Effects of Silane Coupling Agents on the Vulcanization Characteristics of Natural Rubber

Hexiang Yan, Kang Sun, Yong Zhang, Yinxi Zhang, Yongzhong Fan

State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai, China

ABSTRACT: The vulcanization characteristics of silica-filled natural rubber (NR) were studied in the presence of silane coupling agents, 3-octanoylthio-1-propyltriethoxysilane (NXT) and bis [(3-triethoxysilylpropyl) tetra sulfide] (TESPT, or Si-69). The scorch time, cure rate index, and the rate constant of NR were measured using an Oscillating Disk Rheometer in the temperature range of 140–170°C. The scorch time of NR decreases with increasing TESPT and NXT concentrations, and the scorch time of NR compound with NXT is longer than that with TESPT. The apparent activation energies of vulcanization for the compounds with NXT and TESPT both decrease with increasing silane concentration. The apparent activation energy of vulcanization of NR compound with NXT is lower than that with TESPT at various concentrations. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1511–1518, 2004

Key words: natural rubber; silica; NXT silane; scorch; vulcanization

INTRODUCTION

Carbon black and silica have been widely used to improve the mechanical properties of rubber compounds.[1] Silica provides a unique combination of tear strength, abrasion resistance, age resistance, and adhesion properties.[2] Most commonly used rubbers are nonpolar; however, precipitated silica is hydrophilic. Hence, silane coupling agents are usually used to enhance the compatibility of silica and rubbers. Bis [(3-triethoxysilylpropyl) tetra sulfide] (TESPT) and γ-mercaptopropyl trimethoxysilane (A-189) are widely studied.[2–18] Reuvekamp et al.[6,11] concluded that at mixing temperatures over 160°C the coupling agent TESPT can either react with rubber matrix or donate sulfur. 3-Octanoylthio-1-propyltriethoxysilane (NXT silane), which has the structure shown in Scheme 1, offers more scorch safety compared to TESPT.[19] There is no detailed research on the scorch behavior of silica-filled rubber composites with NXT. This paper mainly focuses on the investigation on the NXT silane's influence on scorch behavior and vulcanization of NR.

EXPERIMENTAL

Materials

Natural rubber (NR) RSS1 made in Thailand was supplied by Shanghai Rubber Products Institute. High dispersion silica 7000 GR (Degussa) was supplied by Red Avenue Chemical Co., Ltd. NXT silane was supplied by OSI Specialties (Crompton Corp.); TESPT was provided by Guangzhou Tianhe Science and Technology Co.; *N*-cyclohexyl-2-benzothiole sulfonamide CZ-80, ZnO-80, diphenylguanidine DPG-80, and sulfur *S*-80 with the active content of 80%, respectively, were supplied by Rhein Chemie Corp. Other additives were commercial grades.

Compounding

The compound recipe was rubber, 100; silica, 50; antioxidant, 2; Rhen ZnO-80, 4; stearic acid (SA), 2; Rhen DPG-80, 2; Rhen CZ-80, 2; Rhen *S*-80, 2; silane, variable. In this work, two series of compounds were investigated:

- Series I: with equal quantities of silane coupling agents, the amount of silane coupling agents ranges from 0 to 10 phr;
- Series II: with the equimolar quantities of silane coupling agents, the amount of silane coupling agents from 0 to 0.0275 mol, which was based on molar quantity of NXT silane. The amount of NXT silane used in Series I and Series II was the same.

Sample preparation

The compounds were mixed in three steps, all on a two-roll mill. The first step was to mix the compounds containing rubber, silica, silane, DPG, antioxidant,

---
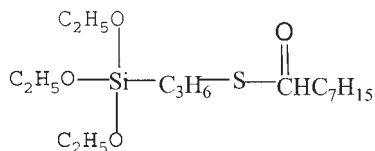
Scheme 1

ZnO, and SA at the temperature range from 50 to 60°C. After uniformly mixing, the compounds were mixed on a mill at 150°C for 10 min. Then, the compounds were charged on the two-roll mill. The accelerator and sulfur were added into the compounds on the two-roll mill.

