

Preblending Effect of Biblends on Properties of the Carbon Black-Filled Rubber Compounds

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Abstract : A premixing effect for the properties of carbon black-filled rubber compounds was investigated using biblends of natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR). Degree of mixing of the biblends was controlled by preblending time of 0.0, 2.5, and 5.0 min. Mooney viscosities of the compounds decreased by increasing the preblending time. Of three carbon black-filled compounds of NR/SBR, NR/BR, and SBR/BR compounds, only the SBR/BR blends showed a specific cure characteristics depending on the preblending time. For the bound rubber composition, the NR content was higher than SBR and BR. The difference in the rubber composition ratio of the bound rubber became smaller with increasing the preblending time. Physical properties of the vulcanizates such as hardness, modulus, tensile property, abrasion loss, and $\tan\delta$ were also compared. Differences in properties of the compounds were discussed with miscibility of the dissimilar rubbers and degree of mixing.

Introduction

Given the economic and technical uncertainties associated with synthesizing new polymeric materials, the utilization of polymer mixtures to achieve a desired combination of properties has obvious attraction. Blends of elastomers¹⁻⁵ are employed in rubber products for a variety of reasons which include improved physical properties, increased service life, easier processing, and reduced product cost. However, there are technological problems arising from some types of mutual incompatibility which can exist between dissimilar elastomers.⁶ Three types of incompatibility have generally been noted; incompatibility due to viscosity mismatch, thermodynamic incompatibility, and incompatibility due to cure rate mismatch.

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.⁷⁻¹³ Cotton⁷ studied the influence of mixing temperature on contents of bound rubber using carbon black-filled rubber compounds and reported that the bound rubber contents increased with the mixing temperature. Influence of the mixing time on the content of bound rubber was studied by several groups.⁸⁻¹¹ The bound rubber content increases with an increase of the mixing time while molecular weight distribution of the rubber becomes lower by increasing the mixing time. In the present work, preblending effect of biblends of raw rubbers on properties of the filled rubber compounds was studied using carbon black-filled binary rubber-based compounds of natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR).

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Table I. Formulations (phr)

Compound No.	1	2	3	4	5	6	7	8	9
SMR CV60	50.0	50.0	50.0	50.0	50.0	50.0	0.0	0.0	0.0
SBR 1500	50.0	50.0	50.0	0.0	0.0	0.0	50.0	50.0	50.0
BR 01	0.0	0.0	0.0	50.0	50.0	50.0	50.0	50.0	50.0
N330	70.0	70.0	70.0	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	5.0	5.0	5.0
Stearic acid	3.0	3.0	3.0	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	2.0	2.0	2.0
Wax	2.0	2.0	2.0	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	1.4	1.4	1.4
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Preblending Time (min)	0.0	2.5	5.0	0.0	2.5	5.0	0.0	2.5	5.0

SMR CV60: standard malaysian rubber with constant viscosity 60.

N330: carbon black.

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

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

Experimental

Carbon black-filled rubber compounds of blends of 50/50 NR/SBR, NR/BR, and SBR/BR were prepared. The formulations are given in Table I. In order to prepare the compounds with different miscibility of the two raw rubbers, raw rubbers were before the carbon masterbatch (MB) stage. The preblending times were 0.0, 2.5, and 5.0 min. The preblending in the MB stage was performed with a Banbury mixer at a rotor speed of 40 rpm. The initial temperature of the mixer was 110°C. The FM was carried out in a two-roll mill. The roll temperature was kept at 100°C during mixing. The mixing time of the MB stage was 2.5 min while that in the FM one was 4.0 min. The MB compounds included rubbers (raw rubbers and premixed blends), carbon black, antidegradants (HPPD and wax), and curing activators (stearic acid and ZnO). The FM compounds contained the MB compound and the curatives (sulfur and TBBS).

