

A Study on the Synthesis and Characteristics of a Blend of Natural Rubber and Hydrogenated Acrylonitrile-Butadiene Rubber

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Abstract: Natural rubber (NR) is a vulcanizing agent that is widely used in industrial applications; thus, its resistance to oil, ozone, and high temperatures should be improved. Similarly, hydrogenated acrylonitrile-butadiene rubber (HNBR) vulcanizers require a better elastic performance. Therefore, in this study, NR and HNBR with polarity differences were mixed via the master batch blend method to prepare a blend, and the vulcanization, basic physical properties, and resilience properties of each blend were evaluated. Changes in the mechanical properties, ozone resistance, and resilience modulus after heat treatment at ~70–120 °C were evaluated for each blend formulation. It was found that, as the NR content increased, the vulcanization rate increased, and as the HNBR content increased, the performance improved in terms of heat and ozone resistance. However, no resilience effect was found because of the crystallinity of HNBR. From the results of this study, it can be concluded that, if NR/HNBR is blended to the specifications required for heat and ozone resistance, it will be useful for applications requiring a superior performance than individual NR and HNBR.

Keywords: NR, HNBR, Blend, Heat resistance, Physical performance, Masterbatch.

INTRODUCTION

The rubber industry has developed since Columbus returned from his exploration on the new continent and introduced natural rubber (NR) in Europe; later on, Goodyear invented vulcanization. Initially, rubber was used to a limited degree, only for office supplies, and not actually in the industry sector. However, as the automobile industry grew and industrialization continued, various types of rubber material for both general and special uses have been developed. In addition to this increase in demand, the features of rubber required in special industry sectors have become more varied and sophisticated.

Rubber is a polymer material that is widely used for automotive tires, belts, hoses, vibration-free rubber, and other special products. Rubber is divided into two types: NR, which is produced by collecting, solidifying, and drying sap of rubber trees, and synthetic rubber, which is produced by polymerizing monomers from the petrochemical industry.

Among the different raw rubber materials, NR is widely used owing to its excellent physical properties, including tensile and tear strength, as well as its low price and outstanding processability [1]. However, NR is disadvantageous in terms of heat, ozone, and oil resistance due to the high degree of unsaturation of cis-1,4-polyisoprene. In addition, the allowable

maximum temperature of rubber products in continued use is known to be approximately 70 °C [2]. As such, approaches to enhance the heat resistance of NR should be investigated.

Acrylonitrile-butadiene rubber (NBR) is a type of synthetic rubber that is widely used in products that require oil resistance. However, the main chain of its monomers includes a double bond that hinders high-heat resistance [3].

To overcome this issue, hydrogenated NBR (HNBR) was developed by inducing selective hydrogenation reactions in NBR, and its commercial production started in Japan in 1984. HNBR is expensive, but the $-\text{CH}_2\text{-CH}(\text{CN})-$ structure of its monomers exhibits oil and fuel resistance and high strength. The $-(\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2)-$ structure exhibits heat resistance, cold resistance, ozone resistance, and elasticity. A small quantity of the $-(\text{CH}_2\text{-CH}_2=\text{CH}_2\text{-CH}_2)-$ structure exhibits the sulfur crosslinking property. Thus, HNBR is widely recognized as a rubber material featuring both oil and heat resistance in extreme conditions as well as high processability and wide applicability [10].

When a rubber product is used, however, more properties are required in addition to heat resistance depending on the desired use, including a higher level of oil resistance and a high-heat compression set. Because it is difficult for one rubber material to satisfy all the physical, chemical, and mechanical conditions of a rubber product, it is preferred to blend two or more rubber materials to overcome their individual disadvantages [4]. Blending of different rubber

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Table 2: Mixing Procedure for the Blend Masterbatches