Scorch measurement

The curing behavior of NR compounds was determined with an Oscillating Disk Rheometer according

to ASTM D2084–92. The scorch time (t_{s2}) is defined as the time required for an increase of 0.2N.m above the minimum torque as determined from a plot of torque versus time.

Methods

The kinetic parameters of vulcanization, such as the cure rate index (CRI) and the rate constant (k), were estimated according to the method reported by Yehia and Stoll.[20]

$$CRI = 100/(t_{90}-t_{s2})$$
$$K = (dM/dt)/(M_H-M)$$

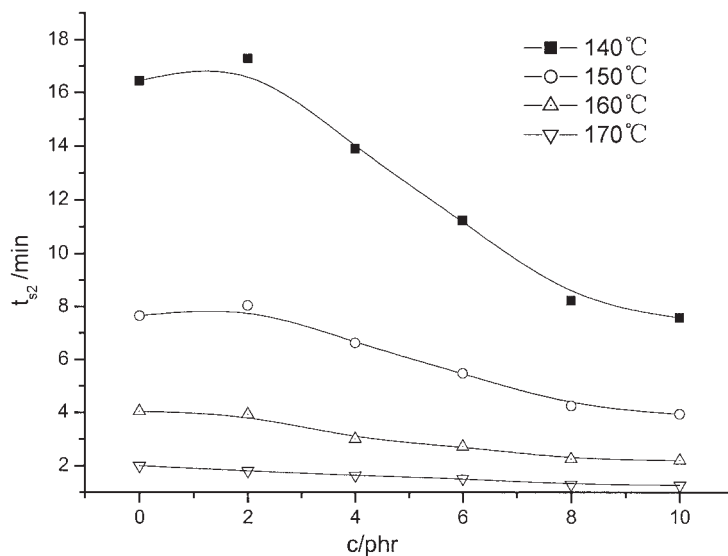The activation energy of cure was calculated according to the method reported by Braker.[21]

Figure 1 Variation of scorch time with NXT concentration for various temperatures of vulcanization.
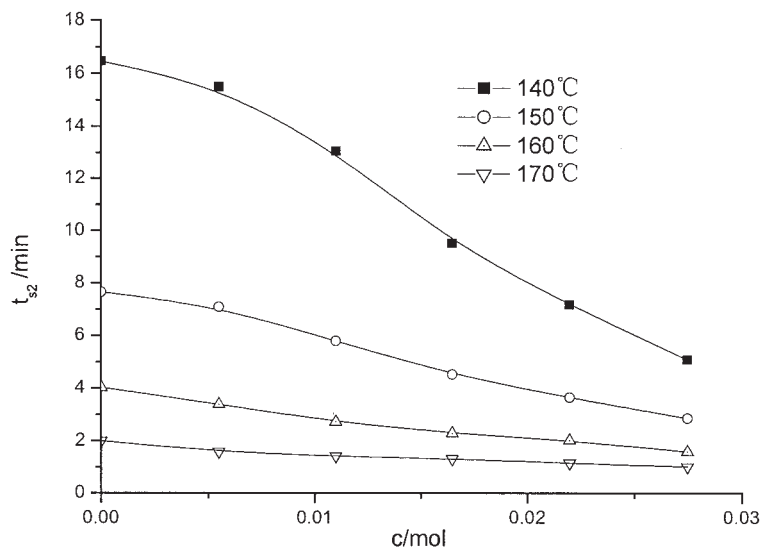

Figure 2 Variation of scorch time with TESPT concentration (mol) for various temperatures of vulcanization.
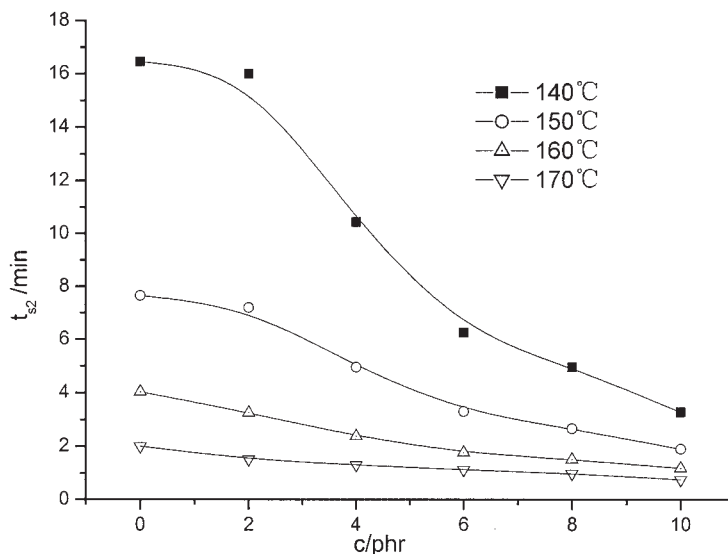
Figure 3 Variation of scorch time with TESPT concentration for (wt) various temperatures of vulcanization.

