

Influence of Mixing Procedure on Properties of Carbon Black-filled Natural Rubber Compounds

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Abstract : Cure characteristics and physical properties of carbon black-filled natural rubber (NR) compounds depending on the mixing procedure were studied using the compounds with different pre-final mixing (FM-1) stages. Carbon master batch (MB) and first and second remilling (1RM and 2RM) stages were employed as the FM-1 stage. Bound rubber content of the FM compound decreased with increasing the mixing steps. This was due to the decrease of the molecular weight distribution of the polymer by the rubber chain scission during the mixing. The Mooney viscosity decreased with increasing the mixing steps. Cure characteristics of the compounds were found to be different with the mixing precedures. The cure times of the compound became slower by increasing the number of the mixing steps. This was explained by the length of rubber chain, the carbon black network, distribution of the curatives in the compound, and immobilization of the polymeric segments. Modulus and tensile strength of the vulcanizate did not show a specific trend with the mixing procedure. Fatigue life of the vulcanizate increased by increasing the mixing stages.

Introduction

Cure characteristics of filled rubber compounds depend on contents and kinds of rubbers, fillers, curatives, and ingredients. Mixing procedure is controlled to improve qualities of rubber compounds. Simple mixing process for carbon black-filled rubber compounds is composed of carbon master batch (CMB or MB) and final mixing (FM) stages. The MB stage includes 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.

Properties of filled rubber compounds and their vulcanizates vary with the mixing conditions.¹⁻⁷ Cotton¹ studied the influence of mixing temperature on contents of bound rubber using carbon black-filled rubber compounds and reported that the contents of bound rubber increased by increasing the mixing temperature. Influence of mixing time

on the content of bound rubber was studied by several groups.^{2,5} The content of bound rubber increases with an increase of the mixing time while molecular weight distribution of the rubber becomes lower by increasing the mixing time.

In general, remilling (RM) for the MB compound is performed to improve the miscibility of filled rubber compounds. In the present work, the influence of the mixing procedure on cure characteristics of rubber compounds was studied using carbon black-filled natural rubber (NR) compounds with different pre-final mixing (FM-1) stages of the MB, first remilling (1RM), and second remilling (2RM) stages. Properties of the compounds and their vulcanizates were also investigated.

Experimental

The carbon black-filled NR compound was composed of SMR CV60 as NR, N330 as carbon black, antidegradants (HPPD and wax), curing activators (stearic acid and ZnO), and curatives (TBBS and sulfur). The formulations were given in

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Table I. Formulations (phr)

Compound No.	1	2	3	4	5	6
SMR CV60	100.0	100.0	100.0	100.0	100.0	100.0
N330	70.0	70.0	70.0	70.0	70.0	70.0
ZnO	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	3.0	3.0	3.0	3.0	3.0	3.0
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	0.6	0.6	0.6	2.4	2.4	2.4
Sulfur	1.8	1.8	1.8	0.8	0.8	0.8
First Remilling (1RM)	No	Yes	Yes	No	Yes	Yes
Second Remilling (2RM)	No	No	Yes	No	No	Yes

SMR CV60: standard malaysian rubber.

N330: carbon black.

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

TBBS: *N*-*tert*-butyl-2-benzothiazole sulfenamide.

Table I. The mixing process was composed of four stages; carbon black master batch stage (MB), first and second remilling stages (1RM and 2RM), and final mixing stage (FM). The compounds obtained from the MB, 1RM, and 2RM stages were used as the FM-1 compounds. Mixing for the MB, 1RM, and 2RM stages were performed with a Banbury mixer at a rotor speed of 40 rpm. The initial temperature of the mixer was 110. The FM stage was carried out in a two-roll mill whose temperature was kept at 100 during mixing.

