

Influence of Mastication on Properties of Carbon Black-Filled NR Compounds

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Abstract : The influence of mastication of natural rubber (NR) on properties of carbon black-filled NR compounds was studied. Variations of viscosities of the masticated NR and the carbon black-filled NR compound by heating were also investigated. The viscosities of the compounds decreased by increasing the mastication time of the raw rubber. The viscosities of the masticated NR and the compounds increased by increasing the heating time. This was explained by the combination reaction between functional groups in the rubber. The viscosity increment of the masticated rubber and the compounds by heating became larger with increased mastication time. Cure rate of the compound became faster by increasing the mastication time. Modulus of the vulcanizate made of the rubber masticated for a long time was higher than that of the vulcanizate made of the rubber masticated for a short time while elongation at break of the former was shorter than that of the latter. This was explained by the content of bound rubber and chain length of the rubber molecules.

Introduction

In the preparation of any kind of rubber mixture, first of all the rubber itself must be plasticized. In other words, compounding ingredients can be mixed into rubber when the rubber has been made soft enough for powders to penetrate the mass and to be dispersed uniformly. The mastication of rubber was of great importance, especially in the earlier days, when natural rubber (NR) was the only elastomer available. NR is difficult to process without prior breakdown because of its rough and nery characters.

Mastication decreases the viscosity of rubber, promotes good dispersion of fillers and chemicals, and increases compound plasticity. This facilitates improved processing of calendering or extruding by reducing the stiffness of the rubber. The rheological properties of die swell, calender shrinkage, and building tack are improved by the mastication. The mastication also plays an important role in the preparation of elastomer blends with elastomers of

widely different viscosities.

Mastication has been studied for a long time.¹⁻¹² The mechanism of mastication was studied by several groups.^{1,3,5,9} Long chain rubber molecules are split by the high shear forces encountered in the mixing equipment such as internal mixers or rubber mills. Chain fragments are formed with terminal free radicals,^{1,6,9} either stabilizing to short chain molecules or recombining into long chain molecules. In the former case, the molecular weight of the rubber is lowered and consequently the plasticity is increased. Important factors influencing the mastication are the presence of oxygen or radical acceptor,^{1,3-6,10} composition of the elastomer,^{7,11,12} and mastication conditions^{2,8} such as temperature, time, and rotor speed of the mixer.

In the present work, the influence of the degree of mastication on properties of the carbon black-filled NR compounds was studied using SMR 20 (standard Malaysian rubber). Viscosity, bound rubber content, and cure characteristics of the compounds and physical properties of the vulcanizates were compared.

Simple mixing process for carbon black-filled

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rubber compounds is composed of carbon master batch (CMB or MB) and final mixing (FM) stages. The MB compound 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. In general, the MB compound sheets are cooled before the FM stage. During the hot summer, temperature of a pile of the sheets in a factory is often over 40°C. 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. In this study, variation of viscosity of the masticated rubber and the rubber compound, which depends on heating time during the storage, was also investigated.

Experimental

SMR 20 was used as a natural rubber. Mastication was performed in a Banbury mixer at a rotor speed of 50 rpm. The initial temperature was 110°C and the mastication times were 1.0, 4.0, and 7.0 min. The carbon black master batches (MB) were prepared in a Banbury mixer at a rotor

speed of 40 rpm. Mixing was started at 110°C for 4 min. The final mixing (FM) was performed using an open mill at 100 for 4 min. *N*-Phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD) was employed as an antiozonant and *N*-*tert*-butyl-2-benzothiazole sulfenamide (TBBS) was used as a cure accelerator. The formulations were given in Table I. Conventional and efficient vulcanization (EV) cure systems were employed. The conventional cure system is a vulcanizing system with very low accelerator ratio while the EV cure system is a vulcanizing system with very high ratio of accelerator. The Compounds 1-3 have the conventional cure system while the Compounds 4-6 have the EV one. The vulcanizates were prepared by curing at 160°C for 20 min.

