

Influence of Kinds of Fatty Acids and Poly(ethylene glycol)s on Properties of Silica-Filled Natural Rubber Compounds

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Abstract : Silica-filled rubber compounds have slower cure characteristics than carbon black-filled ones due to the adsorption of curatives on the silica surface. Fatty acid was used as a cure activator along with zinc oxide in a sulfur cure system. Poly(ethylene glycol), PEG, was used in silica-filled rubber compounds to prevent adsorption of the curatives on the silica surface. In this study, influence of the size of fatty acid and PEG on properties of silica-filled NR compounds was investigated. It was found that the size of fatty acid and PEG affected the cure characteristics and physical properties. The cure rate becomes faster as the PEG size increases. By increasing the size of fatty acid or PEG, the delta torque of the compound decreases while the Mooney viscosity increases. The modulus of the vulcanizate decreases with increasing the molecular weight of fatty acid or PEG. The experimental results were explained by the filler dispersion and by the prevention of the curative-adsorption on the silica surface.

Introduction

Stearic acid is used as a cure activator along with zinc oxide in an accelerated-sulfur vulcanization of a rubber compound. Stearic acid reacts with zinc oxide to form zinc stearate by dehydration. Zinc stearate reacts with sulfur and cure accelerator to form zinc complex.¹⁻³ This complex accelerates crosslinking reaction so that scorch time and cure rate become faster.

Silica has a number of hydroxyl groups on the surface, which results in strong filler-filler interactions and adsorption of polar materials on the surface.⁴ Since silica has strong filler-filler interactions, filler dispersion of a silica-filled rubber compound is worse than that of a carbon black-filled one. The highly polar surface of silica makes hydrogen bonds with polar materials in a rubber compound. The adsorption of curatives by silica results in delay of the scorch time and reduction of the delta torque of a silica-filled rubber compound. In general, silane coupling agent such as bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used in order to

improve the filler dispersion.⁴⁻⁷

Poly(ethylene glycol), PEG, HO-(CH₂CH₂O)_n-H, is used to prevent the adsorption of curatives on the silica surface. Since PEG has many ether linkages, -CH₂-O-CH₂-, it makes hydrogen bonds with silanols of the silica surface. This results in formation of PEG barrier on the silica surface so that the filler-filler interaction is reduced and adsorption of the curatives on the surface is also prevented. Since fatty acids have a carboxyl group, -CO₂H, they also can make hydrogen bonds with the silica. The barrier of fatty acid will reduce the filler-filler interaction of silica and prevent the adsorption of curatives.

It may be considered that intermolecular interactions of the silica with fatty acid or PEG are affected by the size of fatty acid and PEG. In the present work, the influence of the size of fatty acid and PEG on properties of silica-filled natural rubber (NR) compounds was studied. Five fatty acids and five PEGs with different molecular weights were employed.

Experimental

Silica-filled NR compounds containing different

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fatty acids were prepared without PEG to enlarge the influence of fatty acid on properties of the compounds. Five fatty acids were employed: stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$), palmitic acid ($\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$), myristic acid ($\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$), lauric acid ($\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$), and *n*-capric acid ($\text{CH}_3(\text{CH}_2)_8\text{CO}_2\text{H}$). They were obtained from Junsei Chemical Co. and their purities were more than 95%. The formulations are given in Table I.

For silica-filled NR compounds with different PEGs, five PEGs were used. Their average molecular weights were 2×10^3 , 4×10^3 , 6×10^3 , 8×10^3 , and 10×10^3 g/mol. They were obtained from Yakuri Pure Chemical Co. Their molecular weight distributions were about $1.9\text{-}2.2 \times 10^3$, $3.5\text{-}4.5 \times 10^3$, $5.0\text{-}6.0 \times 10^3$, $7.0\text{-}9.0 \times 10^3$, and $8.5\text{-}11.5 \times 10^3$ g/mol, respectively. The formulations were given in Table II.

