Elastomer
Vol. 40, No. 2, pp 112~118 (2005)

Influence of Silane Coupling Agent on Retraction Behaviors of NR Vulcanizates Reinforced with Carbon Black and Clay

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(Received February 2, 2005, Revised & Accepted March 28, 2005)

실란 커플링제가 카본블랙과 점토로 보강된 천연 고무 가황물의 회복 특성에 미치는 영향

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(2005년 2월 2일 접수, 2005년 3월 28일 수정 및 채택)

ABSTRACT : Influence of a silane coupling agent on the reatraction behaviors of NR vulcanizates reinforced with carbon black and clay was studied. Bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) was used as a silane coupling agent. The vulcanizates containing the silane coupling agent were, on the whole, recovered faster than those without the silane coupling agent. However, for the vulcanizate with the higher clay content at low temperature region (below -12℃), the vulcanizate containing the silane coupling agent was recovered slower than that without the silane coupling agent. The recovery difference of the vulcanizates with and without silane coupling agent decreased with increase of clay content. The experimental results were explained with crosslink density, modulus, and bound rubber content.

요 약 : 실란 커플링제가 카본블랙과 점토로 보강된 천연 고무 가황물의 회복 특성에 미치는 영향에 대해 연구하였다. Bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT)를 실란 커플링제로 사용하였다. 실란 커플링제가 함유된 가황물은 실란 커플링제가 함유되지 않은 가황물에 비해 전반적으로 빠른 회복 거동을 보였다. 그러나, 점토 함량이 높은 가황물의 경우 -20℃보다 낮은 온도에서는 실란 커플링제가 함유된 가황물이 실란 커플링제가 함유되지 않은 가황물에 비해 느리게 회복되었다. 실란 커플링제가 함유된 가황물과 실란 커플링제가 함유되지 않은 가황물의 회복량 차이는 점토 함량이 증가할수록 감소하였다. 실험 결과는 가교 밀도, 모듈러스, 그리고 결합 고무량으로 설명하였다.

Keywords : retraction behaviors, silane coupling agent, carbon black and caly, NR vulcanizate

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Ⅰ. Introduction

Rubber materials have been widely used for vibration damping. The low glass transition temperature (T_g) property leads to use of vibration damping at low temperature. A rubber material has a recovery property to return to its original shape from deformation. Hergenrother and Doshak[1] measured the tensile retraction of SBR compounds filled with different carbon blacks. Yun and Kim[2] studied the influence of filler content, curative, and plasticizer on the retraction behaviors.

Polar reinforcing agents uesd in rubber compounds are carbon black and silica.[3-10] Since clay is very cheap, it has been tried to use clay as filler for a rubber compound in a industry. Silane coupling agent is used to improve filler dispersion of inorganic filler such as silica and clay. Bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT), $(C_2H_5O)_3Si\text{-}(CH_2)_3\text{-}S_x\text{-}(CH_2)_3\text{-}Si(OC_2H_5)_3$, is mostly used as a silane coupling agent in a rubber compound.[11-13]

In the present work, we studied the influence of silane coupling agent on retraction behaviors of NR vulcanizates filled with carbon black and clay. Since the silane coupling agent modifies the inorganic filler, it will affect retraction behaviors of rubber compounds filled with clay.

Ⅱ. Experimental

The natural rubber (NR) compounds were prepared using NR (SMR CV60), carbon black (N220), clay, cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). Si69 (Degussa Co., TESPT) was used as a silane coupling agent. The total filler content was 50 phr and the filler compositions were carbon black/clay = 40/10, 30/20, and 20/30 phr. The compounds without the silane coupling agent (Compounds No. 1 - 3) and the compounds containing the silane coupling agent (Compounds No. 4 - 6) were prepared. The formulations are given in Table 1.

Mixing was performed in a Banbury type mixer at a rotor speed of 40 and 25 rpm for master batch (MB) and final mixing (FM) stages, respectively. The initial temperatures of the mixer were 110 and 80℃ for MB and FM stages, respectively. The MB compounds were prepared as follow. (1) The rubber was loaded into the mixer and preheated for 0.5 min. (2) The fillers and silane coupling agent were compounded into the rubber for 2.0 min. (3) The cure activators and antidegradants were mixed for 2.0 min and the compounds were discharged. The FM compounds were prepared by mixing the curatives with the MB compounds for 2.0 min.

