

## CR/NBR 블렌드의 단섬유강화 복합재료 : 1. 블렌드의 물리적 성질, 열노화 및 내유특성

강 창 기 · 김 병 규

부산대학교 고분자공학과

(1991년 4월 13일 접수)

### Short Fiber Reinforced CR/NBR Blends :

#### 1. Physical Properties, Aging, and Oil Resistance of the Blends.

Chang Kee Kang and Byung Kyu Kim

*Dept. of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea*

(Received April 13, 1991)

**요약** : 내열 및 내유성이 공히 좋은 고무를 제조할 목적으로 open mill에서 CR/NBR 블렌드를 제조하였으며, 이들 블렌드의 가류특성, 가류고무의 물리특성, 노화 및 내유특성을 측정하였다. 블렌드의 점도, 경도, 탄성을 및 마모강도는 전반적으로 단순 혼합법칙 이상으로 증가하였으며, 인장강도 및 파단신율은 감소하였다. 또한, heat buildup 및 방향족 기름에서의 체적팽창은 혼합법칙 이하로 억제되었다.

**Abstract** : To obtain rubber compound with satisfactory thermal and oil resistance properties, blends of CR(chloroprene rubber) with NBR(acrylonitrile-co-butadiene rubber) were prepared in a laboratory open mill following the polymer blending method. Cure behavior of the blends, physical properties of vulcanizates, together with the aging and oil resistance properties were measured. The results indicated that the viscosity increased in the blends due to the increased rate of cure. Hardness, modulus, abrasion resistance of the blends increased over the simple additive rule, and tensile strength and elongation showed negative deviation from the additivity. Heat buildup, and volume expansion in aromatic oil showed negative deviation, indicative of effective improvement in thermal and oil resistance upon blending.

#### INTRODUCTION

Since the birth of synthetic rubber, rubber blends have widely been encountered in industry due mainly to the technical reason to obtain the right compromise in properties.<sup>1</sup>

Elastomer blends, especially for vulcanizates, pose some additional difficulties over the plastic blends.<sup>1-3</sup> Rubber is highly elastic, and under all conditions homogeneous blends or molecular solutions are not obtained, i. e., either a distinct dispersed phase or cocontinuous phase occurs. In addi-

tion, elastomer blending accompanies chemical reactions, viz. vulcanization, the characteristics depending on the type of specific rubber, formulations, and cure conditions. Dispersion of the ingredients, notably carbon black again gives significant effects on the final vulcanizate properties. Therefore, technology in rubber blending is essentially empirical.<sup>4</sup>

However there are certain basic rules to obtain rubber blends with predictable vulcanizate properties from those of constituent rubbers.<sup>2,4</sup> The rule requires use of constituent rubbers with similar solubility parameter, similar viscosity, and similar curative characteristics. In addition, mixing method capable of giving good disaggregation of compounding ingredients and satisfactory distribution between the constituent rubbers are also required.

This paper considers blends of chloroprene rubber(CR) with acrylonitril-butadiene rubber(NBR) in an attempt to enhance the oil resistance of CR, and the thermal resistance of NBR. Chloroprene rubber and NBR have excellent thermal and oil resistance properties, respectively. Carbon black affinity, and the solubility parameters of CR(9.55) and NBR(9.26) are not far off.<sup>5,6</sup> Chloroprene rubber and NBR grades with similar Mooney viscosity were chosen. Mixing was done in an open roll mill following the polymer blending method.<sup>7</sup> Cure behavior and physical properties of the vulcanizates together with the aging and oil resistance properties were measured.

## EXPERIMENTAL

Mastication and mixing were carried out on a two-roll mill(150×330mm) following the polymer blend method.<sup>7</sup> That is, after mixing CR (Toyosoda R-100) and NBR (Nipol P-70), ingredients(see basic formulations in Table 1) were added. The mill was operated at 50±5°C, with cold water circulation, at a friction ratio 1 : 1.25 and nip gap, 1.5 mm. Vulcanized sheets(from which test specimens were cut) were produced in an electrically heated press at 170°C. Optimum cure time at 150°C, defi-

