcanization of Silica-filled Polyisoprene*

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Solid-state ^{13}C NMR was utilized in analysis of the crosslink structure in silica-filled polyisoprene. Samples containing either a pre-coated coupling agent, a coupling agent added in the mixing process, or polyethylene glycol (PEG) were vulcanized and the type and density of crosslinking determined. The precoated coupling agent sample gave lower %swelling, lower extraction amounts, and a lower T_2 relaxation than the mixed coupling agent, indicating increased crosslinking or increased filler-rubber interaction. The pre-coated also showed less *cis-trans* isomerization than the mixed, which may be due to its more uniform coating effect on the silica. The PEG sample yielded a ^{13}C spectrum similar to an unfilled sample indicating decreased silica adsorption of vulcanization agents. Neither coupling agent significantly decreased the total sulfurization nor the percent monosulfidic crosslinks from that of a silica-filled sample without coupling agent.

Keywords: Polyisoprene; Rubber; Vulcanization; Silane coupling agent; Silica

1. INTRODUCTION

Polyisoprene has excellent mechanical properties such as tensile strength and tear resistance, as well as low hysteresis which is

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advantageous in reducing heat build-up [1]. Addition of filler material can further enhance mechanical properties [2]. Among the nonblack fillers, silica affords the highest tensile strength [3]. Precipitated silica can improve the tear strength and cut growth resistance of rubber and has better resistance to ozone aging when compared with carbon black [4].

One significant problem with silica filler is its effect on the sulfur-curing mechanism [5]. The silica surface adsorbs curatives, leading to differences in cure rates and state when compared with traditional carbon-black-filled systems. Another significant drawback in the use of silica in rubber is the low interaction between highly polar silica and non-polar polyisoprene.

Organosilane coupling agents have been used extensively in composite systems to promote the interaction of two different materials, usually an organic and inorganic component. The bifunctional agent has an organic end, which reacts with the organic component of the system while an inorganic end reacts with the inorganic part of the system. The coupling agent actually forms a chemical bond between the functional group of the silane and the silanols on the silica.

The silane coupling agent can be added prior to mixing or during the mixing process. Hewitt [5] found that amines, glycols and soluble zinc compounds interfere with the silane–silica reaction. When the coupling agent was pre-added to the silica the problem of silica–zinc interaction was resolved. PPG manufactures silica pretreated with coupling agent under the brand name Ciptane (3-mercapto-propyl-trimethoxy silane coupling agent). The coupling agent is reacted with the silica surface and does not undergo degradation until 250°C, which is still above the rubber mixing and curing temperatures [5].

The effects of the silane coupling agent on the vulcanized rubber have been examined in several different rubber systems. Adhikary [6] found Si-69 (Bis-(3-(triethoxysilyl-propyl) tetrasulfide) in butyl rubber systems increased scorch time, optimum cure time and reversion time. Bandyopadhyay [7] found that 3-amino-propyl triethoxysilane in carboxylated nitrile rubber decreased the minimum rheometer torque, indicating a reduced filler–filler interaction (aggregation).

In this study, silica-filled polyisoprene samples containing a pre-coated coupling agent and a coupling agent added in the mixing

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process were vulcanized and their properties compared. In addition, the effect of polyethylene glycol (PEG) addition was investigated.

2. EXPERIMENTAL

2.1. Materials

The samples include seven groups with the compounding formulations shown in Table I. The samples were mixed on a two-roll mill and vulcanized at 165°C and 610 psi (4.2 MPa) to a 90% cure state as determined by rheometer measurements. In sample 3, the coupling agent Si-69 [Bis-(3-(triethoxysilyl-propyl) tetrasulfide] was added during the mixing process. In samples 4 and 5, the coupling agent A-189 [3-mercapto-propyltrimethoxy silane] was precoated on the silica. The samples were supplied as 10 cm × 10 cm sheets approximately 2 mm thick. Bore samples of approximately 5 mm in diameter, which fit in the NMR sample tube, were used for solid-state NMR analysis.