A. Preparation of the masterbatches Banbury operating conditions	
Speed	77 rpm
Temperature	60 °C
Fill factor	0.7
Ram pressure	3.0 kgf/cm ²
Cooling water	18 °C
Mixing procedure	
	Time (min)
1. Add NR or HNBR	0.0
2. Add half carbon black and additives	0.5
3. Sweep and add the remaining carbon black	1.5
4. Dump	3.0
5. Cool the sample overnight after sheeting off on a mill	
B. Blending of the masterbatches (Banbury operating conditions identical to above)	
	Time (min)
1. Add NR and HNBR masterbatches	0.0
2. Dump	1.5
C. Curative addition on the mill (at ~60 °C–70 °C)	
	Time (min)
1. Set the mill opening to 4 mm and add the NR and HNBR masterbatches	0.0
2. Add curatives	0.5
3. Set the mill opening to 2 mm and make three to four cuts from each side repeatedly	1.5
4. Set the mill opening to 5 mm and sheet off and cool the compound	4.5

Step B. In Step C, the masterbatch blending method was applied to complete the blending process.

3. Evaluation of the Physical Properties

3.1. Vulcanizing Characteristics (Cure Characteristics) Measurements

The torque value was measured for 30 min using a moving die rheometer (RLR-3; rotorless rheometer, Toyoseiki, Japan) at a temperature of 190 °C and under a vibration angle of $\pm 1^\circ$.

3.2. Mooney Viscosity Measurements

The torque value required for metal disk rotation was measured using a Mooney viscometer (Vulchem IND Co., Korea), a type of rotational viscometer. After preheating for 1 min according to ASTM D1646, a large disk (diameter: 38.1 ± 0.05 mm; thickness: 5.5 ± 0.05 mm) was operated at 2 rpm for 4 min at 121 °C, and the value was measured.

3.3. Mechanical Property Measurements

Dumbbell-type specimens with dimensions of 100 (L) \times 25 (W) \times 2 (T) mm³ were produced according to

ASTM D412. The tensile strength and elongation of the produced specimens were measured using a universal tensile machine (KSU-05M-C, KSU Co., Korea). With specimens pressed with a force of approximately 2 kg (19.6 B), the hardness of the vulcanizates was measured five times using a Shore A durometer according to ASTM D2240, and the average was then calculated.

3.4 Resilience Properties

Resilience properties were tested according to ASTM D1054. In general, when a load W falls freely on a rubber surface from height h_0 and then bounces back to height h_1 , the energy loss W ($h_0 - h_1$) is converted into heat inside the rubber. In this study, the energy loss converted into h_1/h_0 at the resilience property tester was converted into the modulus of elasticity (%).

3.5. Post-aging Properties

For testing the post-aging properties, the same specimens used for the measurement of the mechanical properties were employed and were then placed in an aging tester for a week, where heat waves were applied to keep the temperature constant at 70

°C, 100 °C, and 120 °C. The post-aging mechanical properties were then measured using the same equipment and method employed for measuring the mechanical properties, in compliance with ASTM D412. The change in hardness, resilience properties, and other preservation rates at high temperature were calculated in comparison with the measurements at normal temperature and after aging.

3.6. Ozone Cracking Test

On the basis of the KS M 6518 ozone cracking test method, specimens were extended as much as 20% and 50% at a temperature of 40 °C and under an ozone concentration of 50 ± 5 ppm. In order to examine the status of ozone cracking, the static test was continued until cracks occurred in the ozone chamber.

RESULTS AND DISCUSSION

1. Curing and Mooney Viscosity Characteristics

Table 3 shows the vulcanization properties for each blending ratio of the polymers. Table 4 shows the Mooney viscosity. The Mooney viscosity appears to be independent of the blending ratio of the polymers; this is probably because the viscosity of the two blended raw rubber materials is similar, and the mixing method is the same. The proper scorching time and Tc90, which corresponds to the vulcanizing time at which the ideal properties are obtained, increase upon increasing the proportion of NR in the blend owing to its high degree of unsaturation.