The MB compounds included the rubber, carbon black, antidegradants, and curing activators. The mixing times of the MB, 1RM, and 2RM stages were 2.0 min while that of the FM stage was 4.0 min. The FM compounds were prepared by mixing the curatives with the FM-1 compound. The Compounds 1 and 4, 2 and 5, and 3 and 6 have the MB, 1RM, and 2RM stages as the FM-1 stage, respectively. Two cure systems of conventional and efficient vulcanization (EV) cure systems were employed. The EV cure system is a vulcanizing system with low sulfur and high accelerator content while the conventional cure system is a vulcanizing system with high sulfur content. The vulcanizate cured by the EV cure system has low polysulfide and high mono- and disulfides. The compounds 1-3 and 4-6 have the conventional and EV cure systems, respectively.

Viscosities of the compounds were measured using a Mooney viscometer MV 2000 of Alpha Technologies. Contents of bound rubber were determined by extraction of unbound materials including ingredients and free rubbers with toluene for 7 days and with *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. Cure characteristics were obtained using a Flexsys rheometer (MDR 2000) at a frequency of 100 cycles/min and ± 1.5 arc at 145 and 160°C.

The vulcanizates were prepared by curing at 160°C 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. Fatigue life was measured using a Monsanto Fatigue-To-Failure Tester.

Results and Discussion

Viscosity and Bound Rubber. Viscosity of a rubber compound is a very important property in manufacturing of rubber goods. Filled rubber compounds should have proper viscosities to meet good extrusion and calendaring properties.

Table II. Mooney Viscosities, Bound Rubber Contents, and Sulfur Contents of Compounds

Compound No.	1	2	3	4	5	6
Mooney Viscosity (ML 1+4)						
FM-1 Compounds at 120°C	146.7	103.8	89.9	146.7	103.8	89.9
FM Compounds at 100°C	98.8	91.3	86.8	97.7	84.5	80.5
Content of Bound Rubber (%)						
FM-1 Compounds	48.25	53.17	50.79	48.25	53.17	50.79
FM Compounds	53.16	51.96	50.65	50.13	50.02	49.64
Sulfur Content (wt%)	1.60	1.57	1.50	1.32	1.28	1.21

Viscosity and degree of carbon black incorporation of carbon black-filled compounds are changed with the degree of mixing. Mooney viscosities of the FM-1 and FM compounds were measured. The results were summarized in Table II. The Mooney viscosities of the FM compounds were measured at 100°C but those of the FM-1 compounds were measured at 120°C because their initial viscosities were very high. The viscosity of the RM compound is much lower than that of the MB one. This can be explained by the carbon black incorporation and by chain scission of rubber molecules. Viscosities of rubber compounds become lower during the mixing by shear force⁸⁻¹² which leads to scission of rubber chains. Viscosity of a rubber decreases by increasing the mixing time.^{9,10} The chain scission results in decrease of the molecular weight distributions.^{11,12} Viscosities of rubber compounds containing the polymers with a high molecular weight distribution are higher than those containing the polymers with a low one.⁸⁻¹²

Carbon black is incorporated and dispersed in the rubber during the mixing. In general, the incorporation process refers to the wetting of carbon black with rubber and squeezing out entrapped air. It is suggested that during the initial mixing stage the carbon black is compressed by the polymer into many discrete cavities. At that time, the carbon black is being crushed by the shearing and compressive forces. Subsequently, rubber is forced into those voids and air is expelled. Carbon black-filled compounds mixed under the conditions of a long mixing time and a high rotor speed have a better dispersion of carbon black than those mixed under the conditions

of a short mixing time and a low rotor speed.¹³

Since carbon black has a highly structured aggregate, it forms with ease large flock-like agglomerate. The carbon black particles and agglomerates are arranged and the agglomerates can touch or interfere with one other immediately after the incorporation. This interference between agglomerates with some bonding at the points of interference (points of mutual contact) could manifest itself as a network of agglomerates. As these agglomerates become dispersed as isolated aggregates, of course, the agglomerate-agglomerate network would disappear. Aggregate-agglomerate networks could still form even after mixing.¹⁴