Table 1. Formulations of Rubber Mixes

Sample Code	A	B	C	D	E
CR(R-10) <sup>a)</sup>	100	75	50	25	0
NBR(NIPOL P-70) <sup>b)</sup>	0	25	50	75	100
Stearic Acid	1	1	1	1	1
PA <sup>c)</sup>	2	2	2	2	2
MgO <sup>d)</sup>	4	3	2	1	0
SRF <sup>e)</sup>	75	75	75	75	75
A#2 <sup>f)</sup>	15	15	15	15	15
ZnO	5	5	5	5	5
Na <sub>22</sub> <sup>g)</sup>	1	0.75	0.5	0.25	0
DM <sup>h)</sup>	0	0.375	0.75	1.0	1.5
Sulfur	0	0.375	0.75	1.0	1.5

<sup>a)</sup> chloroprene rubber(CR), Toyoda, R-100

<sup>b)</sup> nitrile rubber(NBR), Nipol, P-70

<sup>c)</sup> antioxidant

<sup>d)</sup> vulcanizing agent

<sup>e)</sup> semi-reinforcing furnace carbon

<sup>f)</sup> aromatic oil, processing agent

<sup>g)</sup> accelerator

<sup>h)</sup> dibenzothiazyl disulfide accelerator

ned as the time to reach 90% of the maximum torque, was determined from a rheometer(Monsanto R-100).

Tensile(ASTM D412-51T) and tear(ASTM D 624-54) strengths were measured using an Instron tensile tester. Abrasion and Shore A hardness were determined according to KSM 6158 and ASTM D676-52T, respectively. Heat buildup was measured using a Goodrich Flexometer on 12.7mm (dia)×25.4mm(height) rubber cylinder at 100°C, and 8.75% stroke for 25min. The compression set was determined on a disk sample following KSM 6518. Oil resistance tests were done in ASTM # 3 oil for 70 hrs at 100°C.

## RESULTS AND DISCUSSION

### Cure Behavior

Experimental data obtained using Curastometer and Rheometer are shown in Table 2. It is noted that the Moony viscosity(ML<sub>1+4</sub>) and optimum

**Table 2.** Cure Characteristics of Rubber Mixes

	A	B	C	D	E
MV <sup>a)</sup>	6	8	8	8	3
MT <sup>b)</sup>	64	69	60	48	16.5
T <sub>10</sub> <sup>c)</sup>	1 : 50	1 : 40	1 : 20	1 : 10	3 : 20
T <sub>90</sub> <sup>d)</sup>	4 : 50	3 : 40	3 : 00	2 : 00	10 : 00
CR <sup>e)</sup>	3 : 00	2 : 00	1 : 40	0 : 50	6 : 40
ML <sub>1+4</sub> (100°C) <sup>f)</sup>	85	90	88	88	80
ML <sup>g)</sup>	8	10	10.5	10.5	6.5
T <sub>sl</sub> <sup>h)</sup>	2 : 00	1 : 30	1 : 36	1 : 36	4 : 53
T <sub>c</sub> (90) <sup>i)</sup>	9 : 05	5 : 40	4 : 30	3 : 07	11 : 45
MH <sup>j)</sup>	61	68.5	51	44	22.5

<sup>a)</sup> minimum viscosity(dN · m)

<sup>b)</sup> maximum torque(dN · m)

<sup>c)</sup> time for torque=0.1×maximum torque(min.)

<sup>d)</sup> time for torque=0.9×maximum torque(min.)

<sup>e)</sup> cure rate(min.)

<sup>f)</sup> Mooney viscosity(dN · m)

<sup>g)</sup> Mooney viscosity low(d · Nm)

<sup>h)</sup> scorch time(min.)

<sup>i)</sup> optimum cure time(min.)

<sup>j)</sup> Mooney viscosity high(dN · m)

cure time ( $T_c$ ) of CR and NBR used in the present experiment are similar to each other. The scorch time( $T_{sl}$ ) and optimum cure time are significantly reduced in blends, with a minimum  $T_c$  at 25/75 (CR/NBR). It is also noted that the increased rate of cure is accompanied by increased viscosity of the blends, showing positive deviation from the additive rule, with a viscosity maximum at 75/25 blend.