Changes of viscosities of the masticated rubbers and the MB compounds were measured as a function of the heating time up to 9 h at 40 and 60°C using a convection oven. Viscosities of the compounds were measured using a Mooney viscometer MV 2000 of Alpha Technologies. This is a shearing disk viscometer which is related to the parallel disk type shear flow instrument that has been widely used for polymer solutions and melts.¹³ Contents of bound rubber were determined by extraction of unbound materials includ-

Table I. Formulations (phr), Mooney Viscosities, and Bound Rubber Contents

Compound No.	1	2	3	4	5	6
SMR 20	100.0	100.0	100.0	100.0	100.0	100.0
N330 (carbon black)	50.0	50.0	50.0	50.0	50.0	50.0
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
Mastication time (min)	1.0	4.0	7.0	1.0	4.0	7.0
Mooney viscosity (ML1+4 at 100°C)						
Masticated rubber	81.8	69.7	64.9	81.8	69.7	64.9
MB compound	80.2	77.4	76.0	80.2	77.4	76.0
FM compound	62.5	61.5	53.8	63.3	58.1	53.8
Content of bound rubber of the MB compound (%)						
	42.5	43.7	47.7	42.5	43.7	47.7

ing ingredients and free rubber with toluene for 4 days and *n*-hexane for 1 day and drying for 2 days at room temperature. Cure characteristics were obtained using a Flexsys rheometer (MDR 2000) at a frequency of 100 cycles/min and ± 1.5 arc for the temperatures of 145 and 160°C. Physical properties of the vulcanizates were measured by the Universal Testing Machine (Instron 6021).

Results and Discussion

Dependence of Viscosity on the Mastication Time. Filled rubber compounds should have proper viscosities to meet good extrusion and calendaring properties. Viscosities of rubber compounds become lower during the mixing by shear force.¹⁻¹² The shear force leads to scission of rubber chains. The MB compound included rubber, carbon black, antidegradants (HPPD and wax), and cure activators (ZnO and stearic acid) while the FM compound included the MB compound and curatives (sulfur and TBBS). Table I gives viscosities of the masticated NR and the MB and FM compounds. Viscosities of the FM compounds are lower than those of the MB compounds.

Viscosity of the masticated NR becomes lower by increasing the mastication time. This is because the chain scission of rubber molecules occurs during the mastication. The chain scission causes the molecular weight distribution to shift to lower molecular weight.^{1,6} Mooney viscosity of a rubber is very closely correlated with its molecular weight.¹⁴ The higher the molecular weight is the higher its Mooney viscosity is. The viscosity difference between the rubbers masticated for 1.0 and 4.0 min (12.1 MU) is higher than the difference between the rubbers masticated for 4.0 and 7.0 min (4.8 MU) by about 7 MU (Mooney unit). This may be because the molecular weight distribution of the rubber masticated for 1.0 min is higher than that of the rubber masticated for 4.0 min. Shear force applied to rubber chains becomes stronger as the molecular weight of rubber chain increases.

Viscosities of the MB compounds made of the rubbers masticated for 4.0 and 7.0 min are higher than those of the raw rubbers but the MB com-

pound made of the rubber masticated for 1.0 min is lower than the masticated rubber. This may be due to the high viscosity of the rubber masticated for 1 min. Stronger shear force applied to the rubber masticated for 1 min leads to severe chain scission. The shear force leads to the chain scission. Viscosities of the NR compounds decrease remarkably after the final mixing by adding the curatives. The viscosity difference between the MB and FM compounds are about 16-22 MU. This can be explained by acceleration of the chain scission by the curatives. According to the mastication mechanism,^{1,3-6,10} the chain scission is accelerated by the radical termination. TBBS and sulfur are dissociated with ease and generate radicals. These radicals operate as the radical terminators of the broken rubber chains.

Bound Rubber Content. Carbon black becomes incorporated and dispersed in the rubber during the mixing. In general, the incorporation process comprises the wetting of carbon black with rubber and squeezing out entrapped air. It is suggested that during the initial stages of carbon black incorporation, the carbon black becomes compressed by the polymer. At the time, the carbon black is being crushed by the shearing and compressive forces. Subsequently, rubber is forced into those voids and air is expelled.

Contents of bound rubber for the MB compounds were measured. The results were listed in Table I. The bound rubber contents increase by increasing the mastication time. This is interesting because the molecular weight becomes lower by increasing the mastication time. This can be explained by the mobility of rubber. Fast movement of the rubber molecules favors easy incorporation of carbon black into the rubber. The masticated rubber having a low molecular weight is more mobile than the rubber having a high one.