The viscosity of the MB compound is higher than those of the RM ones and the viscosity of the 1RM compound is higher than that of the 2RM one. This is due to the effect of total mixing time. The viscosity of the compound decreases with increasing the mixing time and mixing stage. The viscosity of the FM compound made of the MB compound is also higher than that of the FM compound made of the RM compound. This is due to the viscosity of the FM-1 compound. The difference in the viscosities of the MB and 1RM compounds (about 43 MU) is much larger than that of the 1RM and 2RM compounds (about 14 MU). The differences in the Mooney viscosities of the FM compounds made of the MB and 1RM compounds are 7.5 and 13.2 MU for the compounds with the conventional and EV cure systems, respectively, while those of the FM compounds made of the 1RM and 2RM compounds are 4.5 and 4.0 MU, respectively. This is due to the viscosity of the FM-1 compound. The shear force applied to rubber compounds during the mixing

causes scission of rubber chains. The rubber chain scission results in lowering of molecular weight distribution of the rubber and decrease of its viscosity. Shear force is more applied to a rubber compound when its initial viscosity is high than when it is low. Since the viscosity of the MB compound is higher than that of the 1RM one, the shear force applied to the MB compound is higher than that applied to the 1RM one. Thus, the viscosity drop between the MB and 1RM compounds is much larger than that between the 1RM and 2RM ones by about 30 MU as discussed in previously.

Contents of bound rubber of the filled compounds are correlated closely with the degree of carbon black incorporation and the length of rubber molecules. The bound rubber contents of the RM compounds are higher than that of the MB one as listed in Table II. This is because carbon black becomes incorporated into the polymer more and more by increasing the mixing stage. However, the bound rubber content of the 1RM compound is higher than that of the 2RM one. This is due to the decrease of the molecular weight by the rubber chain scission. By increasing the mixing stages, carbon black is more and more incorporated into the polymer while at the same

time the rubber chain scission also occurs more and more. This can lead to a conclusion that the incorporation of carbon black is more dominant factor than the rubber chain scission at the beginning of the mixing, and the rubber chain scission occurs predominantly when the incorporation is fully carried out. The bound rubber content of the FM compound decreases as the FM-1 stage changes from MB to 2RM stage. This can be also explained by the rubber chain scission as discussed above.

Cure Characteristics. Cure characteristics of the compounds with the different mixing conditions were investigated at 145 and 160°C. Figures 1-5 show the minimum torque (T_{min}), delta torque ($T_{max} - T_{min}$), scorch time (t_{02} , t_{40}), and optimum cure time (t_{90}). The T_{min} decreases with an increase of the FM-1 stage. This is due to the viscosities of the FM compounds. The T_{min} is very closely related to the viscosity. The lower the viscosity of the compound is the lower the T_{min} is. The delta torque of the compound corresponds to degree of the crosslink density of its vulcanizate. The delta torques of the compounds with the same cure system do not show a specific difference

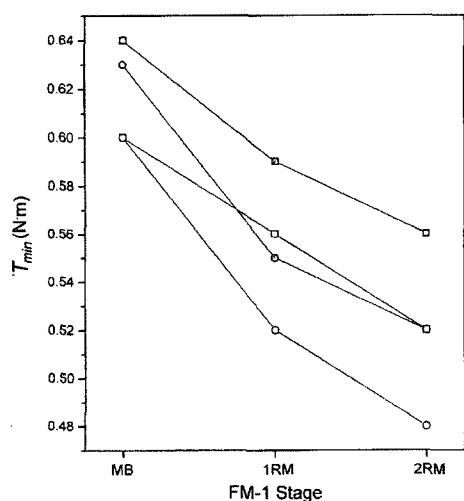


Figure 1. Variation of the minimum torque (T_{min}) of the compounds with the FM-1 stage. Closed and open symbols indicate the measurement temperatures of 145 and 160°C, respectively. Rectangles and circles stand for the conventional and EV cure systems, respectively.

