Cure Characteristics and Physical Properties of Ground-Rubber-Filled Natural Rubber Vulcanizates: Effects of the Curing Systems of the Ground Rubber and Rubber Matrix

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ABSTRACT: Recycling discarded rubber is important for both environmental and economic reasons. One of the most attractive methods of recycling rubber waste is to use ground rubber (GR) as a compounding ingredient or as a replacement for raw polymers. In this study, ground natural rubber was prepared with different curing systems and compounded into the parent compounds. The cure behaviors and physical properties of the GR-filled vulcanizates were investigated, and they were largely affected by the curing systems of the rubber matrix and GR. GR-filled vulcanizates with GR and the rubber matrix, having a conventional curing system, showed the largest changes in the cure char-

acteristics. The greatest decrease in the physical properties was observed for peroxide-cured-GR-filled vulcanizates. The addition of GR decreased the crosslink density of the GR-filled vulcanizates. This was thought to be the main reason for the reduction of the mechanical properties of the GR-filled vulcanizates. However, the adhesion between the GR and rubber matrix may also have caused the differences in the physical properties of the GR-filled vulcanizates with respect to the curing systems of the rubber matrix and GR. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2396–2406, 2007

Key words: crosslinking; recycling; rubber; structure

INTRODUCTION

Unlike general thermoplastic resins, rubber vulcanizates are not soluble with solvents and do not melt down when heated because of the three-dimensional network in their internal structures, that is, crosslinks. Accordingly, scrap rubber is generally incinerated or discarded in landfills. However, these methods cannot be the final solution because they have caused many problems, such as soil and air pollution.[1]

Various attempts to recycle rubber scrap as a useful resource have been reported since the late 1960s.[1–6] They can be classified into two large groups: making ground rubber (GR) from scrap rubber and recycling it as reclaimed rubber.[7] Grinding is the basic step for recycling scrap rubber, and GR has been used as the raw material not only for the production of reclaimed rubber but also for various applications,[8] such as fillers for rubber,[9–16] fillers for thermoplastic compounds,[17–19] and modifiers for asphalt concrete.[20,21] Flooring with urethane binders and GR has also been widely used,[22] and a new method for producing a vul-

canizate sheet from GR with dienophiles and dipolar chemicals has been reported recently; it is called *high-pressure, high-temperature sintering*.[23,24]

From economic and environmental points of view, the use of GR as a filler for rubber compounds has more merit than other methods because it does not need additional processing, reactions, or treatments, and the chemical nature of the various ingredients in GR can be maintained.[25] Many researchers have reported that the addition of GR greatly influences the cure characteristics and physical properties of GR-filled vulcanizates.[2–8,22] The sulfur migration from the rubber matrix to GR and the diffusion of accelerator fragments to the rubber matrix from GR are known to change the cure characteristics.[26] The low adhesion between GR and the rubber matrix is thought to lead to the severe drop in the tensile properties of GR-filled vulcanizates.[13]

In the meantime, the sulfur diffusion rate to crosslinked rubber has been shown to largely depend on the crosslink structures of the vulcanizates, and vulcanizates having polysulfide structures have shown a higher sulfur diffusion rate than those having monosulfide structures.[27,28]

From these reports, it can be inferred that the changes in the cure behaviors and physical properties

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TABLE I
Materials

Description	Ingredient/grade	Source
NR	Natural rubber/SMR-L	
HAF	Carbon black/N330	DC Chemical Co. (Korea)
ZnO	Zinc oxide/KS #2	Hanil Chemical Industry (Korea)
Stearic acid	Stearic acid	LG Chemical (Korea)
Sulfur	Sulfur/MIDAS101	Miwon Chemical Co. (Korea)
CBS	N-Cyclohexylbenzothiazole-2-sulfenamide	Flexsys (USA)
TMTD	N,N,N',N'-tetramethyl thiuram disulfide	Flexsys (USA)
DTDM	4,4-dithiodimorpholine	R. T. Vanderbilt Co. (USA)
DCP	Dicumyl peroxide	Nippon Oil and Fats Co. (Japan)

of GR-filled vulcanizates greatly differ with respect to the curatives used in GR and the rubber matrix; however, these effects have been little investigated. Moreover, the effect of the curing system in GR and the rubber matrix has not drawn much attention.