Figure 1 shows the maximum and minimum torque values measured in a Rheometer vulcanizing test, where the vulcanization properties of a blend are evaluated. The difference between these two values is

related to the vulcanizing density of the blend. As shown in Figure 1, the minimum torque value of the specimens is the same, but the maximum value increases if only one raw material is used. This can be attributed to the deterrent effect of the blend. Thus, even if the compounds are prepared with the same mixing method, the properties of a blend of two raw rubber materials may be different depending on the blending method. Figure 2 shows the vulcanizing rate, which was calculated as follows:

$$(\text{Maximum torque} - \text{Minimum torque}) / (\text{Tc90} - \text{ts2})$$

In particular, the value increases drastically as the NR proportion becomes higher. This indicates that the unsaturation degree of NR is much higher than that of HNBR.

2. Mechanical Characteristics

Table 5 shows how the mechanical properties depend on the blending ratio of the polymers. As for the tensile stress and tensile strength, it can be seen that there is no significant dependence on the blending ratio. However, the tensile strength is relatively low in the case of the N60 and N80 compounds, in which NR is assumed to have a matrix structure. In general, the elongation rate increases as the proportion of NR in the blend increases. The elongation rate of the N50 compound increases at a particularly high rate. This phenomenon was observed in a blend of NR and NBR in a work by Ahamd [13] and is probably related to the fact that the particle size of the dispersoid polymers depends on the blending ratio. The N50 compound, which is a blend of two raw rubber materials with the same viscosity, exhibits the highest elongation rate probably because it has the smallest dispersoid polymer particles.

Table 3: Cure Characteristics of the Compounds with Different Blending Ratios

Mix no.		N0	N20	N40	N50	N60	N80	N100	Remark
MDR 190 °C *30 min	Tc90	2.09	1.57	1.37	1.39	1.24	1.11	1.12	min
	ts2	0.92	0.77	0.73	0.71	0.63	0.57	0.59	min

Table 4: Mooney Viscosity Characteristics of the Compounds with Different Blending Ratios

Mix no.		N0	N20	N40	N50	N60	N80	N100	Remark
Mooney viscosity	ML ₁₊₄	41.7	38.1	40.3	38.8	42.9	43.9	41.3	121 °C
	T ₅	19.53	11.39	10.11	9.57	9.35	8.46	8.17	min

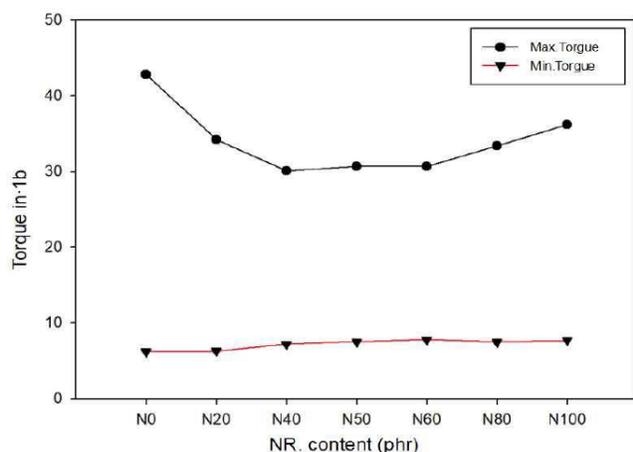


Figure 1: Maximum and minimum torque values of the compounds with different blending ratios.

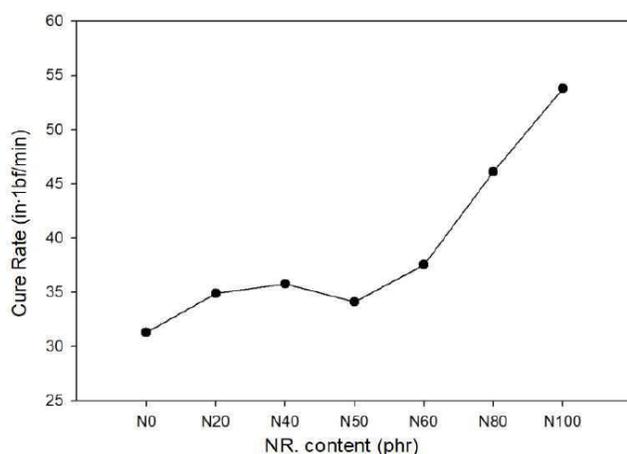


Figure 2: Cure rate of the compounds with different blending ratios.