RESULTS AND DISCUSSION

Effect of silane coupling agent concentration on scorch time

Figures 1 through 3 show the dependence of scorch time on the concentration of silane coupling agent for Series I (Figs. 1, 3) and Series II (Figs. 1, 2) at different vulcanization temperatures. Results indicate that scorch times decrease with increasing the concentrations of NXT and TESPT (Series I and II). The scorch time at 140°C is longest because the thermal energies supplied are not enough to overcome the activation energies of vulcanization. At high temperature, concentration of NXT and TESPT has little effect on the scorch time because the energies at high temperature are available to overcome the activation energies of vulcanization. Joshi et al.[19] reported that the scorch time of rubber compound with NXT silane decreased with increasing NXT silane concentration. Similar reduction in scorch time of rubber compound with TESPT content was also reported by Guan.[22] However, Poh et al.[17] reported that the scorch time increased with increasing TESPT concentration, which is opposite to the result above. This might be attributed to different TESPT silanes used in both experiments.
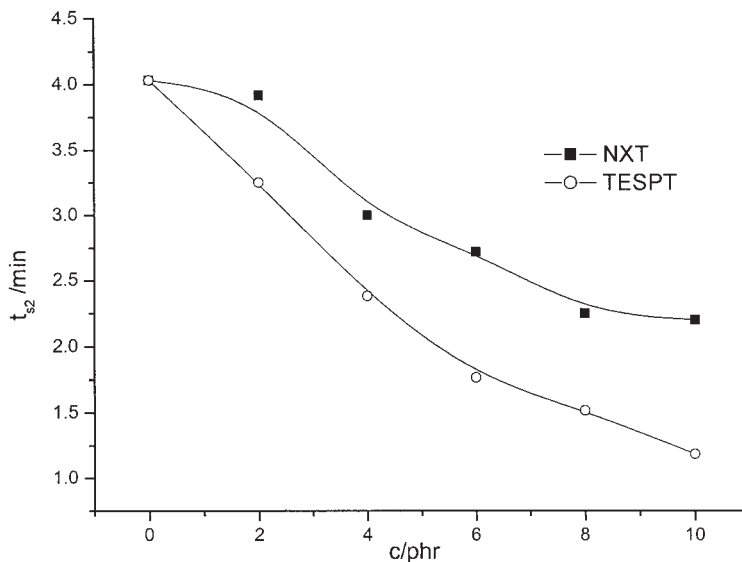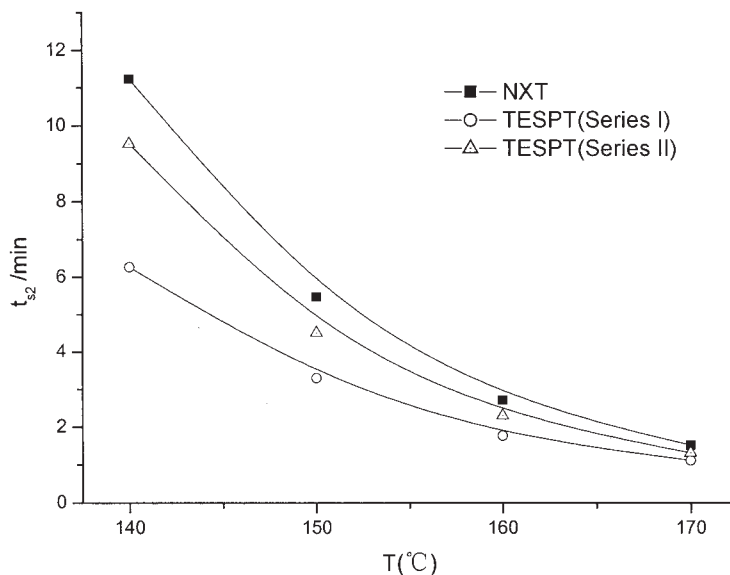
Figure 4 reveals the difference of the effects of

Figure 4 Comparison of scorch time between NXT and TESPT at 160°C.