On the basis of our preliminary study,[29] natural rubber (NR) vulcanizates were prepared with different curing systems such as conventional (CV), semi-efficient (semi-EV), and efficient (EV) or sulfur-donor curing systems. GR from these vulcanizates was mixed into the parent compounds. Peroxide-cured GR was also prepared to be compared with sulfur-cured GR, and this was added to three rubber matrices, which had three different sulfur-curing systems. With the variation of the contents of GR, the cure characteristics and physical properties of GR-filled vulcanizates were investigated. The crosslink densities were also measured, and the fractured surfaces of tensile and tear specimens were observed.

EXPERIMENTAL

Materials and compounding

The materials used in this study are presented in Table I. The compounds were prepared with a two-roll mill according to the mixing schedule shown in Table II. The recipes for the NR vulcanizates and GR-filled NR vulcanizates are presented in Table III. NC, NS, and NE are NR compounds with CV, semi-EV, and EV curing systems, respectively. For comparison with sulfur-cured GR, peroxide-cured natural rubber (ND) was also prepared.

NCG, shown in Table III, represents compounds having a CV curing system, into which ground NC was added. That is, ground NC was mixed into the parent compound (NC), and this compound was designated NCG. In the case of NCDG, ground ND was compounded into the NC matrix. The same rules were applied to NSG, NSDG, NEG, and NEDG.

The amount of GR was varied from 10 to 50 phr. Other additives, such as processing oils, waxes, and antioxidants, were not used to eliminate their influence.

Preparation of GR

Mixed compounds were cured with an electrically heated hydraulic press for the optimum cure times of each compound at 150°C, and ND compounds were cured at 160°C for 40 min. Fully, cured sheets were ground with a crusher (Daeheung Machine Industry, Korea) with a rotary-type cutter. Before the grinding, the sheets were placed in dry ice, and a certain amount of dry ice was added to the crusher at regular intervals to minimize aging of the rubber by heat and to increase the grinding rate.

GR was dried in a vacuum oven at 30°C, and the particle size and distribution were measured with a standard sieve. As shown in Table IV, there were no differences in the particle size and distribution for GR with respect to the curing systems.

The morphology of the rubber particles, as observed with a scanning electron microscope (S200, Hitachi, Japan), is shown in Figure 1. The morphology of GR in this study is similar to that of particles produced by high-speed intensive cutting[30,31] and a cryogenic grinding process.[32,33] The morphology makes little difference among the curing systems.

From these results, it could be expected that the effects of the particle size and morphology of GRs with different curing systems on the cure characteristic and physical properties of GR-filled vulcanizates would be negligible.

Unvulcanized rubber properties and cure characteristics

To confirm the changes in the particle size and morphology of GR after mixing procedures, about 0.5 g of

TABLE II
Mixing Schedules for the NR Compounds

Ingredient	Mixing time (min)
NR	5
ZnO and stearic acid	4
GR	5
HAF	8
Curatives (sulfur, accelerators, and DCP)	5

TABLE III
Formulations for NR and GR-Filled NR Compounds (phr)

Ingredients	NC	NS	NE	ND	NCG	NSG	NEG	NCDG	NSDG	NEDG
NR	100	100	100	100	100	100	100	100	100	100
GR	—	—	—	—	NC[a]	NS[a]	NE[a]	ND[a]	ND[a]	ND[a]
HAF	40	40	40	40	40	40	40	40	40	40
ZnO	3	3	3	—	3	3	3	3	3	3
Stearic acid	1.5	1.5	1.5	—	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	3	0.6	—	—	3	0.6	—	3	0.6	—
CBS	1	2	1.5	—	1	2	1.5	1	2	1.5
TMTD	—	1	1.5	—	—	1	1.5	—	1	1.5
DTDM	—	—	1.5	—	—	—	1.5	—	—	1.5
DCP	—	—	—	2.5	—	—	—	—	—	—
Sum	148.5	148.1	149	142.5	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]

[a] GR.
[b] The sum of the ingredients was variable with respect to the amount of GR.