Table 1. Formulations of the compounds (phr)

Compound No.	1	2	3	4	5	6
SMR CV60	100.0	100.0	100.0	100.0	100.0	100.0
N220	40.0	30.0	20.0	40.0	30.0	20.0
Clay	10.0	20.0	30.0	10.0	20.0	30.0
Si69	0.0	0.0	0.0	1.2	1.2	1.2
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0
HPPD	2.0	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0	2.0
TBBS	1.4	1.4	1.4	1.4	1.4	1.4
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2

SMR CV60: standard Malaysian rubber with viscosity of 60 MU
N220: carbon black
Si69: silane coupling agent, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT)
HPPD: *N*-phenyl-*N'* -(1,3-dimethylbutyl)-*p*-phenylenediamine
TBBS: *N-tert*-butyl-2-benzothiazole sulfenamide

Cure characteristics were obtained using a Flexsys rheometer (MDR 2000) at 160℃. Cure characteristics of the compounds were listed in Table 2. Based on the results of a rheometer test, the rubber compounds were cured at 160℃ for 30 min. Temperature retraction (TR) test according to the ASTM D1329 with a TR tester (ET01, Elastocon Co.) was performed as follow. (1) The sample was strained by 50% and kept in low temperature chamber (about -75℃) for 30 min. (2) The elongated sample was released and the temperature was increased at a rate

Table 2. Cure characteristics of the compounds at 160℃

Compound No.	1	2	3	4	5	6
T_{min} (N·m)	1.21	1.08	0.97	1.27	1.10	1.13
T_{max} (N·m)	4.42	4.17	3.82	4.76	4.36	4.09
ΔT (N·m)	3.21	3.09	2.85	3.49	3.26	2.96
t_2 (min)	6.54	7.21	7.87	5.87	6.28	7.61
t_{90} (min)	12.02	12.40	12.94	13.07	12.95	13.74

of 1 ℃/min. (3) The change of recovery with the temperature was measured. The sample dimension was 50 mm of length, 2 mm of width, and 2 mm of thickness. Physical properties of the vulcanizates were measured with the Universal Testing Machine (Instron 6021).

Ⅲ. Results and Discussion

Figures 1 - 3 show differences in the retraction behaviors of the vulcanizates without and containing the silane coupling agent. The vulcanizates begin to recover at the temperature below -60℃. For the vulcanizates with the fillers of carbon black/clay = 40/10 and 30/20 phr, the vulcanizates containing the coupling agent (squares in Figures 1 and 2) are recovered faster than those without the coupling agent (circles in Figures 1 and 2). The recovery difference between the vulcanizates without and containing the silane coupling agent becomes clear at the temperature higher than -60℃.

Let the 10% recovery be R_{10}. For the the vulcanizates without the silane coupling agent, the temperatures at R_{10} (T_{10}) are -51.9, -52.8, and -54.5℃ for the vulcanizates with the fillers of carbon black/clay = 40/10, 30/20, and 20/30 phr, respectively. For the vulcanizates containing the silane coupling agent, the T_{10}s are -54.7, -52.7, and -52.4℃, respectively. These values are lower than their glass transition temperatures (T_g). The T_gs obtained from the rheovibron test are -46 ~ -50℃. The vulcanizates begin to recover at the lower temperatures than their T_gs. The T_{10}s of the vulcanizates with and without the silane coupling agent show a

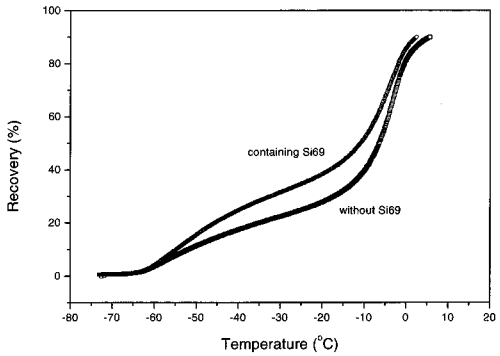


Figure 1. Recovery curves of the vulcanizates with the filler composition of carbon black/clay = 40/10 phr. Squares and circles indicate the vulcanizates with and without Si69, respectively.