In general, the compound characteristics were found to be consistent regardless of the material properties. Although the materials used were noncommercial and showed different polarities, it seems that the high polarity of HNBR and the high degree of unsaturation of NR induced a competitive flowing of the vulcanizing agent at the two phases, resulting in a satisfactory mixing performance.

3. Resilience Properties

Figure 3 shows how the resilience properties depend on the blending ratio of the polymers. It was expected that, owing to the superior elastic performance of NR, the higher the NR content is, the better the resilience properties will be. However, all compounds exhibit similar properties except for the N100 sample. This is probably because the elasticity is affected by the crystallinity of nitrile, which is a raw material of HNBR.

4. Aging Characteristics as a Function of Temperature

Figures 4-8 show the results of the aging tests conducted at different temperatures depending on the ratio of the various compounds. As the aging temperature increases, the tensile stress accordingly increases. In the case of the N60, N80, and N100 compounds, however, the elongation rate decreases drastically at an aging temperature $<100^{\circ}\text{C}$, and no 300% tensile stress is observed. The tensile strength and elongation also decrease as the aging temperature increases, particularly samples with a higher proportion of NR than 50. This result indicates that the heat resistance of NR is inferior. It is known that the aging phenomenon of NR results from the presence of a small amount of oxygen. Therefore, the improvement effect is observed as the content of HNBR increases.

Figure 8 shows how the resilience properties change after the heat resistance treatment. Although the resilience properties before the thermal treatment are the same for all compounds except for N100, after the thermal treatment, an inconsistency can be observed, as the rate of change is the same for all compounds regardless of the temperature. This could be due to the aging characteristics of NR, which are affected by the inconsistent blending property and heat

Table 5: Physical Properties of the Compounds with Different Blending Ratios

Mix no.	N0	N20	N40	N50	N60	N80	N100	Remark
Hardness	72	73	71	69	70	67	62	pts
Tensile strength	279.18	272.48	256.81	271.94	241.91	241.53	269.87	kgf/cm ²
Elongation	475	562	579	644	576	520	534	%
Modulus (100%)	26.92	25.92	26.30	24.15	25.25	25.78	24.63	kgf/cm ²
Modulus (300%)	117.43	93.56	88.95	77.19	92.97	100.29	107.73	kgf/cm ²
Tear strength	70.42	79.82	67.51	88.55	93.57	100.91	99.67	kgf/cm

as raw rubber materials of different polarities are blended. Hence, the resilience properties and heat resistance are independent of the NR content.

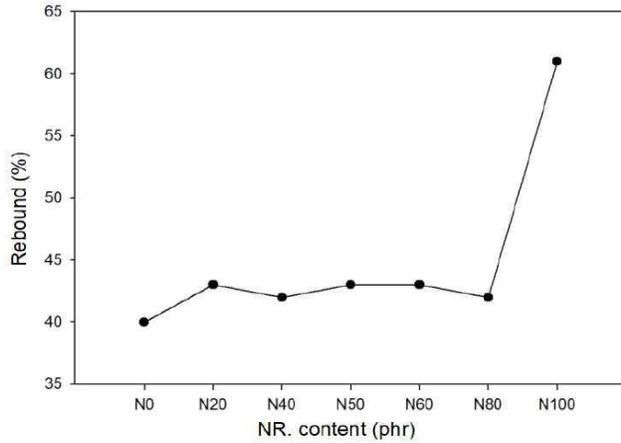


Figure 3: Rebound properties of the compounds with different blending ratios.