Variation of Mooney Viscosity of the Masticated NR during the Storage. Variation of the viscosity of the masticated rubber with the heating time at 40 and 60°C was measured and the initial viscosity effect on the variation was also studied. Figures 1 and 2 give the variations of the viscosity of the masticated rubber as a function of the heating time at 40 and 60°C, respectively. The

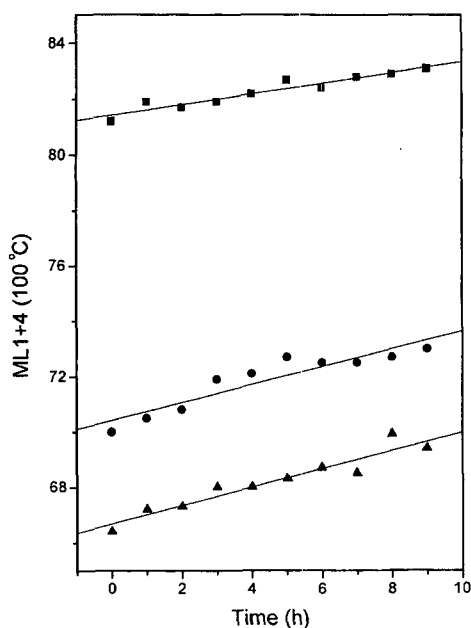


Figure 1. Variation of Mooney viscosity of the masticated NR at 40 as a function of the heating time. Squares, circles, and triangles indicate the rubber masticated for 1.0, 4.0, and 7.0 min, respectively.

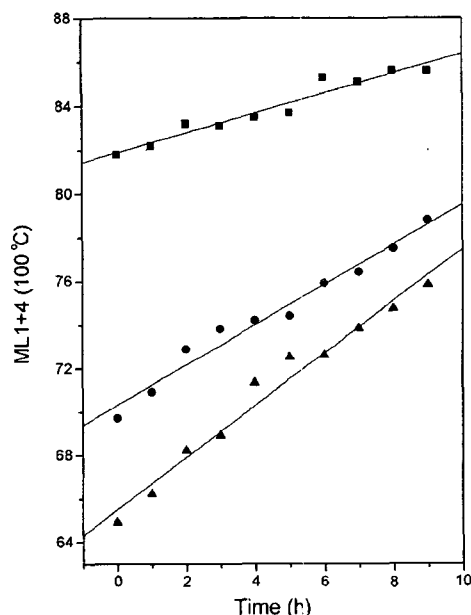


Figure 2. Variation of Mooney viscosity of the masticated NR at 60 as a function of the heating time. Squares, circles, and triangles indicate the rubber masticated for 1.0, 4.0, and 7.0 min, respectively.

viscosities of all the masticated rubbers increase by increasing the heating time. This is due to the intermolecular combination reactions between the rubber molecules. Natural rubber molecules with various functional groups such as epoxy, aldehyde, amino groups^{15,16} combine each other to increase the molecular weight. Increase of the molecular weights leads to an increase of the viscosity.

The viscosity of the masticated rubber increases linearly with an increase of the heating time. The increments of the viscosity of the rubber masticated for 1.0, 4.0, 7.0 min at 40 are about 0.19, 0.32, and 0.33 MU/h, respectively. The increments of the viscosity of the rubber masticated for 1.0, 4.0, 7.0 min at 60 are about 0.45, 0.92, and 1.20 MU/h, respectively. The viscosity increment of the masticated rubber becomes larger by increasing the temperature. This may be due to the enhanced combination reaction by increasing the temperature.

The viscosity increment of the masticated rubber becomes larger by increasing the mastication time. The viscosity increments of the rubber masticated for 7.0 min are much larger than those of the rubber masticated for 1.0 min by about 1.7 and 2.7 times at 40 and 60, respectively. This can be explained in terms of the number of the functional groups in the rubber and the mobility of the masticated rubber. The terminal radicals, formed by the chain scission, react with oxygen or polar chemicals to form small rubber chain terminated by a new functional group.

Rubber molecules with functional groups can react with other molecules. Reactions between the rubber chains result in the increase of molecular weight and Mooney viscosity. By increasing the mastication time, the number of the functional groups increases. The chain length of the masticated rubber becomes shorter with an increase of the mastication time. The chain length of the rubber is related closely with the mobility of the rubber chains. Thus, since the rubber masticated for the long time has the functional groups more than the rubber masticated for the short time and the former is more mobile than the latter, the combination reactions are enhanced by increasing the mastication time.