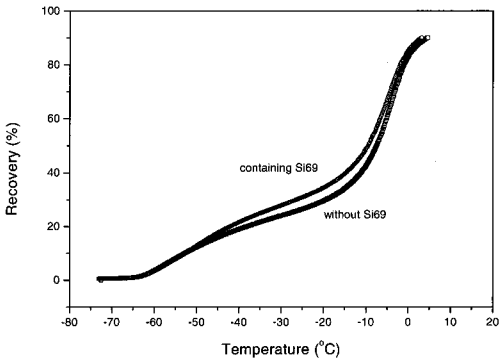


Figure 2. Recovery curves of the vulcanizates with the filler composition of carbon black/clay = 30/20 phr. Squares and circles indicate the vulcanizates with and without Si69, respectively.

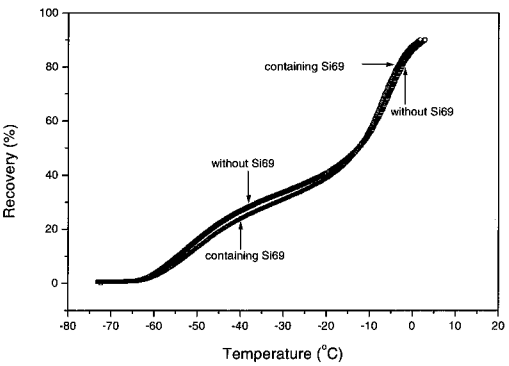


Figure 3. Recovery curves of the vulcanizates with the filler composition of carbon black/clay = 20/30 phr. Squares and circles indicate the vulcanizates with and without Si69, respectively.

reverse trend. The T_{10} of the vulcanizate without silane coupling agent becomes lower as the clay content increases, while that containing the silane coupling agent becomes higher with increasing the clay content. The T_{90}s of the vulcanizates without the silane coupling agent are 5.7, 4.4, and 2.9℃ for the vulcanizates with the filler compositions of carbon black/clay = 40/10, 30/20, and 20/30 phr, respectively. The T_{90}s of the vulcanizates containing the silane coupling agent are 2.5, 3.2, and 1.7℃, respectively. The T_{10}s of the vulcanizates without the silane coupling agent are higher than those containing the silane coupling.

The temparature *vs* the recovery difference and the recovery *vs* the temeprature difference were plotted in order to compare the differences of the retraction behaviors in detail. Figure 4 shows variation of the recovery difference with the temperature. The recovery difference is R_W - R_C, where R_W and R_C are the recoveries of the vulvanizates with and without the silane coupling agent. For the vulcanizates with the filler compositions of carbon black/clay = 40/10 and 30/20 phr, values of the recovery differences are "negative". This means that the vulcanizates containing the silane coupling agent are recovered faster than those without the silane coupling agent. Variations of the recovery differences of the vulcanizates with carbon black/clay = 40/10 and 30/20 phr with the temperature in the range from -60℃ to -10℃ show good linear relations. The slope for the vulcanizates with the filler compositions of carbon black/clay = 40/10 phr is steeper than that for the vulcanizates with the filler compositions of carbon black/clay = 30/20 phr. The slopes are -0.228 and -0.134 %/℃ for the vulcanizates with the filler compositions of carbon black/clay = 40/10 and 30/20 phr, respectively. Values of the recovery difference for the vulcanizates with the filler compositions of carbon black/clay = 20/30 phr are "positive" in low temperature region (below -12℃) but are "negative" in high temperature region.

Figure 5 shows variation of the temperature difference with the recovery. For the vulcanizates

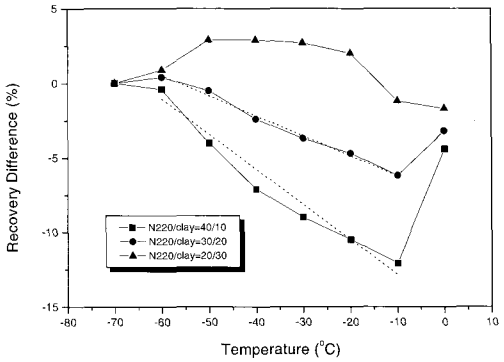


Figure 4. Plot of the recovery difference as a function of the temperature. Squares, circles, and triangles indicate the vulcanizates with the filler composition of carbon black/clay = 40/10, 30/20, and 20/30, respectively.