Because a commercial precoated Si-69 silica was not readily available, pre-treated Ciptane with A-189 silane coupling agent was used. Due to the severe stench of A-189, it was not used as an addition product during mixing. However, because approximately equal mole

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TABLE I Formulations

	Samples						
Ingredients	1	2	3	4	5	6	7
Polyisoprene	100	100	100	100	100	100	100
Zinc oxide	8	8	8	8	8	8	8
Stearic Acid	2	2	2	2	2	2	2
Silica (Hi-Sil 255G)	0	45	45	45	60	30	30
Santocure® TBBS	.80	.80	.80	.80	.80	.80	.80
Sulfur	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Coupling agent	0	0	3.38[a]	1.39[b]	1.86[b]	0	0
Wingstay® (antioxidant)	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Sundex® (oil)	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Polyethylene Glycol	0	0	0	0	0	0.60	0

[a] Coupling agent Si-69 [Bis-(3-(triethoxysilyl-propyl) tetrasulfide]. The coupling agent was added during mixing process.

[b] Coupling agent 3-mercapto-propyltrimethoxy silane. The coupling agent was precoated onto the Hi-Sil 255G silica by PPG Industries and marketed under the tradename of Ciptane 255LD.

amounts of both were used and the reaction products are similar, the results should still reflect some differences due to the mode of addition.

2.2. Methods

The solid-state ^{13}NMR measurements were performed on a Bruker MSL 300 at room temperature, on a CP/MAS probe using magic angle spinning (MAS) at 3500 Hz under gated high power decoupling conditions. A total of 15,000 scans were obtained with a recycle delay of 5 seconds. The solid-state ^{1}H NMR T_2 relaxation measurements were done on the same Bruker MSL 300 instrument at a spinning rate of 2500 Hz with 17 different variable echo times (T_E). A total of 16 scans were obtained for each T_E with a delay of 15 seconds. Solution ^{1}H and ^{13}C NMR was performed on a Varian 200 MHz instrument using $CDCl_3$ as solvent. All infrared (IR) measurements were performed on a BioRad Model FTS-60 Fourier Transform IR Spectrometer. In the IR analysis of the extracted material, the extracted material was dissolved in 3 ml of CCl_4 and analyzed in a 0.2083 mm-thick cell with NaCl windows. Attenuated total reflection (ATR) was performed using a special ATR attachment with a circular Ge crystal at $\theta = 45°$ on both the sample surface and at a depth of 1 mm.

The free induction decay (FID) data from solid-state ^{13}C NMR measurements were transferred to a personal computer equipped with a Grams software program (Galactic Industries Corporation, GRAM/32 Version 4.02 Level 1). Using this software, the FIDs were transformed and the resulting spectra phased, referenced, and baseline corrected. The peak area of the main chain and the vulcanizate carbons were determined using a curve-fitting program in the Grams software utilizing a linear baseline function with Lorentzian peak lineshape. When the carbon vulcanizate peak was so small that the peak could not easily be distinguished from the baseline, the area was recorded as zero although a residual amount is present. Peak areas originating from vulcanizate structures are presented as a percentage of the *cis* main chain carbon peaks of polyisoprene.

Swelling measurements were performed on the samples using benzene as swelling solvent. Circular bore sample of diameter 1.5 cm

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were taken and weighed, and then swollen for 3 days at room temperature. The samples were taken from the benzene solution, gently blotted to remove excess surface solvent, and weighed within 20 seconds after removal. The %swelling was recorded by the formula:

$$\%\text{swelling} = [(\text{wt.solvent uptake})/\text{wt. dry}] \times 100$$

Because the dry weight varies with the amount of filler, correction was made by adjusting the dry weights with the percentage of filler in the sample.

Extraction studies were also performed on the samples. A procedure slightly modified from that used by Gardiner [8] was used for the extractions. The rubber was sliced with a razor blade to the smallest thickness obtainable (approximately 0.1 mm), weighed, and placed in a sealed vial under nitrogen with benzene at 80°C. After each 24 hr. period, the old solvent was removed and fresh benzene added. The removed benzene was evaporated and the amount of extract determined. Extraction was continued for seven days, at which time little or no material was being extracted. The extracted material was dried at room temperature under vacuum for 24 hrs, weighed, and examined by infrared and solution ^{1}H and ^{13}C NMR to determine extract composition. In calculating %extracted, the initial weight was adjusted by the percentage of filler in the sample.