Viscosities of the compounds were measured using a Mooney viscometer MV 2000 of Alpha Technologies. The contents of bound rubber were determined by extraction of unbound materials including ingredients and free rubbers with toluene for 7 days and *n*-hexane for 1 day, followed

by drying for 2 days at room temperature. The weights of the samples before and after extraction were measured and the bound rubber contents were calculated. Composition of the bound rubber was determined using pyrolysis-gas chromatography (Py-GC). Pyrolysis-GC chromatograms of the samples were obtained with a Curie point pyrolyzer JHP-22 and an HP5890 gas chromatograph. The sample (0.6 ± 0.1 mg) was pyrolyzed at 590°C for 5 sec. The analytical conditions for the Py-GC have been described in detail elsewhere.¹⁴ 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 30 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. $\tan\delta$ of the vulcanizates were measured according to ASTM D2231-87 with a Qualimeter Eplexor 150N of Gabo company.

Results and Discussion

Viscosity. Viscosity of a rubber compound is a very important property in manufacturing rubber goods. Filled rubber compounds should have

Table II. Mooney Viscosity, Content and Composition of Bound Rubber

Compound No.	1	2	3	4	5	6	7	8	9
Mooney viscosity (ML1+4) at 100 °C									
FM compounds	82.7	81.9	81.4	94.6	92.7	91.4	102.3	101.4	100.6
Content of bound rubber (%)									
MB compounds	29.27	28.96	28.53	31.91	31.66	32.19	20.01	19.68	20.75
FM compounds	34.89	35.68	35.59	43.19	42.84	41.36	27.91	28.28	28.34
Rubber composition of the bound rubber									
	NR/SBR	NR/SBR	NR/SBR	NR/BR	NR/BR	NR/BR	SBR/BR	SBR/BR	SBR/BR
MB compounds	63/37	60/40	58/42	62/38	59/41	54/46	44/56	47/53	48/52
FM compounds	58/42	56/44	55/45	61/39	60/40	58/42	44/56	46/54	50/50

proper viscosities to meet good extrusion and calendaring properties. Viscosities of rubber compounds become lower during the mixing by shear force arising from scission of rubber chains.¹⁵⁻¹⁹ The chain scission results in the increase of the molecular weight distributions.^{18,19} Viscosities of rubbers or rubber compounds with a high molecular weight are higher than those with a low one.¹⁵⁻¹⁹

The variation of the Mooney viscosities of the compounds with the preblending time is shown in Table II. The Mooney viscosity decreases with an increase of the preblending time, irrespective of the kinds of the biblends. The Mooney viscosities of the NR/SBR, NR/BR, and SBR/BR compounds decrease from 82.7 to 81.4, from 94.6 to 91.4, and from 102.3 to 100.6 by preblending for 5.0 min, respectively. This may be due to the rubber chain scission by the shear force during the preblending.

Bound Rubber Content. Carbon black is incorporated and dispersed in the rubber during the mixing. The amount of bound rubber in carbon black-filled rubber compounds is important because they affect physical properties of their vulcanizates.^{20,21} Bound rubber contents of the MB and FM compounds were measured. The bound rubber contents of the FM compounds are much higher than those of the MB ones (Table II). This is due to the long mixing time of the FM compound and the reaction between the polymer and carbon black activated by sulfur and the cure accelerator (TBBS). Because total mixing time for the FM compound is longer than for the MB one, the more shear force is imposed to the former

than the latter. Carbon black reacts with sulfur and cure accelerator so that $\equiv\text{CS}\cdot$ radicals or $\equiv\text{CX}$ (X is SH or residues of a cure accelerator) are formed.²² The radicals or $\equiv\text{CX}$ on the filler surface can react with rubber chains and this will result in formation of chemical bonds between the rubber and filler.

Bound rubber contents of the compounds containing NR (NR/SBR and NR/BR blends) are higher than those of the SBR/BR ones. This implies that NR is more compatible with carbon black than SBR and BR. Bound rubber content of NR with carbon black is higher than those of SBR and BR.²² The bound rubber contents of the NR/BR compounds are higher than those of the NR/SBR ones.