**Figure 5** Temperature dependence of scorch time for TESPT and NXT at 6phr (or 0.0165 mol) concentration.

TESPT and NXT content (Series I) on the scorch time of NR. The difference in scorch time becomes more apparent with increasing the silane concentration. It is assumed that coupling reaction between silane and rubber will take place by cleavage somewhere in the sulfur linkages during the mixing and/or curing. The molecule structure of TESPT is $(C_2H_5O)_3SiC_3H_6$-$S_4C_3H_6Si(OC_2H_5)_3$. The molecule structure of NXT is as shown above. It was reported that TESPT is a mixture of sulfanes from S_2 to S_{10} with average sulfur chain length of 3.8.[14] The sulfur rank of TESPT is higher than that of NXT. Bonding dissociation energy of NXT silane is higher than that of TESPT according to the following rules of bond dissociation energy[23].

C-S_x-C (where x > 2) <268 kJ mol^{-1}

C-S-C 285 kJ mol^{-1}
C-C 352 kJ mol^{-1}
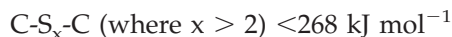
Hence, bonding dissociation energy of NXT silane is higher than that of TESPT. Silane with higher sulfur ranks should react with rubber more easily than silane with lower sulfur ranks. Therefore the scorch time of the compound with NXT is longer than that of TESPT.

Effect of cure temperature on scorch behavior

The dependence of the scorch time on temperature for the compound filled with a certain silane coupling agent concentration is shown in Figure 5. Results indicate that the scorch time of the rubber compound with TESPT is always shorter than that
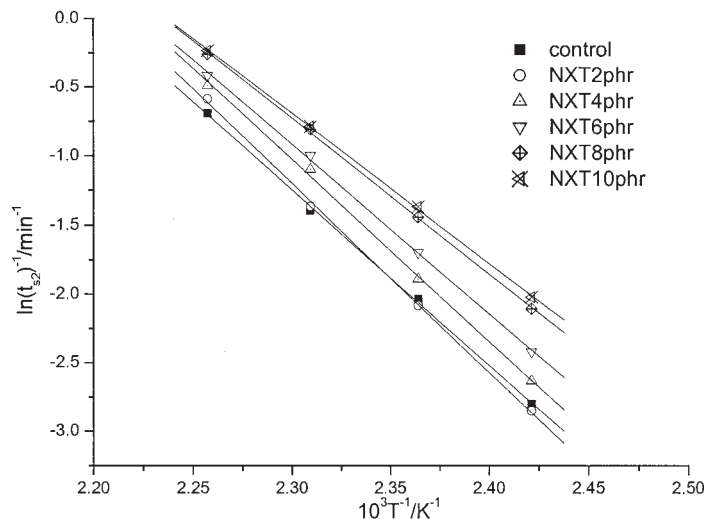
Figure 6 An Arrhenius plot of premature for NXT at various concentrations of silane coupling agent.
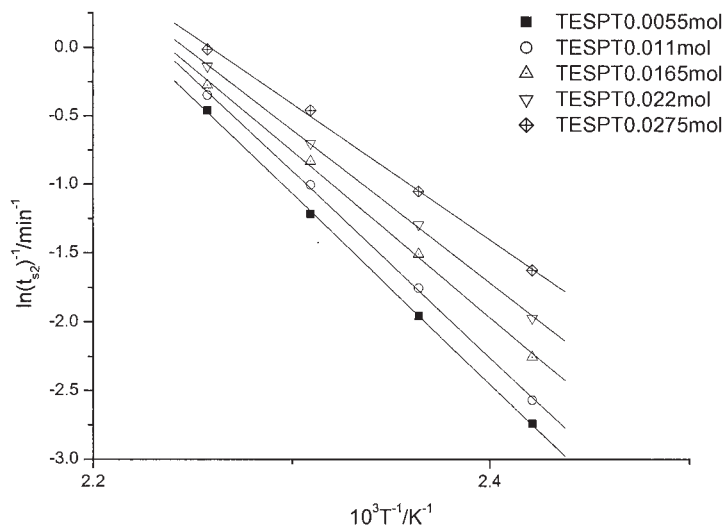
Figure 7 An Arrhenius plot of premature for TESPT (mol) at various concentrations of silane coupling agent.
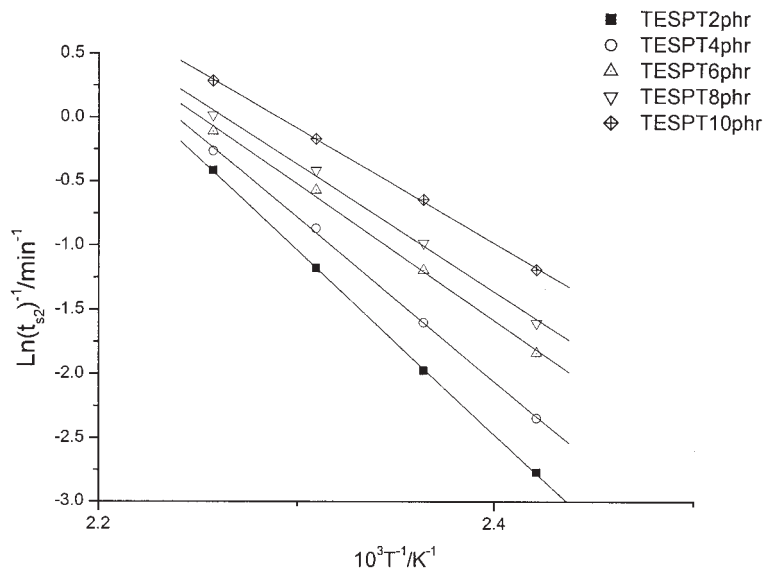