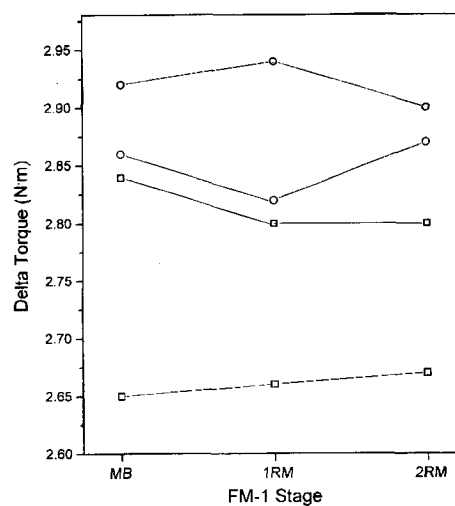


Figure 2. Variation of the delta torque of the compounds with the FM-1 stage. The delta torque is the difference between the maximum and minimum torques ($T_{max} - T_{min}$). Closed and open symbols indicate the measurement temperatures of 145 and 160°C, respectively. Rectangles and circles stand for the conventional and EV cure systems, respectively.

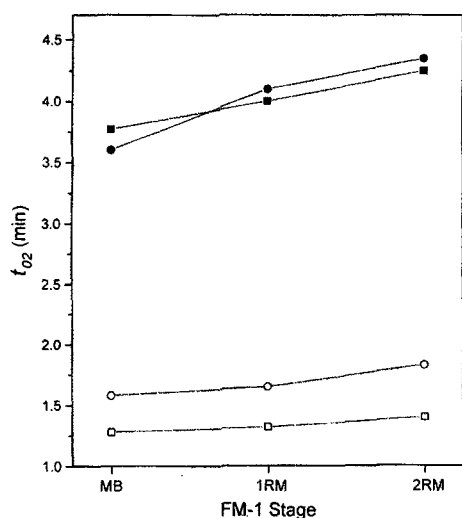


Figure 3. Variation of the scorch time (t_{02}) of the compounds with the FM-1 stage. Closed and open symbols indicate the measurement temperatures of 145 and 160°C, respectively. Rectangles and circles stand for the conventional and EV cure systems, respectively.

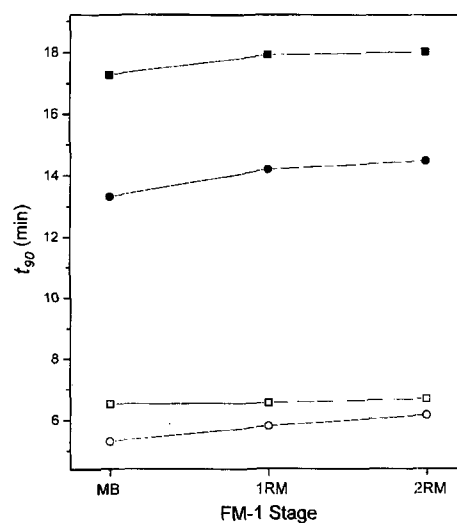


Figure 5. Variation of the optimum cure time (t_{90}) of the compounds with the FM-1 stage. Closed and open symbols indicate the measurement temperatures of 145 and 160°C, respectively. Rectangles and circles stand for the conventional and EV cure systems, respectively.