For the MB compounds, variation of the bound rubber content with the preblending time does not inform a specific trend as shown in Table II. However for the FM compounds, variation of the bound rubber content of the NR/BR compounds with the preblending time shows some trends. The bound rubber content of the NR/BR FM compounds (Compounds 4-6) decreases slightly with an increase of the preblending time. For the NR/SBR and SBR/BR FM compounds, the bound rubber contents of the compounds made of the raw rubbers (preblending time = 0.0) are lower than those of the compounds made of the preblended rubbers.

Composition of Bound Rubber. To investigate the preblending effect on the variation of the bound rubber composition, the composition of bound rubber was analyzed with Py-GC. The

results are summarized in Table II. The NR component ratio of the bound rubbers in the NR/SBR and NR/BR compounds is much larger than the SBR or BR one. The BR component ratio of the bound rubbers of the SBR/BR compounds is larger than the SBR one. This phenomenon can be explained by lowering molecular weight of the rubber and by increasing the compatibility of the rubbers with the filler. The order of the compatibility of the rubber with the carbon black is $\text{NR} > \text{BR} > \text{SBR}$. This compatibility trend reflects to the bound rubber contents. The higher the compatibility between rubber and carbon black make the more abundant bound rubber content. The molecular weight of a natural rubber is higher than one for a synthetic rubber. Thus, the bound rubber contents of the compounds containing NR are higher than the compounds without NR as discussed previously.

Variation of the bound rubber composition with the preblending time shows a unique trend. The bound rubber composition ratios of the two rubbers become smaller by increasing the preblending time. To investigate the variation of the bound rubber composition with the preblending time in detail, the bound rubber composition ratios were plotted against the preblending times of the MB and FM compounds (Figures 1 and 2, respectively). The differences in the bound rubber composition ratios of the MB compounds decrease from 26 to 16%, from 24 to 8%, and from 12 to 4% for the NR/SBR, NR/BR, and SBR/BR compounds after preblending for 5.0 min respectively. For the FM compounds, the differences decrease from 16 to 10%, from 22 to 16%, and from 12 to 0% after preblending for 5.0 min. This may be due to the decrease of the domain sizes of the continuous and disperse phases. By increasing the preblending time, the two rubber phases are dispersed more and more and size of the disperse phase becomes smaller and smaller. The polymer must contact with carbon black to form the bound rubber. Thus, the difference in probabilities of the two rubber phases to meet with carbon black becomes smaller by increasing preblending time though compatibilization of the two rubbers with carbon black are different.

The difference in the bound rubber component

ratios for the SBR/BR compounds is smaller than those for the NR/SBR and NR/BR ones. This can lead to the increase of the compatibility of the

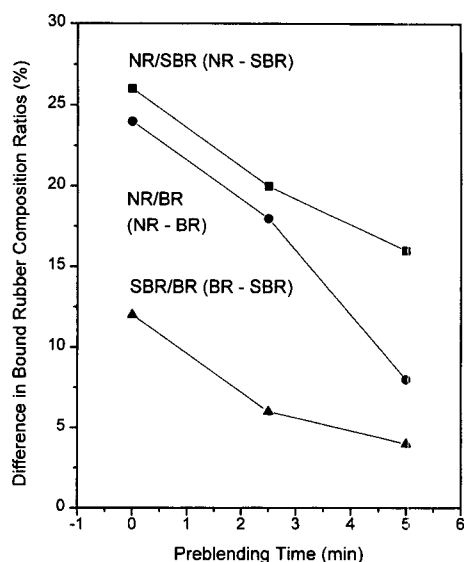


Figure 1. Variation of difference in the bound rubber composition ratios of the MB compounds as a function of the preblending time. Rectangles, circles, and triangles indicate the NR/SBR, NR/BR, and SBR/BR compounds, respectively.