Table I. Formulations (phr)

Compound No.	F1	F2	F3	F4	F5
SMR CV60 ^a	100.0	100.0	100.0	100.0	100.0
Z 175 ^b	50.0	50.0	50.0	50.0	50.0
Si 69 ^c	3.0	3.0	3.0	3.0	3.0
Stearic acid	3.0	0.0	0.0	0.0	0.0
Palmitic acid	0.0	3.0	0.0	0.0	0.0
Myristic acid	0.0	0.0	3.0	0.0	0.0
Lauric acid	0.0	0.0	0.0	3.0	0.0
<i>n</i> -Capric acid	0.0	0.0	0.0	0.0	3.0
ZnO	5.0	5.0	5.0	5.0	5.0
HPPD ^d	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0
DPG ^e	1.0	1.0	1.0	1.0	1.0
TBBS ^f	1.4	1.4	1.4	1.4	1.4
Sulfur	1.2	1.2	1.2	1.2	1.2

^aSMR CV60: standard malaysian rubber with constant viscosity of 60 MU.

^bZ 175: silica of Degussa Co.

^cSi 69: bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT).

^dHPPD: *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine.

^eDPG: diphenylguanidine.

^fTBBS: *N*-*tert*-butyl-2-benzothiazole sulfenamide.

Table II. Formulations (phr)

Compound No.	P1	P2	P3	P4	P5
SMR CV60	100.0	100.0	100.0	100.0	100.0
Z 175	50.0	50.0	50.0	50.0	50.0
Si 69	3.0	3.0	3.0	3.0	3.0
PEG 2000	2.0	0.0	0.0	0.0	0.0
PEG 4000	0.0	2.0	0.0	0.0	0.0
PEG 6000	0.0	0.0	2.0	0.0	0.0
PEG 8000	0.0	0.0	0.0	2.0	0.0
PEG 10000	0.0	0.0	0.0	0.0	2.0
ZnO	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
HPPD	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0
DPG	1.0	1.0	1.0	1.0	1.0
TBBS	1.4	1.4	1.4	1.4	1.4
Sulfur	1.2	1.2	1.2	1.2	1.2

Master batch (MB) stage was performed in a Banbury type mixer at a rotor speed of 40 rpm and final mixing (FM) was carried out in a two roll mill. The initial temperature of the mixer was 110°C. The two-roll mill was kept at 100°C during the mixing. The MB compounds were prepared as follow. (1) The rubber was loaded into the mixer and premixed for 0.5 min. (2) The silica and silane coupling agent were compounded into the rubbers for 2.0 min. (3) The fatty acid or PEG was compounded simultaneously with silica. (4) The cure activators and antidegradants were mixed for 1.5 min and the compounds were discharged. The FM compounds were prepared by mixing the curatives of DPG, TBBS, and sulfur with the MB compounds for 4.0 min in a two roll mill.

Cure characteristics were obtained using a Flexsys rheometer (MDR 2000) at 160°C. Viscosities and Mooney cure times of the compound were measured at 125°C using a Mooney viscometer MV 2000 of Alpha Technologies. The vulcanizates were prepared by curing at 160 for 20 min. Physical properties of the vulcanizates were measured with the Universal Testing Machine (Instron 6021). Abrasion loss was measured according to ASTM 2228 with a Pico abrasion tester of BF Goodrich for 80 cycles. Tan δ of the vulcanizates was measured according to ASTM D2231-87 with a Qualimeter Eplexor 150N of Gabo Co.

Results and Discussion

Influence of Kinds of Fatty Acids. The minimum torque (T_{min}) increases as the fatty acid size increases from *n*-capric acid to stearic acid as shown in Figure 1. The increment is about 0.012 N·m per methylene. On the other hand, the maximum torque (T_{max}) and the delta torque ($T_{max} - T_{min}$) decrease with increase of the fatty acid size. The decrements are about 0.026 and 0.038 N·m per methylene, respectively. This can be explained by the absolute number of the fatty acid molecules in the compound. Since the total fatty acid content was constant (3.0 phr), the relative molar ratio of the fatty acid decreases by increasing its molecular weight. The relative molar ratios are stearic acid : palmitic acid : myristic acid : lauric acid : *n*-capric acid = 1.00 : 1.09 : 1.25 : 1.42 : 1.65. It

