Influence of Mixing Procedure on Properties of Rubber Compounds Filled with Both Silica and Carbon Black

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배합 공정이 실리카와 카본블랙으로 보강된 고무 배합물의 특성에 미치는 영향

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ABSTRACT : Silica-filled rubber compound needs longer mixing time compared to carbon black-filled one since it has poor dispersion of the filler. Influence of the mixing procedure on the properties of natural rubber compound filled with both silica and carbon black was studied. The discharge temperature of the master batch (MB) mixing was 150℃. The mixing time was longer when silica and carbon black were loaded separately than when loaded simultaneously. The mixing time was longer when silica was loaded first than when carbon black is loaded first. The compounds prepared by one MB step (conventional mixing) were compared with the compounds prepared by two MB steps (two-step mixing). Scorch times of the two-step mixing compounds were longer than those of the conventional mixing ones. Bound rubber contents of the formers were lower than those of the latters. The two-step mixing vulcanizates had longer elongation at break, higher tensile strength, and better fatigue life.

요 약 : 실리카로 보강된 고무 배합물은 보강제의 분산이 나쁘기 때문에 카본 블랙으로 보강된 배합물에 비해 더 긴 배합 시간이 필요하다. 실리카와 카본 블랙으로 보강된 천연 고무 배합물에서 배합 공정이 물성에 미치는 영향을 연구하였다. 마스터뱃치(MB) 배합물의 최종 온도를 150℃로 하였을 때, 실리카와 카본 블랙을 따로 투입하는 경우가 함께 투입하는 공정보다 배합 시간을 더 길게 가질 수 있었다. 실리카를 먼저 투입하는 것이 카본 블랙을 먼저 투입하는 것보다 배합 시간이 길었다. MB 배합 공정을 한 단계로 구성한 배합물과 두단계로 구성한 배합물을 비교하였다. 두 단계 공정으로 배합한 배합물의 스코치 시간이 한 단계 공정으로 만든 배합물의 스코치 시간보다 길었고 bound rubber 함량은 작았다. 두단계 공정으로 만든 가황물은 한단계 공정으로 만든 것에 비해 신율이 높고 인장 강도도 강하고 피로 특성도 우수한 것으로 나타났다.

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Ⅰ. Introduction

Mixing procedure is controlled to improve qualities of rubber compounds. Simple mixing process for filled rubber compounds is composed of master batch (MB) and final mixing (FM) stages. The fillers in MB stage include rubbers, fillers, processing aids, antidegradants, and curing activators of zinc oxide and stearic acid. In the FM stage, cure accelerators and sulfur are compounded into the MB compound. In general, in order to improve the dispersion of filler, it is loaded by dividing into 2 steps.[1,2] Properties of filled rubber compounds and their vulcanizates vary with the mixing conditions.[3-12] The mixing time on the content of bound rubber has been studied by several groups.[4-7] The content of bound rubber increases with mixing time while the molecular weight distribution of the rubber becomes lower by increasing the mixing time.

Filler dispersion of a silica-filled rubber compound is worse than that of a carbon black-filled one due to the strong filler-filler interactions of silica.[13-15] The polar surface of silica makes hydrogen bonds with polar materials in a rubber compound. Since the silica surface is acidic, especially it forms a strong hydrogen bond with basic materials. Cure accelerators of benzothiazole sulfenamides have basic functional groups such as amide (=NH) and they are adsorbed well on the silica surface. The adsorption of curatives by silica results in the 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 and in order to prevent adsorption of curatives on the silica surface.

Silica-filled rubber compound needs longer mixing time to disperse the fillers than carbon black-filled one. In the present work, the influence of mixing procedure on the properties of natural rubber compound filled with both silica and carbon black was studied. Mixing procedures with different MB steps were designed. Compounds prepared by two-step MB mixing procedure were compared with compounds prepared by one-step MB mixing procedure. Mixing procedures with different load sequence of fillers were compared.

Ⅱ. Experimental

The compounds had the same formulation of SMR 20 (standard Malaysian rubber, 100.0 phr), N330 (carbon black, 30.0 phr), Coupsil 8108 (silica treated with silane coupling agent, 30.0 phr), processing oil (2.0 phr), stearic acid (3.0 phr), zinc oxide (5.0 phr), wax (1.0 phr), HPPD (antiozonant, N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine, 2.0 phr), TBBS (cure accelerator, N-$tert$-butyl-2-benzothiazole sulfenamide, 2.2 phr), and sulfur (1.2 phr). Mixing of the compounds was performed in a Banbury type mixer at a rotor speed of 40 and 30 rpm for the master batch (MB) and final mixing (FM) stages, respectively. The initial temperatures of the mixer were 110 and 80℃ for the MB and FM stages, respectively. The MB compound included rubber, carbon black, silica, oil, cure activators (stearic acid and ZnO) and antidegradants (HPPD and wax). The MB compounds were discharged at 150℃. The FM compounds were prepared by mixing the MB compounds with the curatives and were discharged at 110℃. The MB compounds had different mixing procedures each other while the FM compounds had the same mixing procedure.