NR compound containing 50 phr GR was stirred in tetrahydrofuran (THF) with a magnetic bar. After vacuum drying, the rubber particles were differentiated with a standard sieve (100 mesh), and scanning electron microscopy (SEM) photographs were taken.

The Mooney scorch times and Mooney viscosities (ML1+4) were determined at 125°C with a Mooney viscometer (Myungji Industry Co., Ltd., Korea). Cure behaviors such as the scorch times, optimum cure times, and torque variations were also measured at 150°C under a 1° arc with an oscillating-disk-type rheometer (ODR 2000, Myungji Industry Co., Ltd., Korea). The data from the Mooney viscometer and oscillating-disk-type rheometer of the parent NR compounds (NC, NS, and NE) are shown in Table V.

From the rheographs, the rate constants k of the vulcanization were calculated as follows:[34]

$$\ln[(1 - (\Delta L_t / \Delta L)] = -k \times t \quad (1)$$

where ΔL is the difference between the maximum torque ($T_{\max}$) and minimum torque ($T_{\min}$) and ΔL_t is the developed torque at arbitrary time T_t torque at a arbitrary time $- T_{\min}$.

Vulcanized rubber properties

Each compound was cured to 2-mm-thick sheets by compression molding with an electrically heated hydraulic press for the optimum cure times at 150°C

TABLE IV
Particle Size Distribution of Ground NR Vulcanizates (wt %)

Particle size		NC	NS	NE	ND
μm	Mesh				
850–600	20–30	66	70	67	62
600–425	30–40	28	24	25	31
425–300	40–50	4	4	5	6
Under 300	Over 50	2	2	3	1

under 14 MPa. Tensile and tear specimens were prepared in accordance with ASTM D 412 and D 624. Tests were performed with a Tensometer 2000 (Myungji Industry Co., Ltd., Korea) at a crosshead speed of 500 mm/min. Seven specimens were used for the tensile test, and five specimens were used for the tear test. The average value was reported, except for the measured maximum and minimum values. The physical properties of the NR vulcanizates are also presented in Table V.

Fractured surfaces of tensile and tear specimens were observed with SEM.

The crosslink densities of the NR vulcanizates and GR-filled vulcanizates were determined with the procedures used by Cuneen and Russell.[35]

RESULTS AND DISCUSSION

Morphology of GR

Photographs of GR, separated from uncured NR compounds, are depicted in Figure 2. There were some insoluble rubber gels, which did not dissolve in THF, on the surface of the GR, which made the GR appear somewhat round. However, except for the rubber gels, the morphology and size of GR did not change much during the mixing procedures. In addition, differences with respect to the curing systems were marginal.