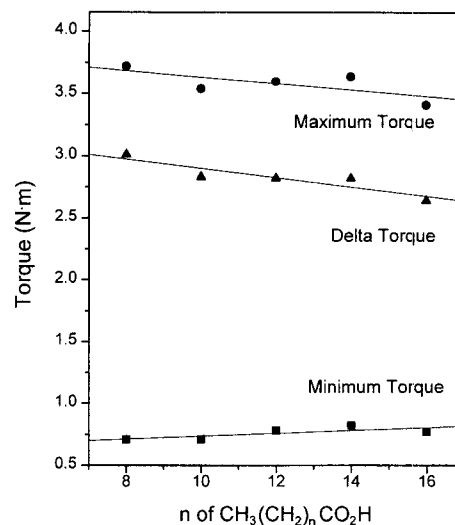


Figure 1. Variation of the torques in rheographs of the silica-filled NR compounds as a function of the fatty acid size. The measurement temperature is 160°C. Rectangles, circles, and triangles indicate the minimum torque (T_{min}), maximum torque (T_{max}), and delta torque, respectively.

can be considered that some of the fatty acids in the compound move to the silica surface and make hydrogen bonds with the silanols or react with the silanols to form chemical bonds. The fatty acid molecules on the silica surface can prevent adsorption of the curatives on the silica surface which results in an increase of the delta torque. The more the number of the fatty acid molecules is, the more the fatty acid molecules on the silica surface is.

Figure 2 shows variation of the Mooney scorch time (t_5) with the fatty acid size. The t_5 is time taken for the Mooney viscosity to increase by 5 MU from the minimum viscosity, where MU is Mooney unit. Variation of the t_5 with the fatty acid size does not show a clear trend. The t_5 , on the whole, increases as the fatty acid size increases. The slow t_5 results from the adsorption of curatives on the silica surface. As discussed above, the number of the fatty acid molecules in the compound decreases with increasing the fatty acid size since the fatty acid content was fixed to 3.0 phr. The more the number of the fatty acid molecules in the compound is, the more the silica surface is covered by the fatty acid. The fatty acid molecules

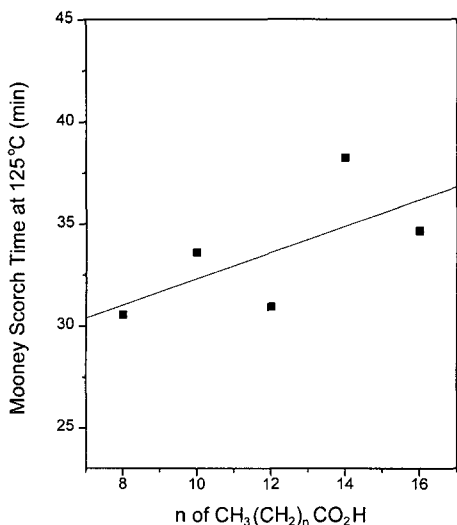


Figure 2. Variation of the Mooney scorch time (t_s) of the silica-filled NR compounds as a function of the fatty acid size. The measurement temperature is 125 °C.

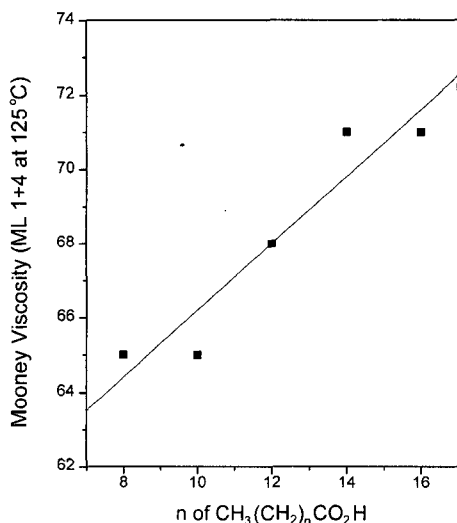


Figure 3. Variation of the Mooney viscosity of the silica-filled NR compounds at 125 °C as a function of the fatty acid size.

on the silica surface can prevent adsorption of the curatives on the silica surface which results in reduction of the scorch time.