The MB compounds with different mixing procedures were prepared (Table 1). The C1, C2, and C3 compounds had only one MB stage (conventional mixing procedure). The T1 and T2 compounds had two MB stages (two-step mixing procedure). The conventional mixing compounds (C1, C2, and C3) were mixed until the temperature reached 150℃. The 1MB compounds of the two-step mixing compounds (T1 and T2) were mixed until the temperature reaches to 140℃ and

Table 1. Mixing Conditions for MB steps

Compound No.	C1	C2	C3	T1	T2
1MB step	Rubber (30 sec) + Carbon black + Silica + Ingredients 110 → 150℃ (300 sec)	Rubber (30 sec) + Carbon black + Ingredients 110 → 130℃ (150 sec) + Silica → 150℃ (330 sec)	Rubber (30 sec) + Silica + Ingredients 110 → 130℃ (140 sec) + Carbon black → 150℃ (380 sec)	Rubber (30 sec) + Carbon black + Ingredients 110 → 140℃ (200 sec)	Rubber (30 sec) + Silica + Ingredients 110 → 140℃ (250 sec)
2MB step				1MB + Silica 110 → 150℃ (270 sec)	1MB + Carbon black 110 → 150℃ (250 sec)
Total MB mixing time (sec)	300	330	380	470	500

the 2MB ones were compounded until the temperature reached 150℃.

The Compound C1 was prepared as follow. (1) The rubber was loaded into the mixer and premixed for 30 sec. (2) The fillers (silica and carbon black) and ingredients (oil, cure activators, and anti-degradants) were compounded into the rubber and mixed. (3) The compound was discharged at 150℃. The Compound C2 was prepared as follows. (1) The rubber was loaded into the mixer and premixed for 30 sec. (2) The carbon black and ingredients were compounded into the rubber and mixed until the temperature reached 130℃. (3) The silica was added and mixed and the compound was discharged at 150℃. The Compound C3 was prepared as follow. (1) The rubber was loaded into the mixer and premixed for 30 sec. (2) The silica and ingredients were compounded into the rubber and mixed until the temperature reached 130℃. (3) The carbon black was added and mixed and the compound was discharged at 150℃.

The 1MB T1 compound was prepared as follows. (1) The rubber was loaded into the mixer and premixed for 30 sec. (2) The carbon black and ingredients were compounded into the rubber and mixed. (3) The compound was discharged at 140℃. The 1MB T2 compound was prepared as follow. (1) The rubber was loaded into the mixer and

premixed for 30 sec. (2) The silica and ingredients were compounded into the rubber and mixed. (3) The compound was discharged at 140℃. The 2MB T1 and T2 compounds were prepared by mixing their 1MBs with silica and carbon black, respectively, until the temparature reached 150℃.

Cure characteristics were obtained with a Flexsys rheometer (MDR 2000) at a frequency of 100 cycles/min and ±1.5 arc at 160℃. Contents of bound rubber were determined by extraction of unbound materials such as ingredients and free rubbers with toluene for 7 days and n-hexane for 1 day and drying for 2 days at room temperature. Weights of the samples before and after the extraction were measured and the bound rubber contents were calculated. Total sulfur content was measured with a sulfur determinator (LECO SC-132). The relative component ratios of carbon black and metal oxide were determined using a TGA 2950 thermogravimetric analyzer of TA Instruments.

The vulcanizates were prepared by curing at 160℃ for 20 min. Crosslink densities of the samples were measured by a swelling method. Organic additives in the samples were removed by extracting with THF and n-hexane for 3 and 2 days, respectively, and they were dried for 2 days at room temperature. The weights of the organic material-extracted samples were measured. They were

soaked in *n*-decane for 2 days and the weights of the swollen samples were measured. Physical properties of the vulcanizates were measured with a Universal Testing Machine (Instron 6021). Fatigue life was measured with a Monsanto Fatigue-To-Failure Tester.

Ⅲ. Results and Discussion

1. Mixing time

The discharge temperature was set at 150℃. The total MB mixing time varies with the load sequence of materials. For the conventional mixing procedures (composed of one MB step), Compounds C2 and C3 with the separate load sequence of the fillers have longer total mixing time than Compound C1 with the simultaneous load sequence. This is due to the highly loaded filler content at the beginning for Compound C1. Heat is generated in the mixer by friction between between the matrix and mixer surface and between the matrices (filler and rubber) during the mixing and so the temperature increases. The heat is generated faster and faster by friction of the fillers as the filler content increases in the mixer. The mixing time of Compound C3 prepared by the first load of silica is longer than that of Compound C2 prepared by the first load of carbon black.