Figure 8 An Arrhenius plot of premature for TESPT (wt) at various concentrations of silane coupling agent.

with NXT. The difference of scorch time between the compounds filled with NXT and TESPT becomes bigger with decreasing temperature. For example, at 140°C, the difference between the compounds with TESPT and NXT (Series I) is 5 min, whereas at 170°C, the difference is only 0.5 min. The difference

TABLE I
Apparent Activation Energy (Es) of Premature at Various Loadings of NXT and TESPT

Concentration phr	Es (kJ/mol)		Concentration mole	Es (kJ/mol)	
	NXT	TESPT (wt)		NXT (mol)	TESPT (mol)
0	105.9	105.9	0	105.9	105.9
2	114.1	119.6	0.0055	114.1	115.3
4	109.8	106.2	0.011	109.8	112.8
6	102.1	88.3	0.0165	102.1	100.6
8	93.8	82.6	0.022	93.8	92.6
10	90.4	74.6	0.0275	90.4	82.5

TABLE II
Kinetic Parameters of Vulcanization

| | 100k(min^{-1}) | | | | CRI (min^{-1}) | | | |
| | Temperature (°C) | | | | Temperature (°C) | | | |
Silane parts	140	150	160	170	140	150	160	170
NXT 0 phr	17.2	37.2	106.5	180.2	11.6	21.9	45.5	81.1
NXT 2 phr	31.9	78.0	160.2	201.3	17.9	26.0	57.1	85.7
NXT 4 phr	37.7	95.7	182.7	300.2	19.5	36.8	65.2	113.2
NXT 6 phr	54.8	112.5	208.5	337.2	21.8	42.9	77.9	139.5
NXT 8 phr	66.8	120.9	223.3	368.1	28.2	44.4	87.0	146.3
NXT 10 phr	79.0	125.8	237.4	360.1	31.6	52.2	88.2	157.9
TESPT 2 phr	35.5	63.8	149.3	216.2	13.0	26.5	54.5	81.1
TESPT 4 phr	43.5	96.9	185.6	267.1	18.0	32.1	62.5	105.3
TESPT 6 phr	41.6	98.9	224.4	358.7	16.7	31.7	75.9	153.8
TESPT 8 phr	36.2	76.4	187.8	289.6	12.7	22.0	41.1	111.1
TESPT 10 phr	34.6	63.7	139.0	241.6	10.1	11.6	19.4	80.0
TESPT 0.0055mol	21.9	58.5	131.2	175.8	12.0	18.6	45.5	72.3
TESPT 0.011 mol	38.3	78.6	167.2	238.0	16.1	28.3	57.7	96.8
TESPT 0.0165 mol	41.9	89.8	219.2	323.0	16.7	30.6	71.4	125.0
TESPT 0.022 mol	42.3	105.4	235.4	347.7	13.5	28.6	83.3	150.0
TESPT 0.275 mol	42.7	81.3	194.1	337.3	13.8	22.8	52.2	125.0

of scorch time between the compounds with TESPT (Series I) and NXT is bigger than that with TESPT (Series II) and NXT. This difference in scorch time narrows with increasing temperature. This is attributed to sufficient thermal energies being available to overcome the activation energy of vulcanization at higher temperatures.

To study the differences of scorch behavior between the compounds with TESPT and NXT, their apparent activation energies were calculated by assuming that the exponential dependence of scorch time t_{s2} on the cure temperature (T) complies with an Arrhenius formulation, $t_{s2} = Ae^{-(E/RT)}$. Arrhenius plots for compounds with NXT and TESPT are shown as Figures 6 through 8. The reciprocal of the

scorch time was plotted against the reciprocal of the temperature. The apparent activity energy of premature (scorch) for the compounds with silane coupling agents, Es, is shown in Table I.

As shown in Table I, the compound with low TESPT content has higher activation energy of premature (scorch) than that with NXT. However, this trend varies when silane concentration is larger than 0.011 mol. The compound with high NXT content has higher activation energy of premature than that with TESPT. The difference of activation energy of premature between the compounds with NXT and TESPT becomes larger with increasing silane concentration, indicating that the compound with NXT has higher activation energy of premature than that with TESPT.
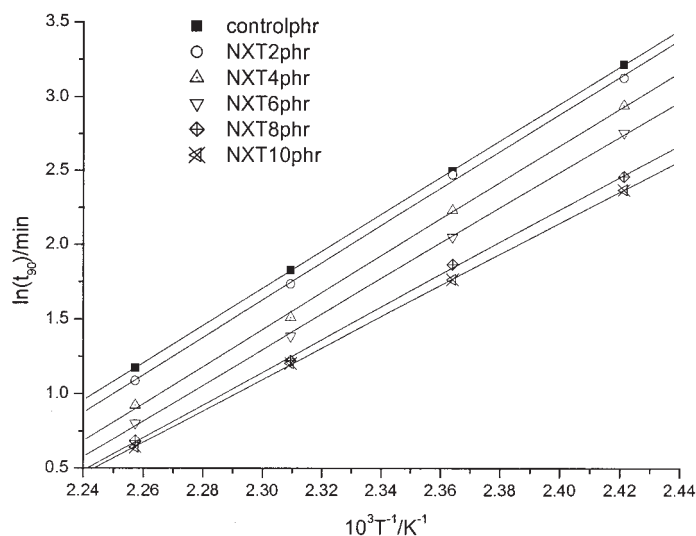