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3. RESULTS

In the swelling measurements (Tab. II), the silica-filled sample without coupling agent (#2) shows the lowest crosslink density of the 5

TABLE II Swelling measurements

Sample	*Dry weight (gm)*	*Corrected dry weight (gm)*	*Solvent weight (gm)*	*%Swelling (solvent/dry) *100*	*Corrected %swelling*
1	.1795	0.1795	0.6176	344	344
2	.2104	0.1528	0.5803	276	380
3	.2165	0.1584	0.5059	234	319
4	.2270	0.1653	0.4570	201	276
5	.2625	0.1756	0.4384	167	250

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samples. This is predictable, as silica is known to absorb vulcanization compounds resulting in decreased crosslinking rate and number. Extraction measurements (Tab. III) support this conclusion, as the percentage of extracted material was highest in sample #2. The unfilled sample shows greater crosslinking density, giving a lower %swelling and %extracted. The filled samples with coupling agents give the lowest swelling percentages, as these agents promote rubber-silica bonding, hinder silica adsorption of vulcanization ingredients, and increase silica dispersion. The precoated coupling agent sample (#4) shows a significant decrease over the mixed sample (#3). However, more material was extracted in these samples than in the unfilled sample, possibly indicating poorer dispersion of vulcanization ingredients in the filled samples. Again the precoated sample (#4) gave better results (lower %extraction) than the mixed sample (#3). Analysis of the extracted material by ^{1}H and ^{13}C NMR and IR analysis showed that it was composed almost entirely of polyisoprene. The NMR spectra showed a small amount of extracted stearic acid in the unfilled sample while none was observed in the filled samples. IR analysis showed some oxidation in the extracted material but it was relatively constant throughout the samples.

Because ^{1}H transverse relaxation (T_2) is inversely proportional to chain mobility, it can give insight into crosslinking and filler–rubber interactions. As shown in Table IV, the relaxation time of the pre-coated sample (#4) was less than that of the mixed sample (#3) indicating a greater crosslink density in the pre-coated sample.

ATR IR spectroscopy was performed on the samples to determine if peak shifts occurred in either the rubber or silica due to the interactions between them or with coupling agents. Shifts of the silica peaks have been reported with an increase in silica loading due to

TABLE III Extraction measurements

Sample	*Wt. initial (gm)*	*Corrected Wt. initial (gm)*	*Wt. extract (gm)*	*% extract*	*% residual*	*% recovered*
1	.1398	0.1398	0.0128	9.2	90.9	100.1
2	.1402	0.1018	0.0289	28.4	71.9	100.3
3	.1867	0.1366	0.0257	18.8	81.1	99.9
4	.2063	0.1503	0.0208	13.8	86.0	99.8
5	.2055	0.1374	0.0262	19.1	81.3	100.4

TABLE IV Relaxation measurements

Sample	T_2 (*methine*) (*msec*)	T_2 (*methylene*) (*msec*)	T_2 (*methyl*) (*msec*)
1	11.2	7.0	12.1
2	11.3	7.3	12.1
3	11.5	7.6	12.1
4	10.2	6.1	11.0
5	10.4	6.9	10.6

physical adsorption [9]. No differences in the polyisoprene rubber peaks were found in the five samples. The silica peaks in the 4 filled samples gave identical broad silica peaks for both the Si—O and the O—H stretch regions at 1250–1000 and 3500–3000 cm^{-1}, respectively.

The ^{13}C NMR of natural rubber and polyisoprene has been extensively studied [10–18]. The possible crosslink structures for polyisoprene vulcanizates are shown in Figure 1. A typical ^{13}C NMR spectrum showing the carbon peaks of these structures is shown in Figure 2. The first two characters indicate the crosslink structure; *c* or *t* is *cis* or *trans*; *m* or *p* represent mono- or polysulfidic linkages; and α,β and γ represent the position on the crosslink structure (α-crosslinked carbon, β-adjacent methylene, γ-methyl group). The integrated area of the vulcanizate peaks given as a percentage of the *cis* main chain carbon peaks for all seven samples is shown in Table V. Although the sample analysis for each group was not repeated, previous ^{13}C NMR studies yield a coefficient of variation of approximately 10% [18]. Analysis of the *trans* carbon peak concentration at 16.1 ppm (Fig. 3) clearly shows *cis*–*trans* isomerization is greatly enhanced by the presence of silica filler. Both coupling agents appear to decrease the isomerization by a small amount with the precoated sample isomerization being slightly less than for the mixed sample. The presence of polyethylene glycol (PEG) also led to a slight decrease in isomerization. Summing the area of the NMR peaks at 50.1, 50.9, 63.9 and 64.4 ppm gives the concentration of polysulfidic linkages, while addition of the areas of the peaks at 44.5 and 57.7 ppm yields the monosulfidic concentration. (The C1cp(α) concentration is very low and will not appreciably effect the concentration) The concentration of poly- and monosulfidic crosslinks is given in Figure 4. A large increase in total sulfurization is clearly evident in the silica-filled samples as