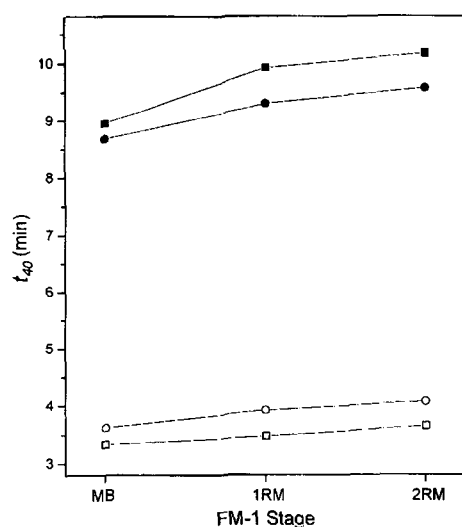


Figure 4. Variation of the t_{40} of the compounds with the FM-1 stage. Closed and open symbols indicate the measurement temperatures of 145 and 160°C, respectively. Rectangles and circles stand for the conventional and EV cure systems, respectively.

depending on the mixing procedure. The delta torques of the compounds with the conventional cure system at 145/160°C are 2.84/2.65, 2.80/2.66, and 2.80/2.67 N·m for the FM compounds

made of the MB, 1RM, and 2RM compounds as the FM-1 compound, respectively, while those with the EV one are 2.92/2.86, 2.94/2.82, and 2.90/2.87 N·m, respectively. Thus, we can say that the delta torque is hardly affected by the mixing procedure.

The t_{02} , t_{40} , and t_{90} increase as the FM-1 stage becomes longer from the MB to the 2RM stage. This is very interesting because the compounds have the same formulations. Cure characteristics of carbon black-filled rubber compounds with a sulfur-accelerated cure system are affected by kinds and contents of materials in the compounds. If the compounds are composed of the same kind and the same content of rubber and carbon black, the cure characteristics are affected predominantly by contents of the curatives. Sulfur contents of the compounds were measured using a sulfur determinator (LECO SC-132) in order to check the error about the weight measurement of the raw curatives. The sulfur contents of the compounds with the same cure system are nearly same as listed in Table II. This implies that there are sources to occur the difference in the cure characteristics of the FM compounds made of the different FM-1 compounds. This may be due to

the different states of the compounds such as degree of carbon black incorporation, molecular weight distribution of rubber, filler-filler interactions, filler-polymer interactions, and so forth.

The FM compounds prepared by the different mixing process will have different viscosities, bound rubber contents, rubber chain length, and degree of carbon black networks. As discussed previously, the viscosity affects the minimum torque. By increasing the mixing stages, the carbon black is more incorporated into the rubber and filler-polymer interactions are enhanced. A better dispersion of the filler leads to reduction of filler networks. The filler-polymer interaction results in additional immobilization of polymeric segments.¹⁵ The torque in the rheograph of the rubber compound begins to increase by the crosslinking reactions which occur mainly between rubber chains. When the compounds have the same formulation, the torque of the compound made of long chain polymers will increase faster than that of the compound made of short ones. If there are agglomerate-agglomerate networks or aggregate-aggregate networks in a carbon black-filled rubber compound, viscosity and green strength of the compound will increase.

One of the principal reasons about the increase of the cure times by increasing the mixing stages may be difference in distribution of the curatives in the agglomerates and the free rubber. Ahagon^{8,16,17} reported that since the high concentration of carbon black reduced the solubility and the diffusivity of the curatives in the polymer, the

distribution of the curatives into the agglomerate phase was suppressed so that the crosslinking reaction occurred mainly in the free rubber phase and less in the agglomerate phase. The agglomerate phase exists more in the compound made by the short mixing procedure than in the compound made by the long one. Therefore, since the concentration of the curatives in the free polymer phase of the compound decreases with increasing the mixing procedure, the t_{02} , t_{40} , and t_{90} of the compounds made by the short mixing procedure will be faster than those of the compounds made by the long one.

Some part of the bound rubber chain is fixed to carbon black (tightly or loosely bound to the filler) so its motion is restricted. The immobilization of the polymeric segments leads to slow rate of crosslinking reaction since two reaction sites have to meet to form a crosslink between rubber chains. Since the degree of carbon black incorporation increases with increasing the mixing stage, the compound prepared by the long mixing procedure has the immobilized polymeric segments more than the compound prepared by the short one. Thus, the cure rate of the compound becomes slower as the number of the mixing stages increases.