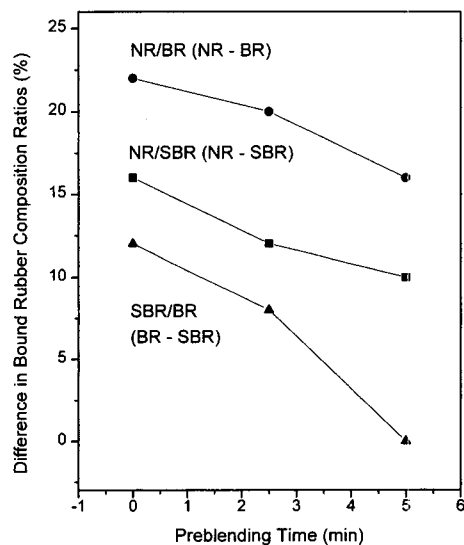


Figure 2. Variation of difference in the bound rubber composition ratios of the FM compounds as a function of the preblending time. Rectangles, circles, and triangles indicate the NR/SBR, NR/BR, and SBR/BR compounds, respectively.

rubbers with the carbon black and the decrease of the molecular weight of the rubber. Since NR is more compatible with filler than SBR or BR and the former has a higher molecular weight than the latters, the bound rubber content of the compound containing NR is larger than that of the compound without NR and the NR ratio of the bound rubber is higher than the other rubber.

Cure Characteristics. Cure characteristics of the compounds were measured at 145 and 160°C. The minimum and the maximum torques (T_{min} and T_{max}), delta torque ($T_{max}-T_{min}$), the scorch time (t_{02}), t_{40} , and the optimum cure time (t_{90}) of the compounds are listed in Table III. The minimum torque of the compound made of the preblended rubbers is lower than that prepared by using of the compound by the raw rubbers, irrespective of the kinds of the biblends. This is due to the increase of the molecular weight distribution of the rubbers by preblending. The delta torque of the compound increases slightly after the preblending.

The t_{02} , t_{40} , and t_{90} of the NR/BR compounds are shorter than those of the NR/SBR and SBR/BR ones because crosslinking reactions of NR and BR are faster than for SBR. In order to compare the curing characteristics of single rubber-based compounds, cure characteristics of carbon black-filled NR, SBR, and BR compounds were measured at 160°C. They contained rubber (100.0 phr), N 330 (50.0), ZnO (4.0), steric acid

(2.0), wax (2.0), HPPD (3.0), TBBS (2.0), and sulfur (1.2). The t_{02} s of the NR, SBR, and BR compounds are 1.58, 3.62, and 2.40 min, respectively, while the t_{90} s are 5.87, 13.42, and 7.45 min, respectively. The t_{02} and t_{90} of the NR and BR compounds are much faster than those of the SBR compound. Since the SBR compound has longer cure times, the vulcanizing reactions of the biblend compounds containing SBR such as NR/SBR and SBR/BR compounds become slower although NR and BR polymers have fast cure characteristics.

No trends for the cure characteristic change of the NR/SBR and NR/BR compounds with the preblending time are observed. But, for the SBR/BR compounds, the cure characteristics vary with the preblending time. The t_{02} , t_{40} , and t_{90} of the SBR/BR compounds become slower by increasing the preblending time as shown in Figure 3. The increments of the t_{02} , t_{40} , and t_{90} of the SBR/BR compounds by the preblending for 5.0 min at 145°C are about 14, 11, and 10%, respectively, while those at 160°C are about 10, 7, and 6%, respectively, because SBR/BR are miscible while NR/SBR or NR/BR are immiscible.

However, the mutual solubility of SBR and BR polymers is very unique. Most useful elastomers are heterogeneous blends. An important example of such a blend is a mixture of NR and SBR. The blends of NR with SBR have been studied by a number of workers. Hess and Chirico²³ reported