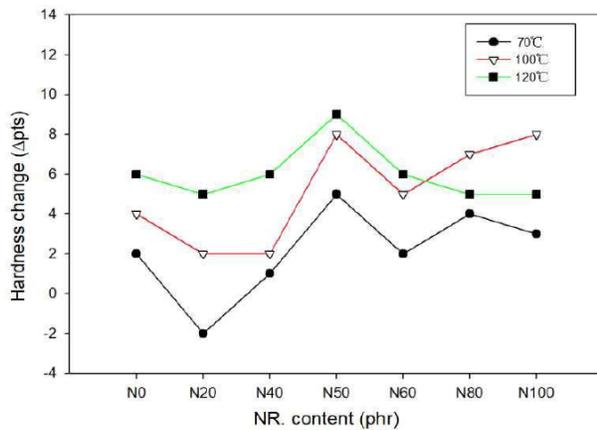


Figure 4: Hardness change observed after aging for 7 days at various temperatures for compounds with different blending ratios.

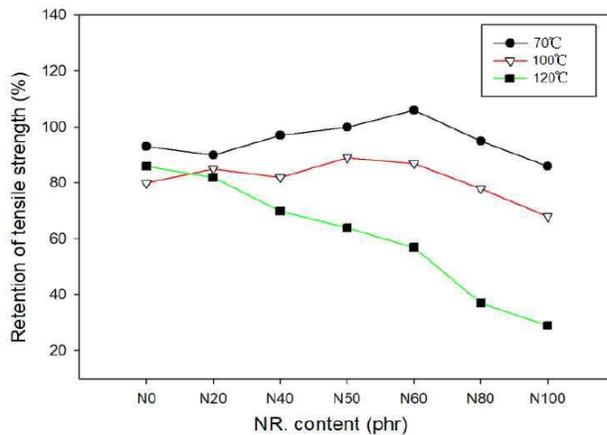


Figure 5: Retention of the tensile strength after aging for 7 days at various temperatures for compounds with different blending ratios.

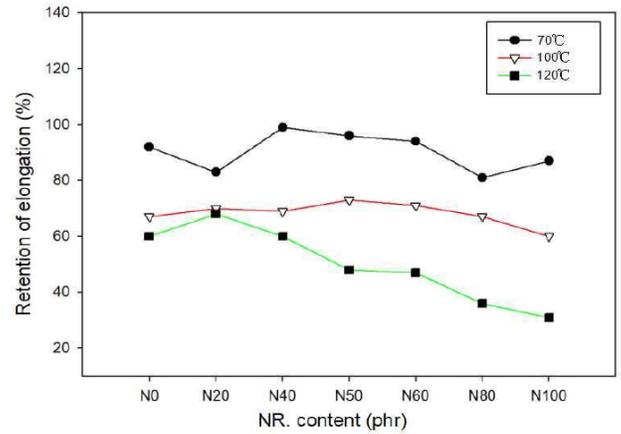


Figure 6: Retention of elongation after aging for 7 days at various temperatures for compounds with different blending ratios.

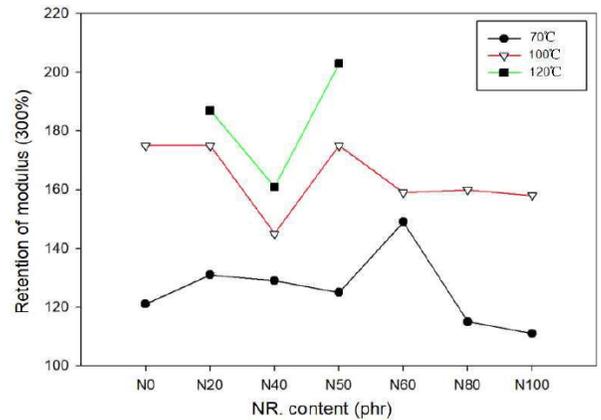


Figure 7: Modulus retention (300%) after aging for 7 days at various temperatures for compounds with different blending ratios.