Unvulcanized rubber properties

The variations of the Mooney scorch times for GR-filled NR compounds are presented in Figure 3. The addition of peroxide-cured GR exercised no influence on the Mooney scorch times, but sulfur-cured GR largely decreased the Mooney scorch times, regardless of the curing systems. This can be explained by the migration of accelerator fragments from GR to the rubber matrix in the case of sulfur-cured GR and the participation of accelerator fragments in the vulcanization of the rubber matrix.[16] Gibala and Hamed[26]
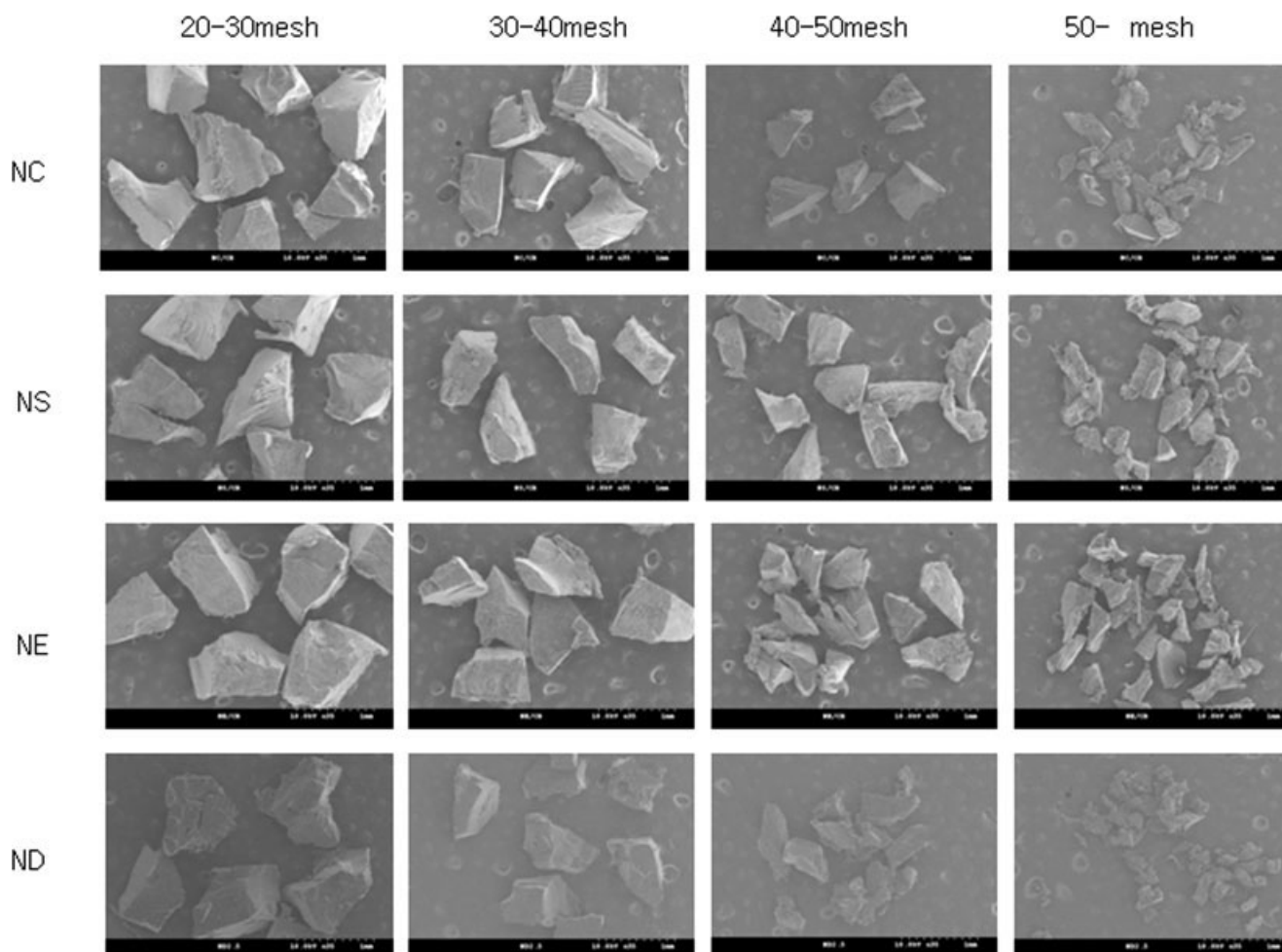
Figure 1 SEM photographs of ground NR vulcanizates with respect to the curing systems and the particle size.

reported that the sulfur migration into GR during mixing and curing procedures triggered the migration of accelerator fragments in GR to the rubber matrix. The variation with respect to the addition of GR was pronounced in the case of NCG with a CV curing system. This is reasonable because an NC matrix has the highest sulfur content and the vulcanization reaction of NC may be heavily influenced even by a small amounts of accelerators. However, the differences between NSG and NEG are marginal.