Figure 9 An Arrhenius plot of vulcanization for NXT at various concentrations of silane coupling agent.
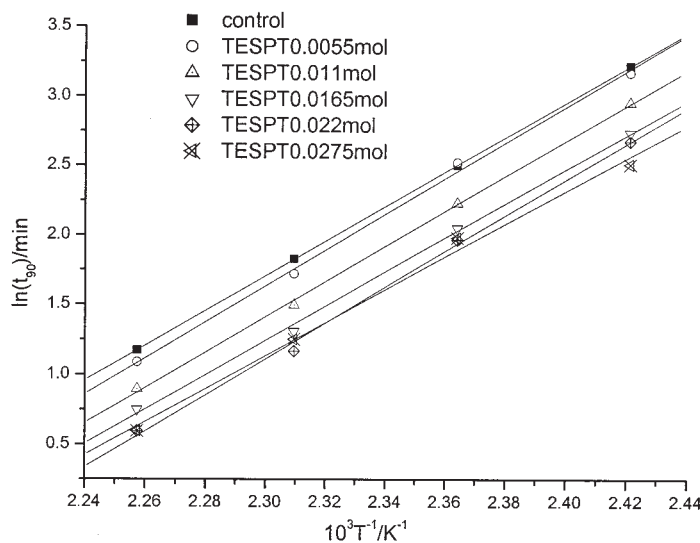
Figure 10 An Arrhenius plot of vulcanization for TESPT (mol) at various concentrations of silane coupling agent.

Kinetic parameters of vulcanization

For the compound with NXT silane, the cure rate index and the rate constant increase with increasing silane concentration as shown in Table II. However, the NR compounds with silane TESPT (Series I or II) show an increase trend and have maximum values. For the NR compounds with NXT and TESPT (Series I or II), the cure rate index is smaller than the rate constant at various concentrations and temperatures. Cure rate index and the rate constant of the NR compound with NXT are smaller than those with TESPT (Series I or II) at low silane concentration. At high silane concentration, however, the opposite trend is observed.

The cure rate index and the rate constant increase with increasing temperature at different concentra-

tions of NXT and TESPT. This should be attributed to the fact that the energy supplied is high enough to overcome the activity energy of vulcanization with increasing temperature; therefore, the crosslinking reaction becomes faster.

Effect of cure temperature on the vulcanization

It is presumed that the crosslinking reaction follows first-order reaction kinetics. Arrhenius plots of vulcanization for NR compounds with NXT and TESPT are shown in Figures 9 through 11. The optimum time was plotted against the reciprocal of the temperature. Table III shows the apparent activity energy of vulcanization for the compounds with different silane concentrations.
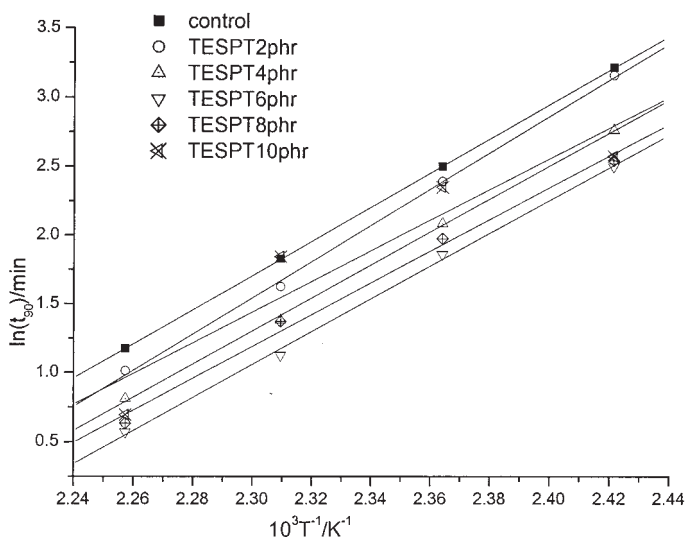

Figure 11 An Arrhenius plot of vulcanization for TESPT (wt) at various concentrations of silane coupling agent.

TABLE III
Apparent Activation Energy (Ea) of Vulcanization of Various Loadings of NXT and TESPT

Concentration phr	Ea (kJ/mol)		Concentration mol	Ea (kJ/mol)	
	NXT	TESPT (wt)		NXT (mol)	TESPT (mol)
0	103.7	103.7	0	103.7	103.7
2	104.5	110.1	0.0055	104.5	107.3
4	103.3	100.3	0.011	103.3	105.3
6	99.5	99.7	0.0165	99.5	102.3
8	91.1	96.5	0.022	91.1	107.2
10	87.6	93.2	0.0275	87.6	98.4

The apparent activation energies of vulcanization for the compounds with NXT and TESPT decrease with increasing silane concentration. The activation energies of vulcanization of the compound with NXT are lower than that with TESPT, which is independent of the silane concentration. This is determined by their structure. TESPT retards the curing process due to the steric hindrance effect of its bulky end group. Steric hindrance of NXT is smaller than that of TESPT as seen from their molecule structures. Poh et al.[17] reported that the apparent activation energy of vulcanization increases with increasing Si-69 concentration. But the apparent activation energy of vulcanization decreases with increasing Si-69 concentration as shown in Table III. This might be attributed to different TESPT silanes used in the experiments.