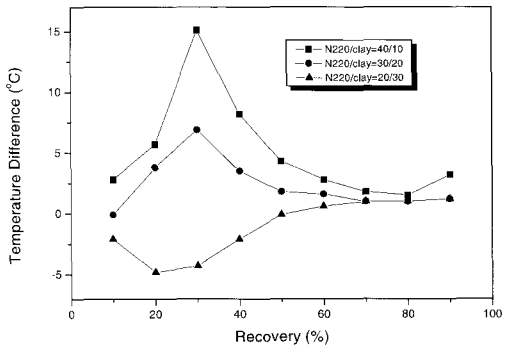


Figure 5. Plot of the temperature difference as a function of the recovery. Squares, circles, and triangles indicate the vulcanizates with the filler composition of carbon black/clay = 40/10, 30/20, and 20/30, respectively.

with the filler compositions of carbon black/clay = 40/10 and 30/20 phr, the values of the temperature differences are "positive", which means that the vulcanizates containing the silane coupling agent are recovered faster than those without the silane coupling agent. The temperature differences increase until 30% recovery and then decreases. The vulcanizate with the filler compositions of carbon black/clay = 20/30 phr shows the different behavior in the temperature difference. For the vulcanizate with the filler compositions of carbon black/clay = 20/30 phr, the temperature differences decreases at the initial region and then increases gradually.

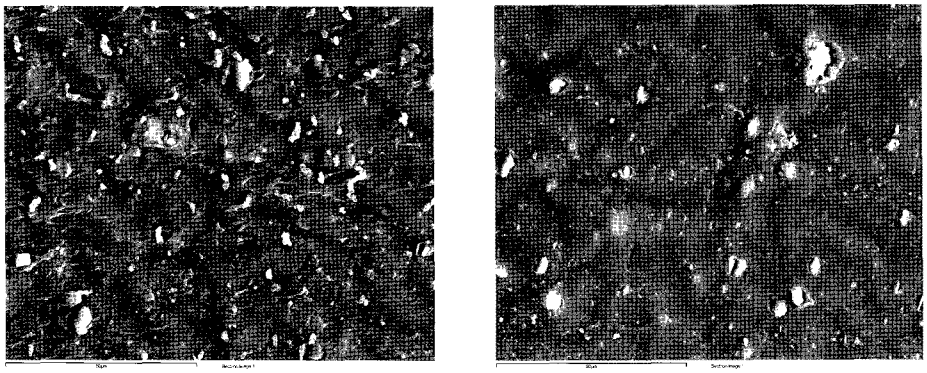
Table 3. Physical properties of the vulcanizates

Compound No.	1	2	3	4	5	6
Hardness (Shore A)	62	58	55	65	60	57
100% Modulus (kg/cm^2)	24.7	21.3	19	28.9	25.9	22.9
300% Modulus (kg/cm^2)	106.4	84.8	64.7	124.5	101.2	81.3
Tensile Strength (kg/cm^2)	279.4	266.6	253.4	289.9	279.0	253.9
Elongation at Break (%)	559.9	568.4	586.2	540.5	551.5	547.2