The Mooney viscosity of the compound increases by increasing the fatty acid size (Figure 3). The increment is about 0.9 MU per methylene. This may be due to the number of the fatty acid mole-

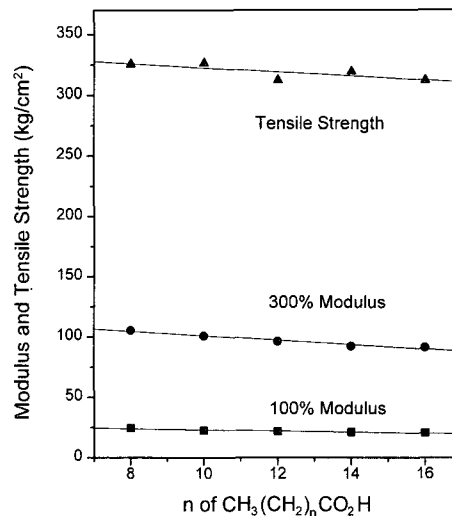


Figure 4. Variation of the moduli and tensile strength of the silica-filled NR vulcanizates as a function of the fatty acid size. Rectangles, circles, and triangles indicate the 100% modulus, 300% modulus, and tensile strength, respectively.

cules in the compound. The fatty acid can act not only as a cure activator but also as a processing aid or a dispersing agent in a rubber compound. If it acts as a dispersing agent, the filler will be dispersed better by increasing the fatty acid molecules. Viscosity of a filled rubber compound is lower when the compound has a good filler dispersion than when it has a bad dispersion.⁸⁻¹²

The modulus and tensile strength of the vulcanizate decrease with increasing the fatty acid size (Figure 4). The decrements are about 1.86 and 1.66 kg/cm² for 300% modulus and tensile strength, respectively. This can be explained by the delta torque. Since the torque in the rheograph starts to increase by formation of crosslinks, the delta torque is very closely related to the crosslink density.¹³⁻¹⁵ The larger the delta torque is, the higher the crosslink density is. In general, modulus of a rubber vulcanizate increases with increasing the crosslink density.³ Since the delta torque of the compound decreases with increase of the fatty acid size as shown in Figure 1, the modulus of the vulcanizate also decreases.

Variation of the elongation at break of the vulcanizate with the fatty acid size is given in Figure 5. The elongation at break, on the whole, increases

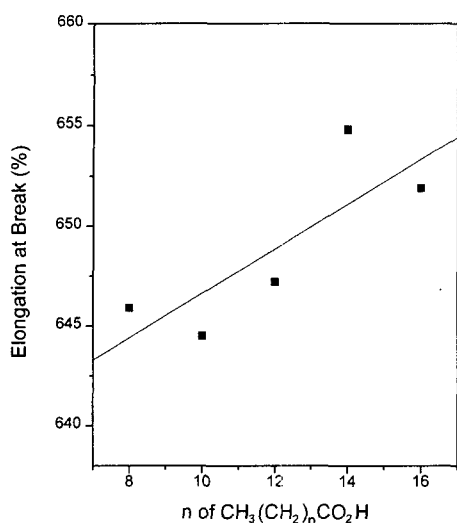


Figure 5. Variation of the elongation at break of the silica-filled NR vulcanizates as a function of the fatty acid size.

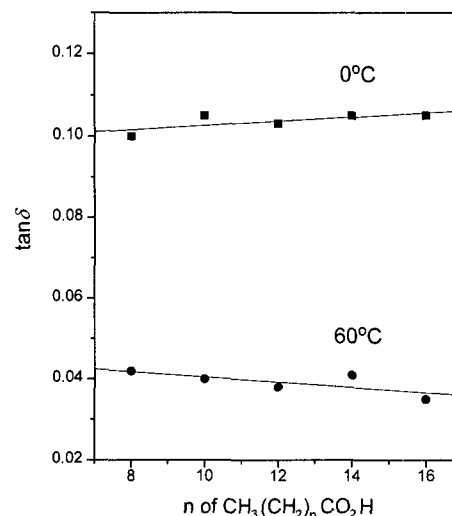


Figure 7. Variation of the $\tan \delta$ of the silica-filled NR vulcanizates as a function of the fatty acid size. Rectangles and circles indicate the $\tan \delta$ at 0 and 60°C, respectively.