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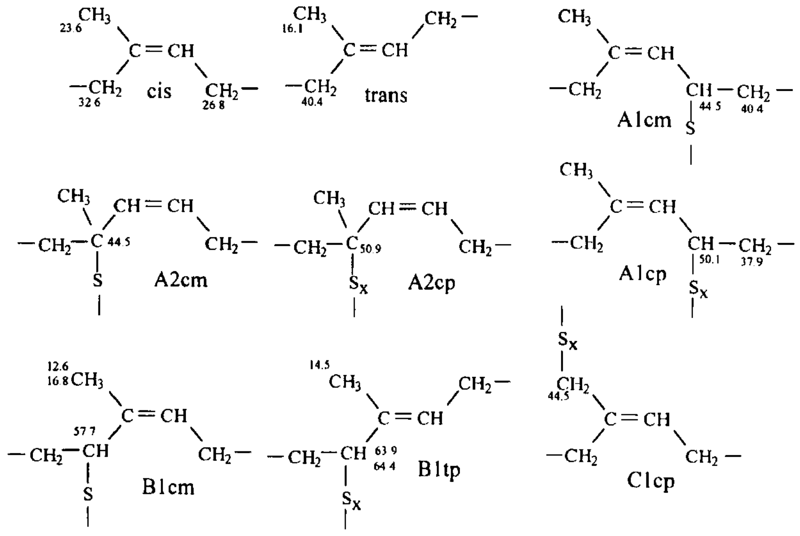

FIGURE 1 Polyisoprene crosslinked structures.

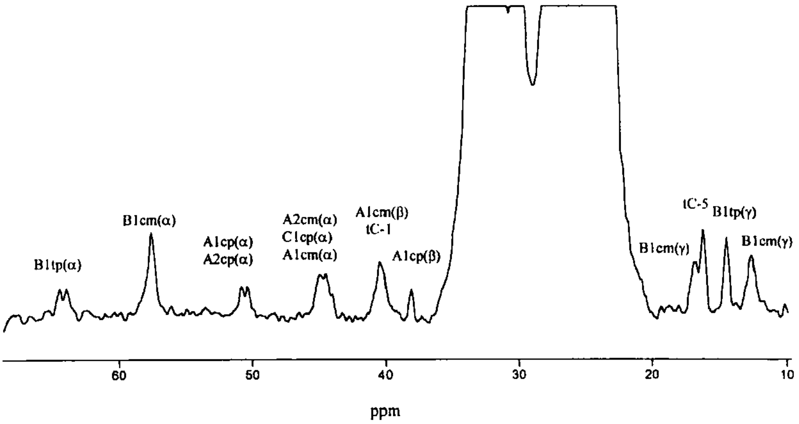

FIGURE 2 ^{13}C NMR spectra of crosslinked carbons.

compared with the unfilled sample. Although the concentration of polysulfidic linkages is relatively constant in all samples, the monosulfide concentration is much higher in the silica-filled samples as shown by the concentration of the 44.5 and 57.7 ppm monosulfide

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TABLE V Integrated area of vulcanizate peaks

	Samples						
^{13}C *NMR peak (ppm)*	1	2	3	4	5	6	7
12.6	1.60	1.61	1.34	1.61	1.28	0.78	1.35
14.5	0.61	0.67	0.53	0.54	0.51	0.72	0.54
16.1	2.10	2.78	2.63	2.47	2.51	2.21	2.29
16.9	0.56	0.65	0.46	0.73	0.38	0.19	0.49
40.4	2.14	2.42	2.47	2.13	1.76	1.99	2.21
44.5	1.82	4.53	3.53	4.28	3.16	1.89	4.31
47.3	0.37	0.61	0.68	0.38	0.32	0.44	0.39
50.1 + 50.9	1.06	1.41	1.99	1.62	1.12	1.44	1.47
57.7	0.85	1.53	1.37	2.15	1.96	0.75	1.25
63.9 + 64.4	0.47	0.34	0.42	0.42	0.30	0.43	0.44