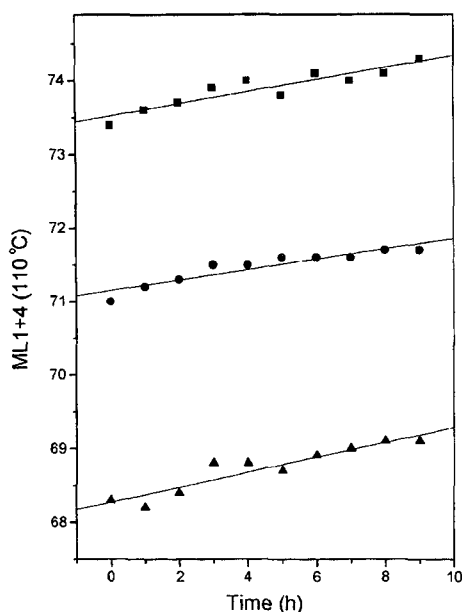


Figure 3. Variation of Mooney viscosity of the carbon black-master batch compound at 40 as a function of the heating time. Squares, circles, and triangles indicate the rubber masticated for 1.0, 4.0, and 7.0 min, respectively.

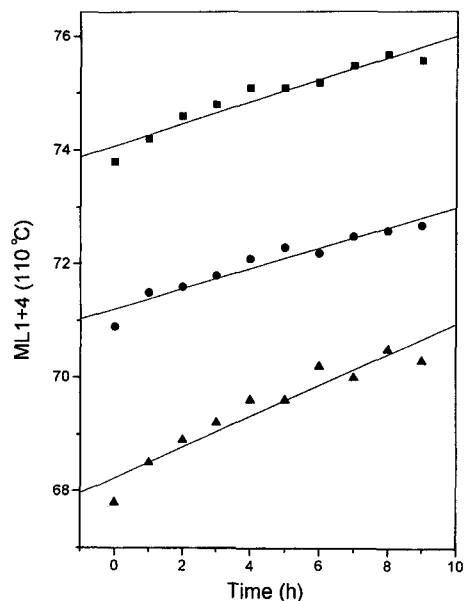


Figure 4. Variation of Mooney viscosity of the carbon black-master batch compound at 60 as a function of the heating time. Squares, circles, and triangles indicate the rubber masticated for 1.0, 4.0, and 7.0 min, respectively.

Variation of Mooney Viscosity of the MB Compound during Storage. Variation of the viscosity of the MB compound with the heating time at 40 and 60°C was also investigated. Figures 3 and 4 give the variations of the viscosity of the MB compound as a function of the heating time at 40 and 60°C, respectively. The viscosities of all the MB compounds increase by increasing the heating time as similar to the masticated rubber. However, the viscosity increments are small. The viscosity increments for the MB compounds made of the rubbers masticated for 1.0, 4.0, and 7.0 min at 40°C are about 0.08, 0.07, and 0.10 MU/h, respectively, while those at 60°C are about 0.20, 0.18, and 0.27 MU/h, respectively. The viscosity increments of the MB compounds at 60°C are more than twice higher than those at 40°C. The difference in the viscosity increments of the MB compounds, which depends on the mastication time, is smaller than that of the masticated rubbers. The average viscosity increment of the MB compound made of the rubber masticated for 7.0 min at 60°C is higher than that of the MB compound made of the rubber masticated for 1.0

min by about 2.7 times while that of the rubber masticated for 7.0 min at 60°C is higher than that of the rubber masticated for 1.0 min by about 3.6 times.

The viscosity increments of the MB compounds with an increase of the heating time are much smaller than those of the masticated rubbers by about 2.4-4.4 times. This can be explained by the presence of polar materials and binding of rubber to carbon black. Some of rubber molecules in the MB compound are bound to the carbon black so they become less mobile. The less flexible rubber molecule has a low probability to meet the other molecule. The polar chemicals such as HPPD and stearic acid in the MB compound can stay around the functional groups in the rubber molecules by the polar-polar interactions. The solvation of the functional groups will inhibit the combination reactions between the functional groups of the rubbers.