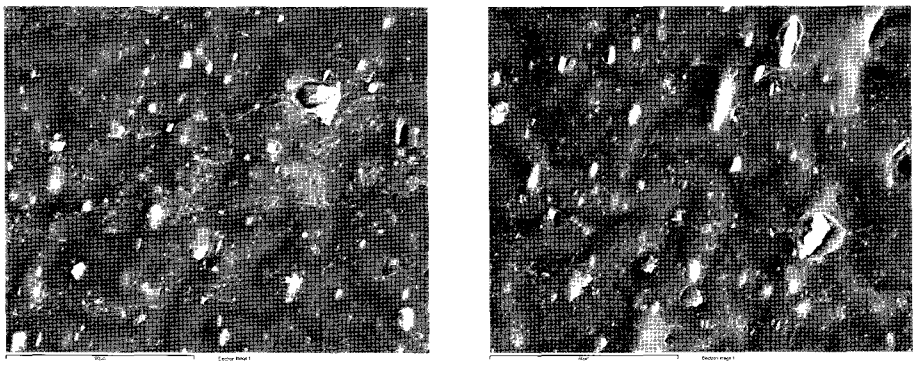
For the vulcanizates with the filler compositions of carbon black/clay = 40/10 and 30/20 phr, the faster retraction behaviors of the vulcanizates containing the silane coupling agent can be explained with the higher crosslink density and higher modulus. Delta torque (ΔT), the difference between the maximum and minimum torque in the rheograph, was used as the crosslink density. The ΔTs of the vulcanizates containing the silane coupling agent are larger than those without the silane coupling agent by 8.7 and 5.5% for the vulcanizates with the filler compositions of carbon black/clay = 40/10 and 30/20 phr, respectively (Table 2). Moduli of the vulcanizates containing the silane coupling agent are also larger than those without the silane coupling agent by about 20% (Table 3). Samples were elongated by the same strain rate of 50% but the stresses were applied to them by different levels. When a sample has higher crosslink density and higher modulus, the stress applied to the sample will be larger at the same strain rate. The larger stress will lead to faster return to its original form.

Experimental results for the vulcanizates with the filler compositions of carbon black/clay = 20/30 phr cannot be explained with the crosslink density and modulus. Crosslink density and modulus of the vulcanizates containing the silane coupling agent are larger than those without the silane coupling agent as listed in Tables 2 and 3. However, the recovery rate at low temperature region (below -12℃) are slower for the vulcanizate containing the silane coupling agent than for the vulcanizates without the silane coupling agent as discussed previously. We can say that clay is not a good reinforcing filler from the SEM images and from the experimental measurements of bound rubber contents. Figure 6 shows SEM images of the vulcanizates. Clay particles are separated from rubber matrix, which means that clay is not compatible with NR and cannot play a role as a good reinforcing agent. The bound rubber contents of the compounds without the silane coupling agent are 17.49, 15.42, and 13.56% for the compounds with the filler compositions of carbon black/clay = 40/10, 30/20, 20/30 phr, respectively. The bound rubber contents of the compounds containing the silane coupling agent are 23.59, 15.84, and 13.28%, respectively. The bound rubber content of the compound compounds with the filler compositions of carbon black/clay = 40/10 phr increases notably (about 35%) by adding the silane coupling agent. This is due to the improved filler dispersion. However, the bound rubber content of the compound with the filler composition of carbon black/ clay = 30/20 phr increases slightly by about 3% and that of the compound with the filler composition of carbon black/clay = 20/30 phr decreases by adding the silane coupling agent.

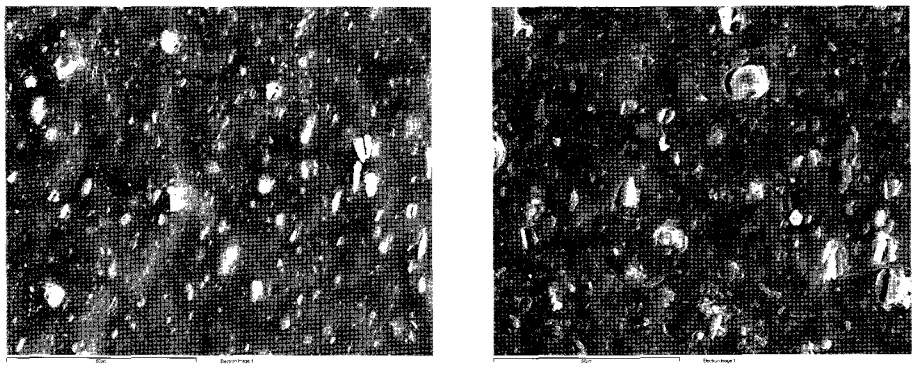
We can consider that the retraction behaviors of the vulcanizate with the filler composition of carbon black/clay = 20/30 phr will be related with the bound rubber content and unreacted silane coupling agent. The bound rubber content of the compound without the silane coupling agent (13.56%) is slightly larger than that containing the silane coupling agent (13.28%). The lower bound rubber content implies the lower reinforcement. The elastic property will increase as the bound rubber content increases. Slippage between rubber chains or between rubber chains and filler will increase and elastic property will decrease as the unreacted silane coupling agent increases. It can be considered that there are unreacted silane coupling agents from the result of the bound rubber content of the compound with the filler of carbon black/clay = 20/30 phr.