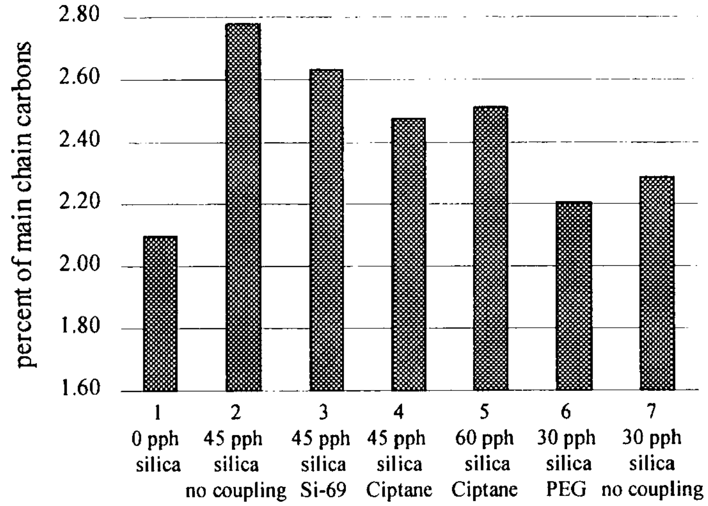

FIGURE 3 Concentration of *trans* monomers (16.1 ppm).

peaks (Figs. 5 and 6), thus yielding a higher overall percentage of monosulfides (Fig. 7). This result has been reported in a previous study [19]. Sample #6, containing PEG, gives results in total sulfurization and %monosulfidic crosslinks very close to those of the unfilled sample. Polyethylene glycol (PEG) is known to coat the surface of silica and prevent vulcanization compounds from adsorbing on the surface [20].

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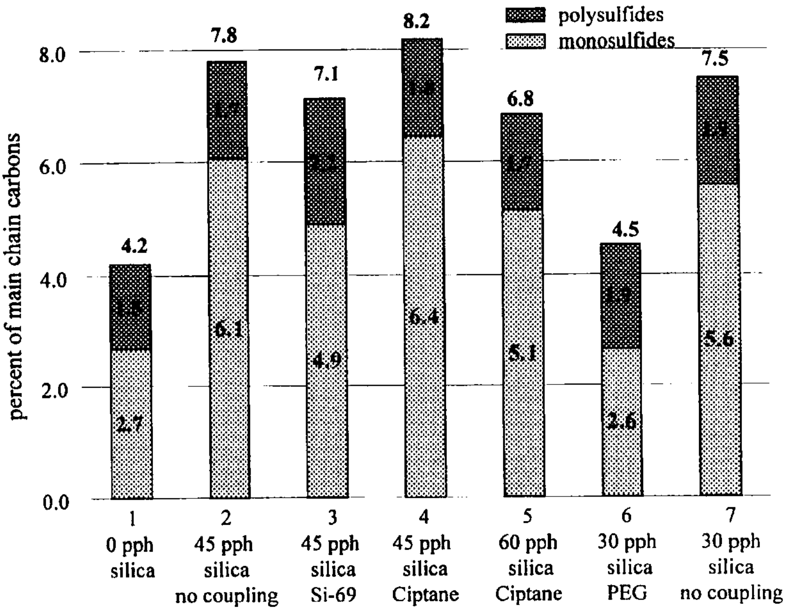

FIGURE 4 Concentration of poly- and monosulfidic crosslinks.

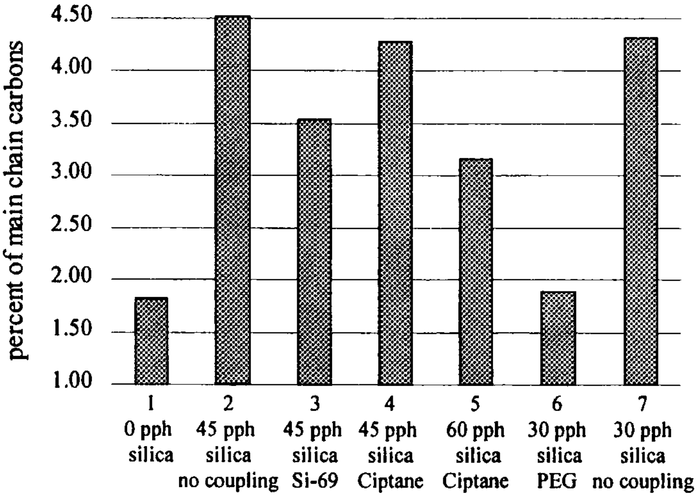

FIGURE 5 Concentration of monosulfide carbons (44.5 ppm).