Cure Characteristics. Table II gives the cure characteristics of the compounds at 145 and 160°C. The minimum torque (T_{min}) of the compound becomes lower by increasing the mastication

Table II. Cure Characteristics

Compound No.	1	2	3	4	5	6
at 145°C						
T_{min} (N·m)	0.42	0.40	0.34	0.42	0.38	0.34
T_{max} (N·m)	2.85	2.83	2.78	2.82	2.81	2.80
Delta torque (N·m)	2.43	2.43	2.46	2.40	2.43	2.46
t_{02} (min)	4.22	4.50	4.07	4.22	4.77	4.12
t_{40} (min)	9.65	9.77	8.97	9.62	9.58	8.95
t_{90} (min)	18.00	17.83	15.57	17.52	16.15	15.23
Cure rate (N·m/min)*	0.155	0.160	0.174	0.158	0.188	0.194
at 160°C						
T_{min} (N·m)	0.38	0.37	0.32	0.36	0.35	0.32
T_{max} (N·m)	2.62	2.64	2.73	2.43	2.72	2.72
Delta torque (N·m)	2.24	2.27	2.41	2.07	2.37	2.40
t_{02} (min)	1.07	1.12	1.07	1.07	1.82	1.60
t_{40} (min)	3.12	3.25	3.72	3.17	3.97	3.65
t_{90} (min)	6.12	6.37	6.05	6.18	6.68	6.08
Cure rate (N·m/min)*	0.390	0.382	0.427	0.357	0.431	0.471

* Cure rate = $(T_{90} - T_{02}) / (t_{90} - t_{02})$

Table III. Physical Properties

Compound No.	1	2	3	4	5	6
Hardness (kg/cm ²)	60.0	60.0	62.0	59.0	62.0	63.0
Modulus at 50% (kg/cm ²)	13.9	13.4	14.7	13.4	15.1	15.2
Modulus at 100% (kg/cm ²)	23.0	23.2	27.8	22.5	27.9	28.0
Modulus at 200% (kg/cm ²)	61.3	61.0	78.6	60.1	78.6	79.0
Modulus at 300% (kg/cm ²)	117.7	117.0	146.1	115.8	145.2	145.3
Tensile strength (kg/cm ²)	284.1	279.0	279.6	287.8	294.9	283.9
Elongation at break (%)	573.9	545.1	497.1	576.7	522.1	505.2
Tear resistance (kg/cm)	86.0	80.5	92.5	82.0	89.0	88.0

tion time. This is because the viscosity of the compound decreases with an increase of the mastication time. The cure rate of the compound also becomes faster by increasing the mastication time. This may be due to the increase of functional groups in rubber chains and the decrease of the length of the rubber chain by the rubber chain scission. The cure rates of the compounds with the EV cure system are, on the whole, faster than those of the compounds with the conventional one. The difference of the cure rates of the compounds with the EV cure system depending on the mastication time is larger than that of the compounds with the conventional one. The differences of the cure rates of the compounds made of the rubbers masticated for 1.0 and 7.0 min

with the EV cure system are 0.036 and 0.114 N·m/min for 145 and 160°C, respectively, while those with the conventional cure system are 0.019 and 0.099 N·m/min, respectively. This means that the EV cure system is more sensitive to the cure rate depending on the mastication than the conventional cure system.

Mastication Effect on Physical Properties.

Table III gives the physical properties of the vulcanizates. The hardness of the vulcanizate made of the rubber masticated for the long time is higher than that of the vulcanizate made of the rubber masticated for the short time. The moduli of the vulcanizate increase by increasing the mastication time. The elongation at break of the vulcanizate decreases as the mastication time increases. The

differences in the physical properties of the vulcanizates depending on the mastication time may be due to the length of the rubber chain. Since the chain length of the rubber masticated for the long time is shorter than that of the rubber masticated for the short time, the vulcanizate made of the former is stiffer than that made of the latter.

Conclusion

The viscosity of natural rubber decreases with increased mastication time. The cure rate of the compound becomes faster by increasing the mastication time. The vulcanizate made of the rubber masticated for the long time is stiffer than that made of the rubber masticated for the short time. The viscosities of the masticated rubber and the MB compounds increase linearly as the heating time increases. This is because of the combination reaction between the functional groups in the rubber chains. The viscosity increment by heating became larger by increasing the mastication time. This is due to the mobility of the rubber chain and the number of the functional groups in the rubber molecules. The viscosity increments for the MB compounds are much smaller than those of the masticated rubbers. This can be explained by inhibition of the combination reaction by binding of the rubber to the carbon black and by solvation of the functional groups by the polar chemicals.

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