For the two-step mixing procedures, the silica 1MB compound (T2) has longer mixing time than the carbon black 1MB compound (T1). The total MB mixing times of the two-step mixing compounds (T1 and T2) are longer than those of the conventional mixing ones (C1, C2, and C3). This is due to the cool 1MB compound of the two-step mixing procedure. For the two-step mixing procedure, the 1MB compounds had cooling time of about 2 hours after discharge and cooled down to room temparature before the 2MB mixing. The cold compound needs extra mixing time to be heated.

2. Cure characteristics

Cure characteristics of the compounds were investigated at 160℃. The results were summarized in Table 2. The minimum torque (T_{min}) reflects the viscosity. The lower the T_{min} is, the lower the viscosity is. The T_{min} of the two-step mixing compounds are lower than those of the conventional ones. This is due to the total mixing time. The total mixing times of the two-step mixing compounds are much longer than those of the conventional ones (Table 1). The delta torque is correlated closely with the crosslink density since the torque is increased by crosslinking reactions. The C1 compound has lower delta torque than the other compounds.

The t_5 (scorch time), t_{40}, and t_{95} (optimum cure time) mean the times taken for the torque in a rheograph to reach from the minimum point to 5, 40, and 95% of the delta torque, respectively. The t_5 is used as the starting point to occur the crosslinking reaction. The cure rate index is the reciprocal of the difference between t_{95} and t_5, $1/(t_{95} - t_5)$. For the conventional mixing procedures, the t_{40} and t_{95} of the separately loaded compounds (C2 and C3) are slower than that of the simultaneounsly loaded one (C1) while the t_5 are the same. This is due to the total mixing time. The t_{40} and t_{95} become slower as the mixing time increases.[12] The cure rate index varies with the mixing time. The cure rate index becomes slower with mixing time. For the two-step mixing procedures, the t_{40}, t_{95}, and cure rate index show the same trend as the conventional mixing procedures. The t_{40}, t_{95}, and cure rate index of the T2 with longer mixing time are slower than

Table 2. Cure Characteristics

Compound No.	C1	C2	C3	T1	T2
T_{min} (N·m)	0.57	0.59	0.59	0.54	0.53
T_{max}(N·m)	2.65	3.07	3.08	3.04	2.92
Delta torque(N·m)	2.08	2.48	2.49	2.50	2.39
t_5(min)	2.17	2.17	2.17	2.28	2.27
t_{40}(min)	4.18	4.27	4.45	4.20	4.48
t_{95}(min)	6.95	7.00	7.13	6.85	7.08
Cure rate index(min^{-1})*	0.209	0.207	0.202	0.219	0.208

* Cure rate index = $1/(t_{95} - t_5)$

those of the T1 with shorter one. Considering the total mixing time, however, the two-step mixing compounds have faster cure rate compared to the conventional mixing compounds.

3. Chemical analysis

Bound rubber is an important factor in reinforcement. Bound rubber is a parameter which is simple to measure but the factors which influence the test results are very complicated. The filler-polymer interaction leading to the formation of bound rubber involves physical adsorption, chemisorption, and mechanical interaction. Moreover, bound rubber also shows a dependence on the processing conditions of the compound, such as mixing and storage times. The bound rubber contents were summarized in Table 3.

For the conventional mixing procedures, the bound rubber content has an order of C1 < C2 < C3. This is because the mixing time increases with the same order of C1 < C2 < C3. Bound rubber content increases with increase in the mixing time.[12] For the two-step mixing procedures, the bound rubber contents are nearly the same. Bound rubber contents of the conventional mixing compounds are higher than those of the two-step mixing ones, though the total mixing times of the formers are shorter than those of the latters. This may be due to the decreased molecular weight. Scission of rubber chains occurs during the mixing by shear force,[16-20] which leads to the decreased molecular weight. Bound rubber content depends on the molecular weight of a rubber chain.[21,22] Bound rubber content decreases as the molecular weight of a polymer decreases. The two-step mixing compounds were prepared by mixing for longer time compared to the conventional mixing compounds and extra shear force was applied to their 1MB compounds in the 2MB mixing stage. Thus, the rubber chain scission will be more progressed and the molecular weight will be also decreased. If the rubber is incorporated sufficiently into the fillers, the too long mixig time results in decrease of the

Table 3. Chemical Analysis

Compound No.	C1	C2	C3	T1	T2
Bound rubber content (%)	35.08	37.28	38.64	33.36	33.96
Total sulfur content (wt%)	1.37	1.36	1.39	1.38	1.36
Carbon black content (wt%)	17.24	17.80	17.70	17.90	17.48
Metal oxide content (wt%)	17.57	18.01	17.49	18.10	18.06
1/Q*	0.950	1.008	1.028	1.008	0.983

* reciprocal of the swelling ratio

bound rubber content due to the rubber chain scission.