Table III. Cure Characteristics

Compound No.	1	2	3	4	5	6	7	8	9
at 145°C									
T_{min} (N·m)	0.72	0.71	0.70	0.88	0.84	0.82	0.91	0.90	0.90
T_{max} (N·m)	4.56	4.50	4.55	5.03	5.01	5.01	4.66	4.77	4.76
Delta Torque (N·m)	3.84	3.79	3.85	4.15	4.17	4.19	3.75	3.87	3.86
t_{02} (min)	5.55	5.53	5.83	5.02	4.87	4.93	6.40	6.98	7.30
t_{40} (min)	14.83	14.50	14.67	10.57	10.20	10.72	15.55	16.58	17.33
t_{90} (min)	23.38	22.27	22.62	14.07	13.58	14.03	22.15	23.35	24.40
at 160°C									
T_{min} (N·m)	0.66	0.66	0.66	0.84	0.81	0.79	0.87	0.86	0.86
T_{max} (N·m)	4.26	4.28	4.31	4.89	4.90	4.89	4.72	4.72	4.71
Delta Torque (N·m)	3.60	3.62	3.65	4.05	4.09	4.10	3.85	3.86	3.85
t_{02} (min)	2.03	2.12	2.17	1.80	1.83	1.88	2.42	2.50	2.67
t_{40} (min)	5.85	5.92	5.83	4.23	4.32	4.37	6.27	6.55	6.70
t_{90} (min)	9.55	9.28	9.18	5.83	5.88	5.87	9.12	9.47	9.70

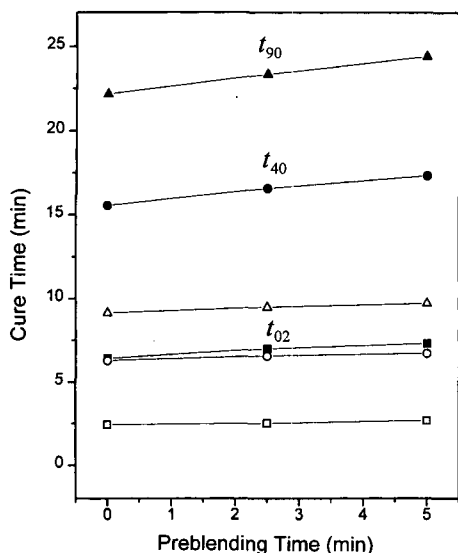


Figure 3. Variation of cure times of the SBR/BR compounds as a function of the preblending time. Rectangles, circles, and triangles indicate the t_{02} , t_{40} , and t_{90} , respectively. Closed and open symbols are data obtained at 145 and 160 °C, respectively.

that SBR was the continuous phase in 50/50 blends of NR/SBR, while for 50/50 NR/BR blends it was the NR that formed the continuous phase. Since SBR and BR polymers are miscible at the mixing temperature, the intrinsic properties of the single rubber-based compounds of SBR and BR will disappear by preblending. When SBR and BR polymers are mixed completely to a molecular level, BR polymer chain will be crosslinked with SBR not another BR since BR will be surrounded by SBR polymers. Scorch time and optimum cure time of a BR compound are much faster than

those of a SBR compound as discussed previously. Thus, the t_{02} and t_{90} of the SBR/BR blends become slower by increasing the preblending time.

Physical Properties. The physical properties of the vulcanizates, such as hardness, modulus, tensile strength, elongation at break, tear resistance, abrasion loss, and $\tan\delta$ were measured. The results are summarized in Tables IV and V. The physical properties of the vulcanizates do not show a specific change with the preblending time except the moduli. The moduli of the vulcanizates made of the premixed rubbers are higher than those of the vulcanizate made of the raw rubbers. Especially, the moduli of the NR/SBR vulcanizates notably increase with an increase of the preblending time.

In general, the wear resistance of a vulcanizate made of rubbers with a high molecular weight is better than that of a vulcanizate made of rubbers with a low one. The NR/SBR and NR/BR vulcanizates follow this trend. Some rubber chains are dissociated by shear force during the preblending so the molecular weight becomes lower. Amounts of abrasion loss of the NR/SBR and NR/BR vulcanizates made of the preblended rubbers are larger than those of the vulcanizates made of the raw rubbers. However, the SBR/BR vulcanizates do not follow this trend. The amounts of the abrasion loss of the SBR/BR vulcanizates made of the premixed rubbers are smaller than that of the SBR/BR vulcanizate made of the raw rubbers. This may be due to the relatively short rubber chains of SBR and BR compared to NR and the miscibility of SBR and BR polymers. The molecular