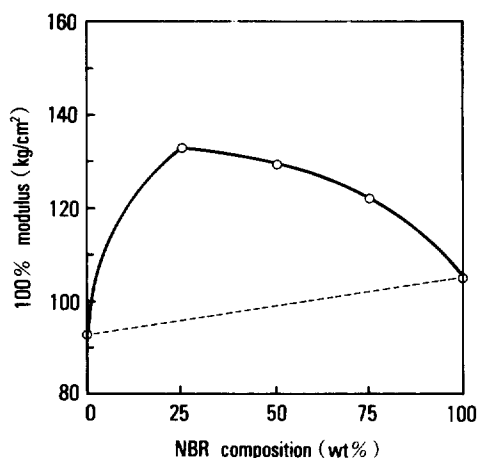
In incompatible polymer blends, positive deviation of viscosity has often been observed when the interactions between droplets, and interfacial interactions are strong, or when the morphology is an interlocked one.<sup>8,9</sup> Especially, the viscosity maximum is generally obtained when there are chemical reactions between the phases.<sup>10-14</sup> With regard to rubber blends, Hess et. al.<sup>15</sup> reported torque maximum for natural rubber/butadiene rubber blends, and from solubility measurement they found that insoluble high molecular weight graft copolymers were formed during mixing. For the

same blends, conflicting results were also reported by Folt and Smith.<sup>16</sup> These authors reported torque maximum but with no insoluble parts.

The reason for viscosity and torque departure with maximum is not clear in the present CR/NBR blends. However this should be related to the increased rate of cure of the blends, which is primarily determined by the rubber formulations. Chloroprene rubber is typically cured by metallic oxide, whereas NBR by sulfur(see the formulation in Table 1). However, during the mastication and blending in a roll, chain scissions occur, and therefore cross cure between the two types of rubber is also possible.<sup>1,17</sup>

### Physical Properties of the Vulcanizates

Tensile moduli of CR and NBR(Fig. 1) are significantly increased in the blends, with a maximum at 75/25 blend, the composition at which the viscosity and torque maxima were observed. In rubbery materials, modulus is a measure of the degree of crosslinking and physical entanglements,<sup>18</sup> i.e., with increasing crosslinking and/or entanglement density, the modulus is increased. The CR/NBR blends prepared following the present formulation should give more physical and/or chemical entanglements. Hardness of the blend(Fig. 2), like the modulus, also shows positive deviation(more in CR-rich and less in NBR-rich blends, generally)



**Fig. 1.** Tensile moduli of the blends.

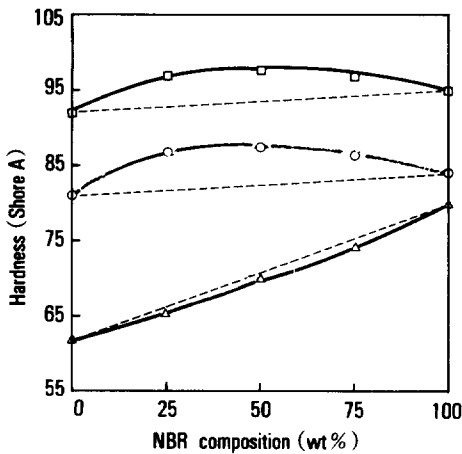


Fig. 2. Hardness of the blends : (○) virgin, (□) after aging, and (△) after immersion in oil.

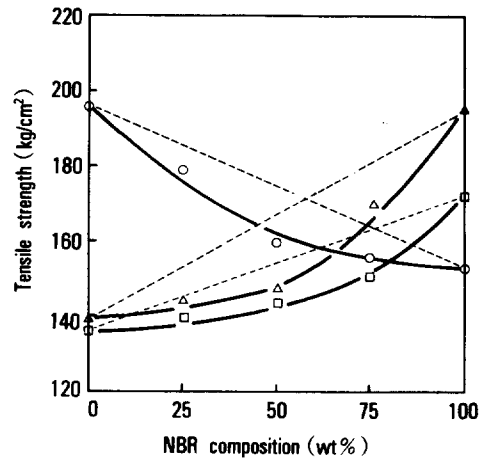


Fig. 3. Tensile strength of the blends : same symbol with Fig. 2.

from the additivity. However, the departure from the simple additivity is relatively small when compared with the modulus variation. When the modulus and hardness data are put together, it may be concluded that the CR was subjected to a bit excessive cure, which is mostly governed by the formulation (Table 1). Though CR is typically cured by metallic oxide, it is also curable by sulfur. The sign of excessive cure especially in CR-rich blends will also be seen from the reduced ductility of the blends to follow.

Tensile strength (Fig. 3) and elongation at break (Fig. 4) show negative deviation from the additivity, and this is most likely due to the incompatible nature of the rubber blends.<sup>19,20</sup> It is noted that the ductility of CR is significantly reduced upon blending with NBR due, at least in part, to the excessive cure, mentioned above.