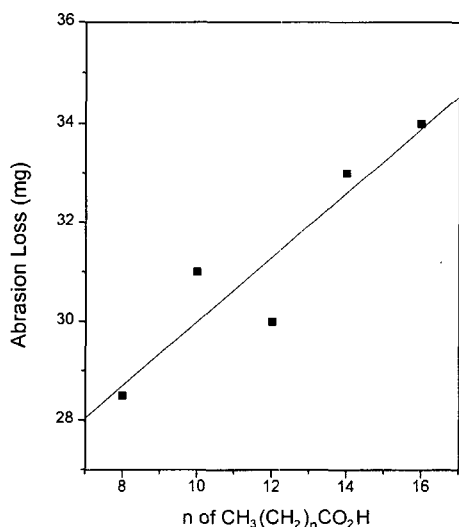


Figure 6. Variation of the abrasion loss of the silica-filled NR vulcanizates as a function of the fatty acid size.

with increase of the fatty acid size. This can be explained by the crosslink density. Breaking elongation of a rubber vulcanizate is inversely proportional to the degree of crosslink density.¹⁶ Breaking elongation of a rubber vulcanizate with a high crosslink density is shorter than that of a rubber vulcanizate with a low one. The crosslink density of the vulcanizate decreases with increase of the fatty acid size

as discussed previously.

The abrasion loss of the vulcanizate increases by increasing the fatty acid size (Figure 6). This may be due to the modulus. In general, wear property is improved by increasing the modulus.³ Since the modulus decreases with increasing the fatty acid size, the wear property becomes worse and worse.

$\tan \delta$ values at 0 and 60°C reflect the wet traction and the rolling resistance, respectively. The larger the $\tan \delta$ at 0°C is, the better the wet traction property of a vulcanizate is. The smaller the $\tan \delta$ at 60°C is, the better the rolling resistance of a vulcanizate is. Variation of the $\tan \delta$ at 0 and 60°C of the vulcanizate with the fatty acid size is given in Figure 7. Change of the $\tan \delta$ values with the fatty acid size is negligible. The $\tan \delta$ at 0°C, on the whole, increases with increase of the fatty acid size. The $\tan \delta$ at 60°C, on the whole, decreases with increasing the fatty acid size.

Influence of Kinds of PEG. The T_{min} of the compound almost does not change with the PEG size as shown in Figure 8. The T_{max} and delta torque decrease slightly with increasing the PEG size. The decrement is about 0.013 N m per 1×10^3 g/mol.

The t_{35} is the time taken for the Mooney visco-

sity to increase by 35 MU from the minimum point. The cure rate index (Δt) is the difference between the t_{35} and t_5 . The reciprocal of the cure rate index is used as a cure rate. Variations of the t_5 , t_{35} , and Δt with the PEG size were shown in

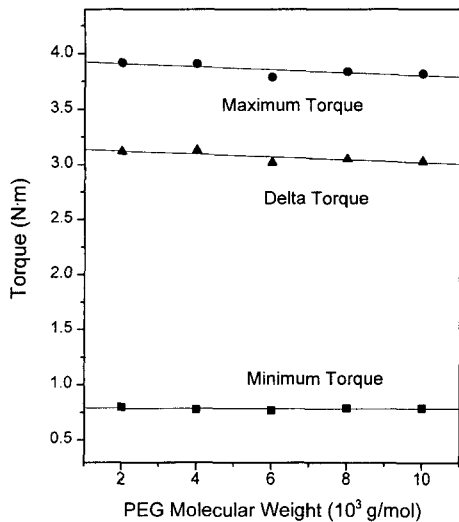


Figure 8. Variation of the torques in rheographs of the silica-filled NR compounds as a function of the PEG size. The measurement temperature is 160 °C. Rectangles, circles, and triangles indicate the minimum torque (T_{min}), maximum torque (T_{max}), and delta torque, respectively.

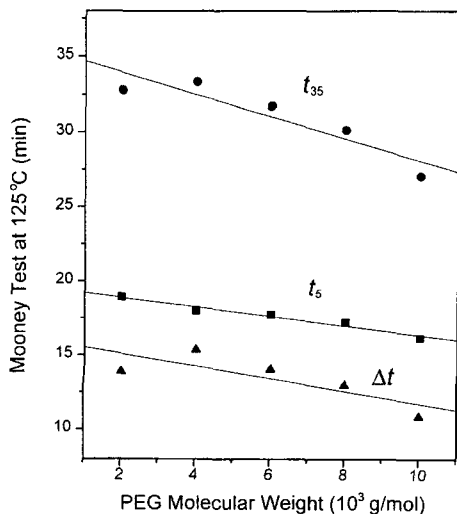


Figure 9. Variation of the t_5 , t_{35} , and Δt of the silica-filled NR compounds as a function of the size. The measurement temperature is 125 °C. Rectangles, circles, and triangles indicate the t_5 , t_{35} , and Δt , respectively.