Cure characteristics of a filled rubber compound are affected by the type and content of materials in the compound. Especially, curatives affect significantly the cure time, cure rate, and delta torque. Contents of sulfur, carbon black, and metal oxide (silica and zinc oxide) were measured in order to investigate the influence of weighing error for the materials on the cure characteristics and physical properties. The results were listed in Table 3. The total sulfur content and filler contents are nearly the same irrespective of the compounds. This implies that the variation of the properties with the mixing procedure does not result from the weighing error.

Physical properties of a rubber vulcanizate cured by the accelerated sulfur cure system depend on the crosslink density.[23] The crosslink densities were measured with a swelling method. The swelling ratio is correlated closely to the crosslink density. The swelling ratio was calculated: $Q = 100 \times (W_s-W_u)/W_u$, where W_s and W_u are weights of the swollen and unswollen samples. The reciprocal swelling value, $1/Q$, was used as crosslink density.[24] For the conventional mixing vulcanizates, the crosslink density increases with mixing time: the order of C1 < C2 < C3. The crosslink density of the C1 vulcanizate is much lower than those of the C2 and C3 ones. For the two-step mixing vulcanizates, the crosslink density of the T1 vulcanizate is slightly higher than that of the T2 one.

4. Physical properties

The physical properties were summarized in

Table 4. Physical Properties

Compound No.	C1	C2	C3	T1	T2
Hardness (Shore A)	61.0	63.0	62.0	62.0	60.0
50% Modulus (kg/cm^2)	13.8	14.6	14.5	14.2	13.2
100% Modulus (kg/cm^2)	25.5	27.2	26.6	26.3	23.4
200% Modulus (kg/cm^2)	67.8	73.8	73.6	72.1	65.0
300% Modulus (kg/cm^2)	129.9	137.4	137.9	135.1	125.3
Tensile strength (kg/cm^2)	249.6	283.9	259.1	285.1	288.6
Elongation at break (%)	479.5	530.3	485.6	539.8	558.6
Fatigue life (10^3 cycles)	57.3	71.3	69.1	72.0	96.6

Table 4. For the conventional mixing vulcanizates, the physical properties of the C2 and C3 ones with the separate load sequence are better than those of the C1 one with the simultaneous load sequence. The vulcanizates prepared with the separate load sequence have higher tensile strength, longer elongation at break, and longer fatigue life as well as higher modulus than the vulcanizate prepared with the simultaneous load sequence. This is because the formers have better filler dispersion as well as higher crosslink density than the latter. Modulus is a proportional property to the degree of crosslink density, while elongation at break is an inversely-proportional property to the degree of crosslink density.

The C1 and T1 vulcanizates have almost the same crosslink density. The physical propreties of both vulcanizates do not show a big difference as demonstrated in Table 4. Elongation at break and fatigue life reflect flexibility of a vulcanizate. The flexibility is dependent on degree of the filler dispersion when compounds have the same formulation. Thus, it can lead to a conclusion that the two-step mixing procedure is not much favorable to improve the filler dispersion compared to the conventional mixing procedure though the two-step mixing procedure has longer mixing time when carbon black is loaded first.

The T2 vulcanizate has longer elongation at break and higher tensile strength than the T1 one. Especially, the fatigue life of the T2 vulcanizate is much longer than that of the T1 one. This implies that the T2 compound has better filler dispersion than the T1 one. becouse of to the longer mixing time of silica. Since silica has lots of hydroxyl groups to cause the strong filler-filler interactions, filler dispersion of a silica-filled rubber compound is worse than that of a carbon black-filled one. Thus, for rubber compounds filled with both silica and carbon black, the longer mixing time for silica is more favorable to improve the filler dispersion than the longer mixing time for carbon black.

Ⅳ. Conclusion

Properties of filled rubber compounds were found to vary with the mixing procedures while they have the same formulation. The two-step mixing procedure has longer mixing time than the conventional one (one-step mixing procedure) when the discharge temperature is set the same. For the two-step mixing procedures, the filler dispersion is better when silica is loaded first (the silica 1MB, T2) than when loading carbon black first (the carbon black 1MB, T1). For the mixing procedures of the first load of carbon black, the physical properties of the two-step mixing vulcanizate (T1) is not much better than those of the conventional mixing one (C2) cobile the two-step mixing compound has longer mixing time.

Acknowledgement

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