CONCLUSION

The scorch time of natural rubber decreases with increasing NXT and TESPT concentrations. The scorch time of NR compound with NXT is longer than that with TESPT. NXT silane offers longer scorch safety than TESPT silane.

At high temperatures, the dependence of scorch time on the silane concentration becomes less significant because sufficient thermal energy is available to overcome the activation energy of the vulcanization.

The activation energies of vulcanization of NR compound with NXT and TESPT decrease with increasing silane concentration. The activation energies of vulcanization of NR compound with NXT are lower than that with TESPT at a given concentration.

References

1. Bokobza, L.; Rapoport, O. J Appl Polym Sci 2002, 85, 2301.
2. Hashim, A. S.; Azahari, B.; Ikeda, Y.; Kohjiya, S. Rubber Chem Technol 1998, 71, 289.
3. Boretti, L. G.; Gradwell, M. H. S.; McGill, W. J. Plast Rubber Compos 2000, 29, 144.
4. Kralevich, M. L.; Koenig, J. L. Compos Interfaces 1997, 5, 125.
5. Hasse, A.; Klockmann, O.; Wehmeier, A.; Luginsland, H.-D; Kautsch Gummi Kunstst: Köln, 2002, 55, 236.
6. Reuvekamp, L. A. E. M.; Ten Brinke, J. W.; Van Swaaij, P. J.; Noordermeer, J. W. M. Kautsch Gummi Kunstst 2002, 55, 41.
7. Adikary, A.; Mukuopadhyay, R.; Deuri, A. S. J. Mater Sci 1995, 30, 4112.
8. Nakamura, M.; Takagishi, Y.; Noguchi, K. Rubber World 1998, 218, 30.
9. Wang, M. J. Rubber Chem Technol 1998, 71, 520.
10. Choi, S. S. Polym Test 2002, 21, 201.
11. Reuvekamp, L. A. E. M.; Ten Brinke, J. W.; Van Swaaij, P.; Noordermeer, J. W. M. Rubber Chem Technol 2002, 75, 187.
12. Pal, P. K.; De, S. K. Rubber Chem Technol 1983, 56, 737.
13. Datta, R. N.; Das, P. K.; Manda, S. K.; Basu, K. Kautsch Gummi Kunstst 1988, 41, 157.
14. Luginsland, H. D. Kautsch Gummi Kunstst 2000, 53, 10.
15. Ten Brinke, J. W.; Van Swaaij, P. J.; Reuvekamp, L. A. E. M.; Noordermeer, J. W. M. Rubber Chem Technol 2003, 76, 12.
16. Ladouce-Stelandre, L.; Bomal, Y.; Flandinö Labarre, L. D. Rubber Chem Technol 2003, 76, 145.
17. Poh, B. T.; Ng, C. C. Eur Polym Mater 1998, 34, 975.
18. Jeong, J. H.; Moon, C. W.; Leonov, A. I.; Quirk, R. P. Rubber Chem Technol 2002, 75, 93.
19. Joshi, P. G.; Pickwell, R. J.; Weller, K. J.; Hofstetter, M. H.; Pohl, E. R.; Stout, M. E.; Osterholtz, F. D. Tire Technol Int 2002, 80.
20. Menon, A. R. R.; Pillai, C. K. S.; Nando, G. B. Polymer 1998, 39, 4033.
21. Braker, L. R. J Inst Rubber Ind 1973, 121.
22. Guan, S. H.; Liu, R. D.; Chen, X. Y. LunTaiGongYe 1997, 17, 535.
23. Cruse, R. W.; Hofstetter, M. H.; Panzer, L. M.; Pickwell, R. J. 150th ACS Rubber Division Meeting 1996, 75, 8.