Figure 9. The t_5 decreases with increase of the PEG size. The decrement is about 0.32 min per 1×10^3 g/mol. This implies that adsorption of the curatives on the silica surface is more prevented when using PEG with higher molecular weight. The t_{35} also decreases with increase of the PEG size. The decrement is about 0.73 min per 1×10^3 g/mol. The Δt also decreases with increasing the PEG size. This implies that the cure rate becomes faster as the PEG size increases. Thus, it can lead to a conclusion that PEG with higher molecular weight is more effective to prevent the adsorption of curatives on the silica surface.

The Mooney viscosity of the compound, on the whole, increases with increasing the PEG size (Figure 10). The increment is about 0.6 MU per 10^3 g/mol. This may be due to the molecular weight of the PEG. Viscosities of materials depend upon their molecular weight.¹⁷

The modulus of the vulcanizate decreases slightly with increasing the PEG size (Figure 11). The decrements are about 0.17 and 0.29 kg/cm² per 1×10^3 g/mol for 100 and 300% moduli, respectively. This can be explained by the delta torque. Since the delta torque of the compound slightly decreases with the increase of the PEG size as shown in Figure 8, the modulus of the vulcanizate also decreases. However, the tensile strength

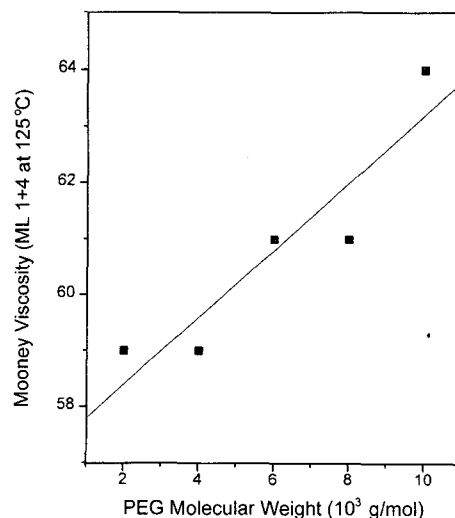


Figure 10. Variation of the Mooney viscosity of the silica-filled NR compounds at 125 °C as a function of the PEG size.

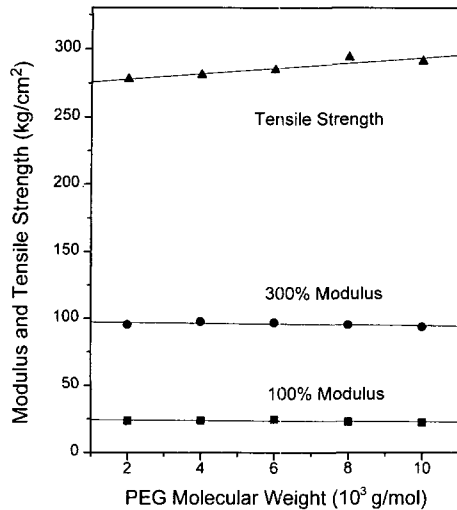


Figure 11. Variation of the moduli and tensile strength of the silica-filled NR vulcanizates as a function of the PEG size. Rectangles, circles, and triangles indicate the 100% modulus, 300% modulus, and tensile strength, respectively.

increases by about 2 kg/cm^2 per $1 \times 10^3 \text{ g/mol}$ with the increase of the PEG size. This is very interesting because the crosslink density decreases with the increase of the PEG size. In general, tensile strength of a rubber vulcanizate increases with the increase of the crosslink density.¹⁶ This can be explained by the filler dispersion. A filled rubber vulcanizate with a good filler dispersion will have a stronger tensile strength than that with a bad filler dispersion. Thus, it can lead to a conclusion that the PEG with a high molecular weight improves the silica dispersion better than the PEG with a low one.

The elongation at break of the vulcanizate, on the whole, increases with the PEG size as shown in Figure 12. The increment is about 2.9% per $1 \times 10^3 \text{ g/mol}$. This can be explained by the crosslink density. In general, elongation at break of a vulcanizate with a higher crosslink density is shorter than that of a vulcanizate with a lower one. The crosslink density of the vulcanizate decreases with increase of the PEG size as discussed previously.