Table IV. Physical Properties

Compound No.	1	2	3	4	5	6	7	8	9
Hardness (Shore A)	74.0	74.0	74.0	71.0	71.0	71.0	72.0	74.0	73.0
50% Modulus (kg/cm ²)	22.4	22.8	23.1	21.9	22.3	21.9	22.2	23.0	23.4
100% Modulus (kg/cm ²)	41.2	42.8	44.3	41.2	42.7	41.8	40.1	43.2	43.0
200% Modulus (kg/cm ²)	112.2	117.0	119.7	111.9	115.3	112.4	109.1	114.2	111.8
300% Modulus (kg/cm ²)	185.4	188.7	191.7	182.6	187.2	182.7	179.5	186.6	182.1
Tensile strength (kg/cm ²)	244.7	254.9	237.7	233.3	231.3	238.2	205.6	204.3	199.3
Elongation at break (%)	410.5	424.9	381.8	385.8	373.6	395.6	343.4	329.4	332.8
Tear resistance (kg/cm)	89.0	94.0	92.5	84.0	88.5	81.0	86.0	90.5	85.5
Abrasion loss (mg)	19.0	22.5	20.5	10.5	12.0	12.0	14.0	12.5	13.0

Table V. Tan δ

Compound No.	1	2	3	4	5	6	7	8	9
-40°C	0.562	0.557	0.562	0.306	0.309	0.296	0.291	0.333	0.273
-30°C	0.375	0.367	0.395	0.251	0.241	0.241	0.247	0.264	0.230
-20°C	0.279	0.272	0.291	0.216	0.215	0.212	0.222	0.208	0.213
0°C	0.213	0.208	0.225	0.191	0.189	0.178	0.216	0.205	0.212
10°C	0.212	0.211	0.222	0.173	0.173	0.169	0.220	0.204	0.208
50°C	0.187	0.191	0.197	0.157	0.154	0.153	0.175	0.169	0.179
60°C	0.184	0.189	0.194	0.154	0.150	0.150	0.171	0.164	0.175
70°C	0.181	0.187	0.192	0.151	0.147	0.148	0.167	0.161	0.172

weight of the natural rubber is usually higher than those of the synthetic rubbers. Thus, during the preblending, the decrement of the molecular weight distribution of the former is larger than those of the latters. Since SBR and BR polymers are miscible, the SBR/BR compounds are more homogeneous than the NR/SBR and NR/BR ones and the homogeneity of the SBR/BR blend will increase by increasing the preblending time.

Tan δ values at 0 and 60°C imply the wet traction and the rolling resistance of the sample, respectively. The larger tan δ at 0°C informs the better wet traction property of a vulcanizate. The smaller tan δ at 60°C indicates that the better rolling resistance of a vulcanizate retains. The tan δ values at 0 and 60°C of the NR/BR vulcanizate made of the raw polymers are higher than those of the vulcanizates made of the premixed blend (Table V). This means that the rolling resistance of the NR/BR vulcanizate is improved by the preblending but the property for wet traction may not be improved. The tan δ at 60°C of the NR/SBR vulcanizate made of the raw polymers is lower than those of the vulcanizates made of the premixed blends, but the tan δ at 0°C does not show a specific trend with the preblending time. This implies that the wet traction and the rolling resistance of the NR/SBR vulcanizate can not be improved by the preblending of the two rubbers. The tan δ at 0°C of the SBR/BR vulcanizate made of the raw polymers is higher than those of the vulcanizates made of the premixed rubbers, but the tan δ at 60°C does not show a specific trend with the preblending time. This also implies that the wet traction and the rolling resistance of the SBR/BR vulcanizate can not be improved by the preblending of the two rubbers.

Conclusion

Some properties of the binary rubber-based carbon black-filled rubber compounds are changed by premixing of the biblends of raw rubbers. The Mooney viscosity decreases with increasing the preblending time. The bound rubber content is not effected by premixing of the biblends. Of the bound rubber composition, the NR content is higher than SBR or BR and the BR content is also higher than SBR. The difference in the bound rubber composition ratio is decreased with an increase of the preblending time. The $t_{0.2}$, t_{40} , and t_{90} of the SBR/BR compounds become slower by increasing the preblending time, but this trend is not observed in the NR/SBR and NR/BR compounds. Most physical properties measured are not affected by premixing of the biblends.

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