As shown in Figure 4, the use of GR slightly increases the Mooney viscosities of GR-filled compounds. However, the increase is much smaller than in other reports.[33] A two-roll mill was used for the mixing procedures in this study, and so extra time was needed to compound GR in the rubber compounds. It is thought that this extended mixing time caused more shear-induced breakdown of polymer chains in NR, which is known for mastication. The Mooney viscosity of SMR-L, rolled for 5 min, was 26.2; after 20 min, it was reduced to 1.9.

NC compounds showed higher sensitivity to the Mooney viscosity with the addition of GR.

The Mooney viscosities in Figure 4 are not the lowest values but the ML1+4 values, so they can be affected by the induction time of the cure, such as the scorch time of the rubber matrix. This is also the reason for NCDG, NSDG, and NEDG having lower values than NCG, NSG, and NEG.

TABLE V
Cure Characteristics and Physical Properties of the NR Compounds

	NC	NS	NE
Mooney viscometer at 125°C			
Mooney scorch time (min : s)	16 : 13	12 : 36	17 : 12
Mooney viscosity (ML1+4)	53.2	46.3	36.7
Oscillating-disk-type rheometer at 150°C			
Scorch time (min : s)	3 : 50	3 : 07	5 : 08
Optimum cure time (min : s)	9 : 42	6 : 44	13 : 36
Physical properties			
Hardness (Shore A)	62	62	61
Modulus at 100% elongation (kgf/cm^2)	29.7	25.6	28.4
Modulus at 300% elongation (kgf/cm^2)	149	142	152
Tensile strength (kgf/cm^2)	245	255	251
Elongation at break (%)	442	451	428
Tear strength (kgf/cm)	80.8	60.0	43.8
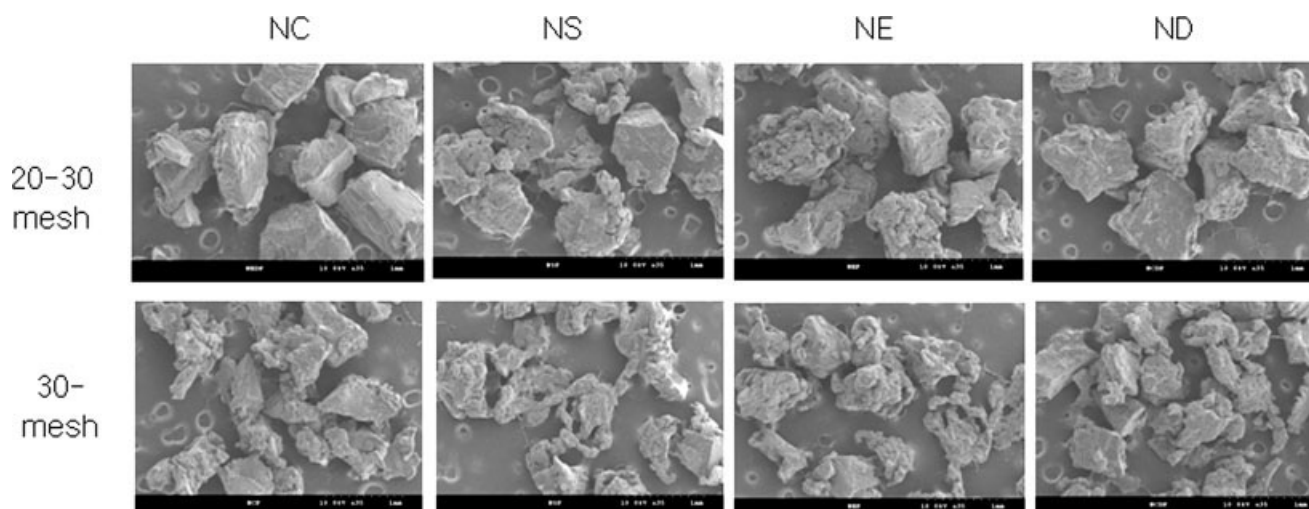
Figure 2 SEM photographs of ground vulcanizates after mixing procedures.