Tear strength, compression set, and abrasion are shown in Fig. 5. Abrasion is decreased in blends due probably to the increased hardness of the blends. Tear strength and compression set are, more or less, kept at CR level for 75/25, and 50/50 blends. This may imply that the CR forms a continuous phase in these blends. In incompatible polymer blends, major component generally takes the continuous phase, and at 50/50 composition the lower viscosity component forms the continuous

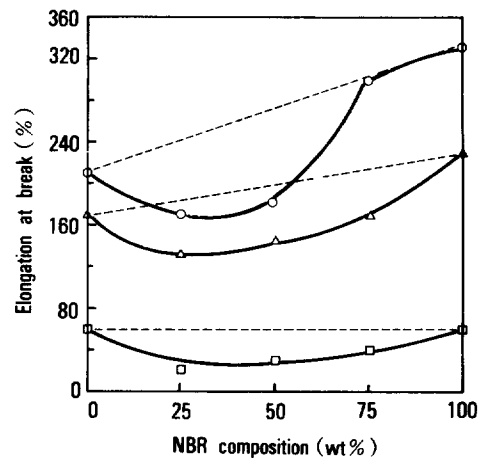


Fig. 4. Elongation at break of the blends : same symbol with Fig. 2.

phase.<sup>1,2</sup> In this experiment, CR of slightly higher viscosity than NBR was used. However, during the mastication process, CR was first fed to the roll, followed by NBR to approach viscosity match, and hence CR was subject to excessive breakdown during mixing and its viscosity could possibly be lowered below that of NBR.

The results of heat buildup test are given in Fig. 6. It is seen that heat buildup of CR is less than the half of NBR, which upon blending with CR temperature rise is significantly reduced showing

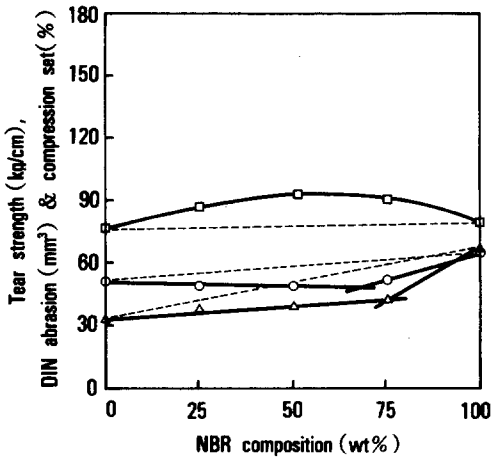


Fig. 5. Tear strength (○), DIN abrasion (□) and compression set (△).

negative deviation from the linear additivity. The change of compression set of NBR is subsequently reduced in blends and the level is, more or less, the same as CR.

**Aging and Oil Resistance**

Rubber compounds have a propensity to deteriorate in properties with exposure to heat, oxygen, ozone, and oil.<sup>1</sup> Hardness is increased upon aging, and decreased by immersion in hot oil (Fig. 2), due probably to the post cure during the aging test, and swelling of aromatic oil into the rubber, respectively. It is seen that the oil resistance of NBR in terms of hardness is significantly higher than that of CR, and the blends generally follow the additive rule.

Tensile strength of CR and CR-rich blends are deteriorated by aging and oil immersion (Fig. 3), and increased for NBR. When the drastically reduced elongation (Fig. 4) is considered together, rubbers and their blends are subject to hardening during the aging test. Hardening may be caused by simultaneous chain scission and crosslinking leading to brittle material. In oil resistance test, rubber is subject to less hardening, and oil penetrated into the rubber gives lubrication effect, leading to less brittle (Fig. 4) compared to aging treatment. Finally the volume and weight changes ( $\Delta V$  and  $\Delta W$ )

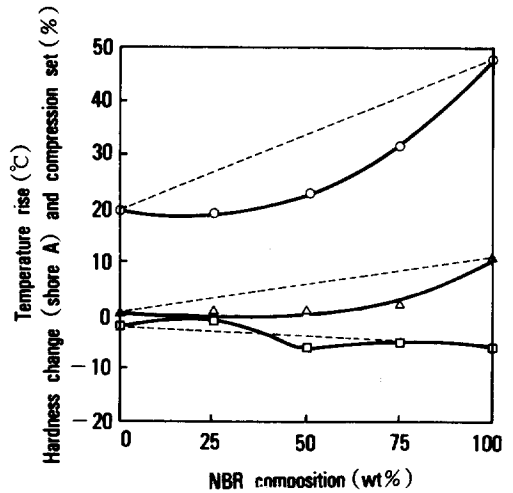


Fig. 6. Temperature rise (○) and change of compression set (□) and hardness (△), before and after heat buildup test.