The abrasion loss of the vulcanizate decreases by increasing the fatty acid size (Figure 13). The decrement is about 1.3 mg per $1 \times 10^3 \text{ g/mol}$. This is an unexpected result because the modulus de-

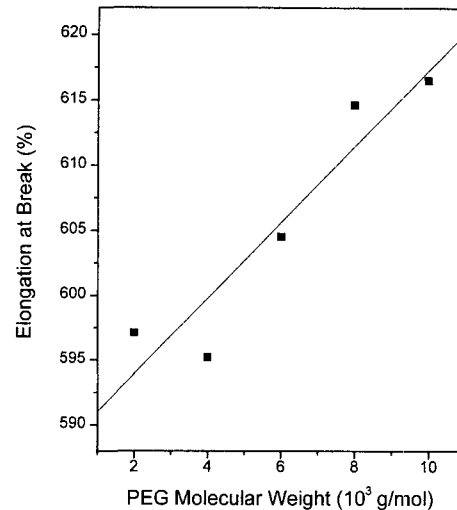


Figure 12. Variation of the elongation at break of the silica-filled NR vulcanizates as a function of the PEG size.

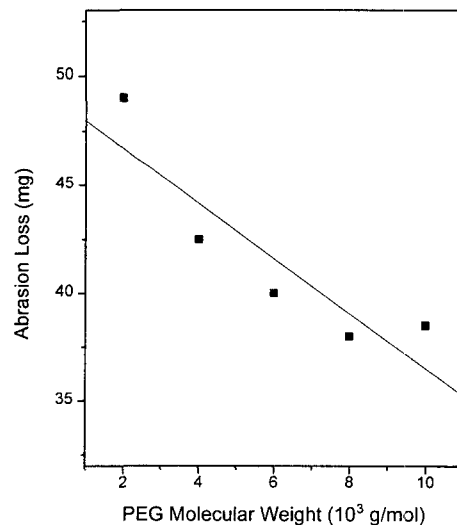


Figure 13. Variation of the abrasion loss of the silica-filled NR vulcanizates as a function of the PEG size.

creases with the increase of the PEG size as discussed above and the wear property is improved by increasing the modulus. This may be due to the filler dispersion. In general, a filled rubber vulcanizate with a good filler dispersion has a good wear property. Another evidence about a good dispersion when using the PEG with high molecular weight is the tensile strength as discussed above.

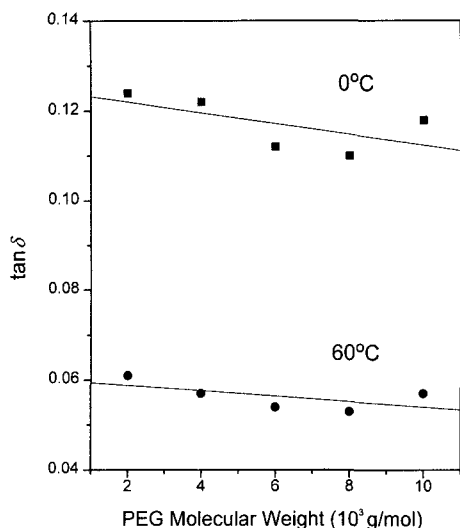


Figure 14. Variation of the $\tan \delta$ of the silica-filled NR vulcanizates as a function of the PEG size. Rectangles and circles indicate the $\tan \delta$ at 0 and 60°C, respectively.

The $\tan \delta$ at 0 and 60°C of the vulcanizate, on the whole, decrease with increasing the PEG size. The decrements are about 0.0012 and 0.0006 per 1×10^3 g/mol, respectively (Figure 14). This is a negligible variation.

Conclusions

Properties of the silica-filled NR compounds were affected by types of the fatty acids and poly(ethylene glycol)s. By increasing the fatty acid size, the delta torque decreased, the Mooney viscosity increased, and the moduli and the tensile strength decreased. By increasing the PEG size, the delta torque decreased, the Mooney viscosity increased, the moduli decreased, and the tensile strength increased. The cure rate became faster

with the increase of the PEG size. The PEG with a high molecular weight was better for the silica dispersion than the PEG with a low one.

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