Cure characteristics

Rheographs of GR-filled compounds are presented in Figures 5–7. The digits in the sample names indicate the amount of GR in the rubber compounds. For example, NCG10 is the rubber compound with a CV curing system (NC), having 10 phr ground NC.

The variations of the cure characteristics from rheographs, such as the scorch time, optimum cure time, and torque development ($T_{max} - T_{min}$), with respect to the curing systems are shown in Figures 8–10.

Similarly to the Mooney scorch times, the rheometric scorch times also decreased with the addition of sulfur-cured GR. In particular, the NC compounds showed the greatest decrease (Fig. 8). With sulfur-cured GR, optimum the cure times also diminished, but the dependence on the curing systems was not large (Fig. 9). Peroxide-cured GR little affected the

scorch times and optimum cure times of GR-filled compounds (Figs. 8 and 9).

As depicted in Figure 10, as the amount of GR increased, the torque development from rheographs decreased, regardless of the curing system of GR. The torque development is the difference between T_{max} and T_{min} on rheographs, which is known to be related to the crosslink densities of rubber vulcanizates.[36] It has been reported that the sulfur migration from the rubber matrix into GR can cause a reduction of sulfur in the rubber matrix available during vulcanization and consequently a drop of the crosslink densities of GR-filled vulcanizates.[26] In addition, it has been ascertained that the concentration gradient of sulfur between GR and the rubber matrix is the main reason for sulfur migration and that the chemical structures of GR also influence sulfur migration.[27]
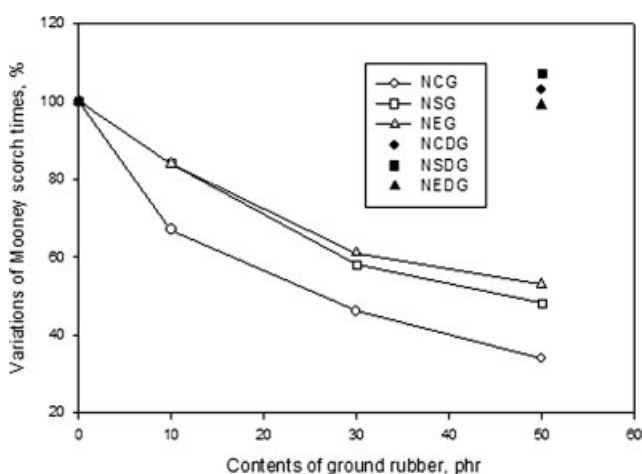
Figure 3 Variations of the Mooney scorch times for NR compounds.
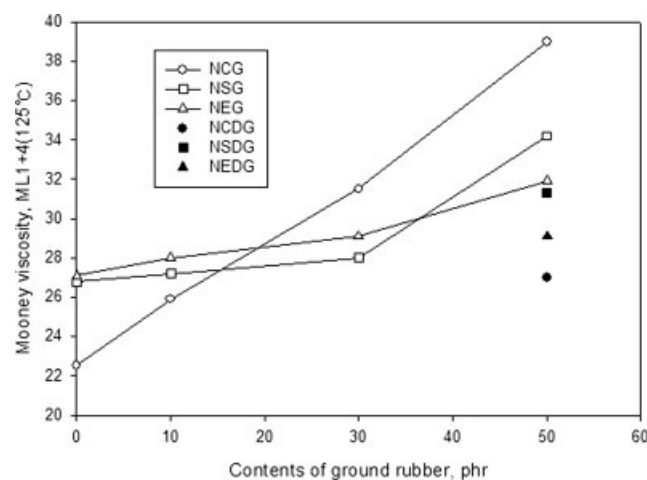
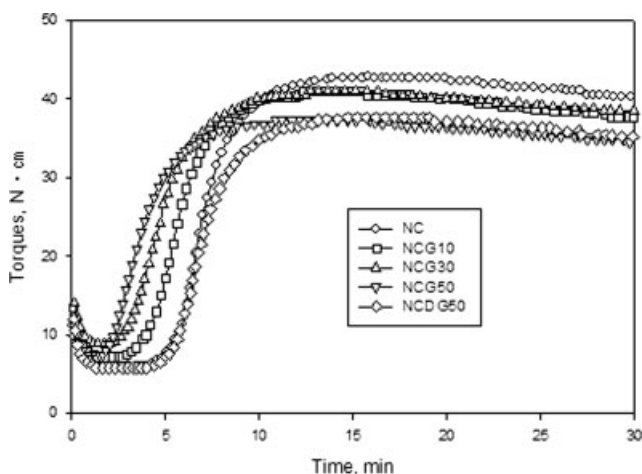**Figure 4** Variations of the Mooney viscosities for NR compounds.