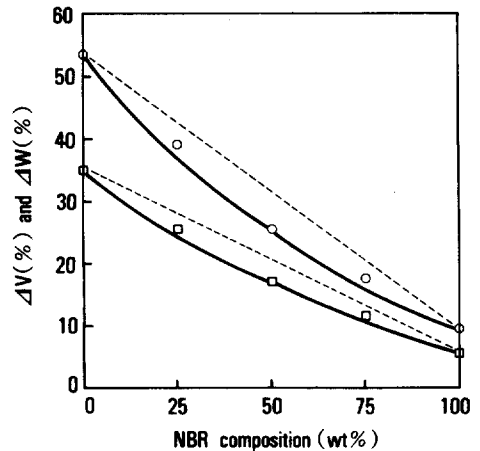


Fig. 7. Volume (○) and weight (□) change, before and after immersion in oil (ASTM #3 oil, 100°C, 70 hrs).

$\Delta W$ ) after immersion in oil are shown in Fig. 7. It is seen that the changes are much smaller for NBR than CR, due to the better oil resistance of NBR. With regard to the blends,  $\Delta V$  and  $\Delta W$  show negative deviation from the linear additivity, a desired property.

**Acknowledgement** : The financial support from the Korean Ministry of Education is gratefully acknowledged.

## REFERENCES

1. E. T. McDonel, K. C. Baranwal, and J. C. Andries in "Polymer Blend" (D. R. Paul and S. Newman eds.), Vol 2, Chap. 19, Academic Press, New York, 1978.
2. P. J. Corish, *Rubber Chem. Tech.*, **40**, 324 (1967).
3. G. N. Avgeropoulos, F. C. Weissert, P. H. Biddison, and G. G. A. Bohm, *ibid*, **49**, 93 (1976).
4. Y. Sakaura in "Science of Rubber", Chap. 14, *Jap. Inst. Rubber. Tech.*, Tokyo, 1982.
5. J. E. Callan, W. M. Hess, and C. E. Scott, *Rubber Chem. Tech.*, **58**, 350 (1985).
6. A. F. M. Barton, "CRC Handbook of Solubility Parameters and Other Cohesion Parameters", CRC Press, Boca Raton, Florida, 1983.
7. Denka Technical Report #66, 1969.
8. C. D. Han, "Multiphase Flow in Polymer Processing", Academic Press, New York, 1981.
9. H. Van Oene, in Ref. 1, Chap. 7.
10. D. Heikens, N. Hoen, W. Barentsen, P. Plet, and H. Leiden, *J. Polym. Sci., Polym. Symp.*, **62**, 309 (1978).
11. W. Berger, H. W. Kammer, and C. Kummerlowe, *Makromole. Chem. Suppl.*, **B**, 101 (1984).
12. S. J. Park, B. K. Kim, and H. M. Jeong, *Eur. Polym. J.*, **26**, 131 (1990).
13. B. K. Kim, S. Y. Park, and S. J. Park, *ibid*, **27**, 349 (1991).
14. B. K. Kim and S. J. Park, *J. Appl. Polym. Sci.*, in press.
15. W. M. Hess, C. E. Scott, and J. E. Callan, *Rubber Chem. Tech.*, **40**, 371 (1967).
16. V. L. Folt and R. W. Smith, *ibid*, **46**, 1193 (1973).
17. S. Mukhopadhyay, T. K. Chaki, and S. K. DE, *J. Appl. Polym. Sci.*, **28**, 25 (1990).
18. I. M. Ward, "Mechanical Properties of Solid Polymer", Wiley, 1983.
19. T. Kyu, S. Hu, and R. S. Stein, *J. Polym. Sci., Polym. Phys.*, **25**, 89 (1987).
20. T. O. Ahn, C. K. Kim, B. K. Kim, H. M. Jeong, and J. D. Huh, *Polym. Eng. Sci.*, **30**, 341 (1990).