Physical Properties. Tensile properties and abrasion resistance of the vulcanizates were measured. Table III gives the results for hardness, modulus, tensile strength, elongation at break, tear resistance, and abrasion resistance of the vulcanizates. The hardness, moduli at low strains,

Table III. Physical Properties of Vulcanizates

Compound No.	1	2	3	4	5	6
Hardness (Shore A)	71.0	71.0	71.0	74.0	73.0	73.0
50% Modulus (kg/cm ²)	18.6	18.9	18.5	21.9	21.7	20.9
100% Modulus (kg/cm ²)	35.6	36.7	35.9	46.0	45.3	43.4
200% Modulus (kg/cm ²)	99.7	104.7	102.6	126.8	128.2	126.7
300% Modulus (kg/cm ²)	168.8	175.9	174.1	198.7	205.1	204.6
Tensile Strength (kg/cm ²)	266.7	259.5	263.6	264.3	258.8	273.3
Elongation at Break (%)	492.2	458.3	467.3	418.6	390.7	417.8
Tear Resistance (kg/cm)	87.0	84.5	87.5	96.5	96.5	96.0
Abrasion Loss (mg)	25.0	27.5	26.5	21.5	26.0	25.0
Fatigue Life (10 ³ cycles)	109.59	112.10	121.69	52.58	57.48	63.01

tensile strength, and tear resistance of the vulcanizates with the same cure system are, on the whole, nearly the same, irrespective of the mixing procedure. The modulus at 300% strain of the vulcanizate made of the RM compounds is slightly higher than that of the vulcanizate made of the MB compound. The elongation at break of the vulcanizate made of the RM compounds is slightly shorter than that of the vulcanizate made of the MB compound. This can be explained by the rubber chain length. The length of rubber chain in the compound made by the long mixing procedure is shorter than that in the compound made by the short one.

Amounts of the abrasion loss of the vulcanizate made of the RM compounds are higher than that of the vulcanizate made of the MB compound, especially for the vulcanizates with the EV cure system. This can be also explained by the rubber chain length. Abrasion properties of rubber vulcanizates are closely related with the rubber chain length. A rubber vulcanizate with a long rubber chain has a better wear resistance than a vulcanizate with a short one. Fatigue life of the vulcanizate with the long mixing procedure is longer than that of the vulcanizate with the short one as shown in Table III. This can be explained by the carbon black dispersion. Homogeneity of a filled rubber compound depends on degree of the filler dispersion. Since the fatigue life test of a rubber vulcanizate is performed under the repeated motion of extension and contraction with a constant strain, the stress will be concentrated on the less homogeneous phase. If the carbon black is not dispersed well into the polymer, the stress will be concentrated on the point where the carbon black is clustered. Thus, the fatigue life of the vulcanizate with a good homogeneity is longer than that of the vulcanizate with a poor one.

Conclusion

Properties of the carbon black-filled NR compounds and their vulcanizates were found to be different with the mixing procedure although they had the same formulation. The viscosity of the compound decreased by increasing the mixing procedure. The cure times such as the t_{90} , t_{40} , and

t_{30} of the compound became slower as the number of the mixing stages increases. Hardness, modulus, tensile property, and tear resistance of the vulcanizates did not show a big difference with the mixing procedure. The abrasion resistance of the vulcanizate made of the short mixing procedure was better than that of the vulcanizate made of the long one. The fatigue life of the vulcanizate became longer by increasing the mixing procedure. Differences in the properties of the compounds and the vulcanizates depending on the mixing procedure were explained by the degree of the filler dispersion, the bound rubber content, the length of the rubber molecules, difference in distribution of the curatives in the free polymer phase and the agglomerate phase, and the immobilized polymeric segments.

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