(aW) (aC)



(bW) (bC)



(cW) (cC)

Figure 6. SEM images of the vulcanizates with the filler compositions of carbon black/clay = 40/10 phr (a), 30/20 (b), and 20/30 phr (c). The "W" and "C" mean the vulcanizates with and without containing the silane coupling agent.

Ⅳ. Conclusion

For the vulcanizates with the filler compositions of carbon black/clay = 40/10 and 20/30 phr, the vulcanizates containing the silane coupling agent had faster retraction behaviors than those without the silane coupling agent. However, for the vulcanizate with the filler composition of carbon black/clay = 20/30 phr, the vulcanizate containing the silane coupling agent had slower retraction behaviors than those without the silane coupling agent at low temperature region (below -12℃). The faster retraction behaviors of the vulcanizates containing the silane coupling agent, for the vulcanizates with the filler compositions of carbon black/clay = 40/10 and 20/30 phr, were due to the higher crosslink density and higher modulus. For the vulcanizate with the filler composition of carbon black/clay = 20/30 phr, the slower retraction behaviors of the vulcanizate containing the silane coupling agent were due to the lower reinforcement and slippage between rubber chains or between rubber chains and filler.

Acknowledgements

This work was supported by Korea Reserch Foundation Grant (KRF-2004-003-D00100).

References

1. W. L. Hergenrother and J. M. Doshak, "Tensile retraction measurements. V. The effect of carbon black on the crosslink density of cured rubber", *J. Appl. Polym. Sci.*, **48**, 1621 (1993).
2. J. H. Yun and T. H. Kim, "A study on the low temperature retraction of NR", *Elastomer*, **35**, 303 (2000).
3. S. Wolff and M.-J. Wang, "Filler-elastomer interactions. Part IV. The effect of the surface energies of fillers on elastomer reinforcement", *Rubber Chem. Technol.*, **65**, 329 (1992).
4. A. Y. Coran and J.-B. Donnet, "The dispersion of carbon black in rubber. Part I. Rapid method for assessing quality of dispersion", *Rubber Chem. Technol.*, **65**, 973 (1992).
5. A. Y. Coran and J.-B. Donnet, "The dispersion of carbon black in rubber. Part II. The kinetics of dispersion in natural rubber", *Rubber Chem. Technol.*, **65**, 998 (1992).
6. A. Y. Coran and J.-B. Donnet, "The dispersion of carbon black in rubber. Part III. The effect of dispersion quality on the dynamic mechanical properties of filled natural rubber", *Rubber Chem. Technol.*, **65**, 1016 (1992).
7. T. C. Gruber and C. R. Herd, "Anisometry measurements in carbon black aggregate populations", *Rubber Chem. Technol.*, **70**, 727 (1997).
8. M.-J. Wang, S. Wolff, and J.-B. Donnet, "Filler-elastomer interactions. Part I. Silica surface energies and interactions with model compounds", *Rubber Chem. Technol.*, **64**, 559 (1991).
9. M.-J. Wang and S. Wolff "Filler-elastomer interactions. Part V. Investigation of the surface energies of silane-moidified silicas", *Rubber Chem. Technol.*, **65**, 715 (1992)..
10. A. Blume, "Analytical properties of silica - A key for understanding silica reinforcement", *Kautsch. Gummi Kunstst.*, **53**, 338 (2000).
11. U. Görl and A. Hunsche, "Advanced investigations into the silica/silane reaction system", in *Proceedings of the Rubber Division 150th Meeting, American Chemical Society*, Paper No. 76 (1996).
12. U. Görl and A. Hunsche, "Investigation unto the chemistry of the TESPT sulfur chain", in *Proceedings of the Rubber Division 151st Meeting, American Chemical Society*, Paper No. 38 (1997).
13. A. S. Hashim, B. Azahari, Y. Ikeda, and S. Kohjiya, "The effect of TESPT on silica reinforcement of styrene-butadiene rubber", *Rubber Chem. Technol.*, **71**, 289 (1998).