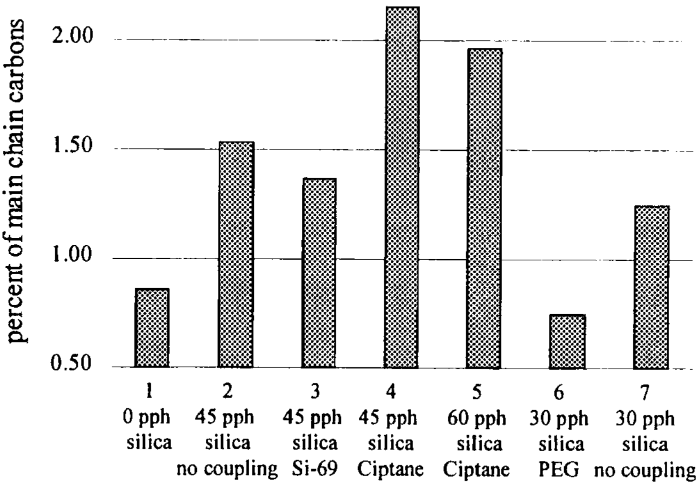

FIGURE 6 Concentration of monosulfide carbons (57.7 ppm).

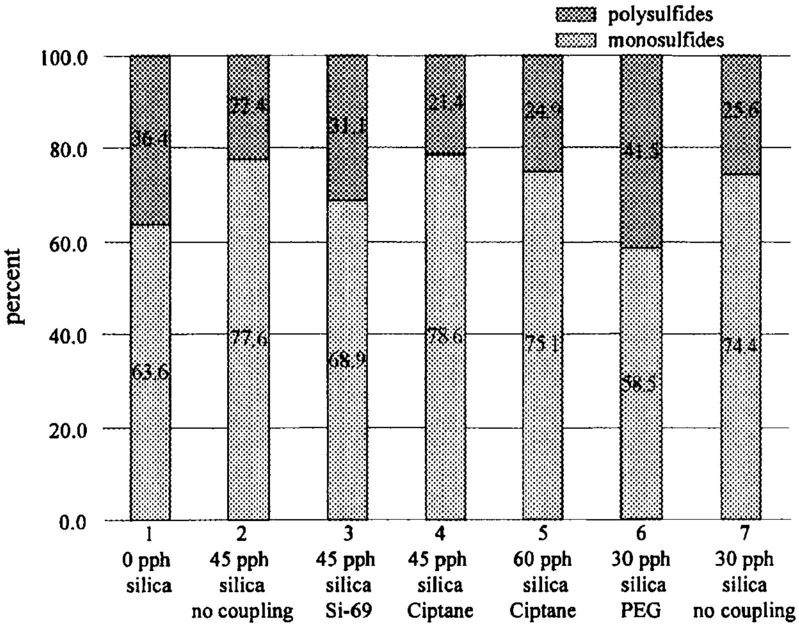

FIGURE 7 Percentage of poly- and monosulfidic crosslinks.

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4. CONCLUSIONS

PEG prevents the adsorption of vulcanization agents on the surface of silica, yielding a ^{13}C spectrum similar to that of an unfilled sample. Coupling agents did not significantly decrease either total sulfurization or the percent monosulfidic crosslinks from the values for the silica-filled sample without coupling agent. The presence of PEG in a silica-filled sample (#6) only slightly decreased *cis–trans* isomerization as compared with an identical sample without PEG (#7).

Stearic acid, ZnO, and TBBS are known to be adsorbed on the silica surface [20, 21]. With a high concentration of these additives at the silica surface, monosulfidic crosslinks should predominate in this region. In the bulk rubber phase, a decrease in these additives would result in an increase in polysulfidic and a decrease in monosulfidic crosslinks. This would explain why the silica-filled samples have higher extractibles (indicating decreased bulk crosslinking) than the unfilled sample, while ^{13}C NMR results show a substantial overall increase in crosslinking, especially the monosulfidic linkages, as compared with the unfilled sample.

The precoated coupling agent sample gives lower %swelling, lower extraction amounts, and a lower T_2 relaxation than the mixed coupling agent indicating increased crosslinking or increased filler–rubber interaction. The precoated sample also shows less *cis–trans* isomerization than the mixed sample, possibly due to its more uniform coating effect on the silica.

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Acknowledgments

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