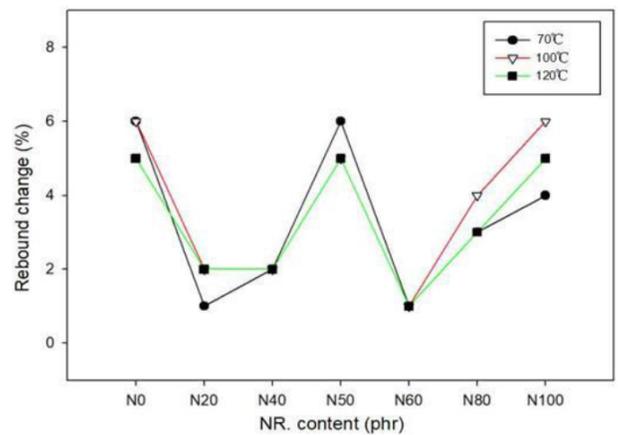


Figure 8: Rebound change after aging for 7 days at various temperatures for samples with different blending ratios.

5. Ozone Characteristics

Table 6 shows how the ozone resistance properties depend on the blending ratio of the polymers. At a

Table 6: Ozone Resistance of Vulcanizates with Different Blending Ratios

Mix no.		N100	N80	N0-N60	Remark
Time to the first crack (at static strain)	Type 1	<1 day	>3 weeks	>3 weeks	20%
	Type 2	<1 day	<1 day	>3 weeks	50%

deformation rate of 20%, the ozone resistance performance is stable for all compounds except for the N100 compound. At a rate of 50%, however, cracks occur within 1 day in the case of N100 and N80. It was also reported that, in order to secure the proper ozone resistance performance at a deformation rate of 20%, the ratio of EPDM should be at least 30% in weight [1], which is as low as 60 phr. In this study, however, the ozone resistance performance is improved with 20 phr HNBR at a deformation rate of 20%. At a deformation rate of 50%, the ozone resistance performance is improved with 40 phr HNBR. This result shows that HNBR is a superior material to EPDM in improving the ozone resistance performance of NR.

CONCLUSIONS

In order to improve the elasticity of HNBR and the heat and ozone resistance of NR in rubber materials, the vulcanization properties, mechanical properties, and their corresponding changes after heat resistance were investigated for samples with different NR-to-HNBR blending ratios and compared with the single-material compounds. On the basis of the experiment results, the following conclusions can be drawn:

- 1) Because of the unsaturated content of NR, the vulcanization rate increased as the NR content increased. As the viscosity of NR and HNBR is the same, the viscosity of the NR/HNBR compounds remained the same. Hence, the vulcanization properties of the NR/HNBR blended compounds were in general the same as those of the single-material compounds.
- 2) As the stiffness of NR and HNBR is similar, the properties were consistent among the compounds. However, the tensile strength in the compounds with high NR content decreased to some extent, which the acrylonitrile crystallinity of HNBR. In addition, as the NR content increased, it was expected that the resilience properties of HNBR improved to match those of the NR/HNBR blended compounds. However, there was no significant improvement due to the crystallinity of HNBR.

- 3) The heat resistance of the NR/HNBR compounds was improved upon increasing the HNBR content. Taking N50 as the reference point, a significant change could be observed. It was also expected that, as the NR content increased, the resilience rate would accordingly increase after heat resistance. However, the result was inconsistent. This is probably because NR is vulnerable to heat, and polar and nonpolar elements were blended at a nonuniform rate.
- 4) When the elongation condition of ozone-resistant specimens is 20% or 50%, the ozone resistance was improved when NR was blended with 20 and 40 phr HNBR. This result indicates that HNBR is effective to improve the performance of NR, which is vulnerable to ozone.
- 5) As NR and HNBR were blended, the heat and ozone resistance performance were improved. HNBR is an unsaturated rubber material, but sulfur vulcanizing can be applied to it just as in the case of NR. Thus, there is no problem in the vulcanization because the vulcanization properties of the blended compounds were similar.
- 6) Considering changes in overall physical properties, such as basic properties, heat resistance, ozone resistance and resilience, the mixture of NR 20 phr shows the most improved changes in physical properties.

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