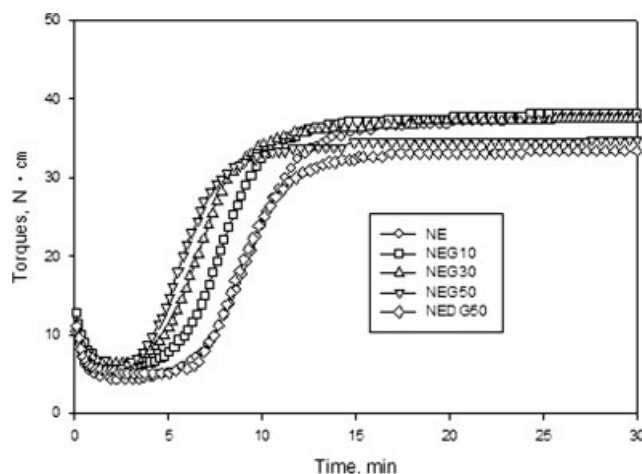**Figure 5** Cure curves of NCG and NCDG compounds.

Figure 7 Cure curves of NEG and NEDG compounds.

The NCG series shows the largest variation of the torque development, and it is reduced in the order of NSG and NEG compounds. Although the addition of peroxide-cured GR decreases torque development, the differences with respect to the curing system of the rubber matrix are marginal.

One of the plots for calculating crosslink rate constants with eq. (1) is illustrated in Figure 11, which is for the NE series. The rate constants, acquired from the slopes from the linear region of each plot, are shown in Table VI.

With the addition of GR up to 30 phr, the cure rate for NCG and NSG decreases. Over that amount, it increases a little. However, for NEG, it increases a little up to 50 phr GR.

The cure rate for rubber compounds with peroxide-cured GR varies in a different way. NSDG50 and NEDG50 show higher cure rate constants than NS and NE compounds, but NCDG50 does the opposite.
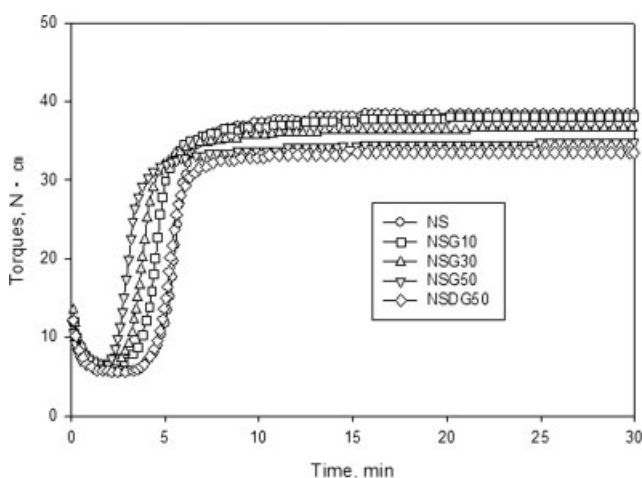
Physical properties

Figures 12 and 13 show the moduli at 100 and 300% elongation for GR-filled vulcanizates. Measurement error bars are shown in the figures. As the amount of GR increases, the moduli are reduced. This tendency is exactly the same as that of the torque development in Figure 10. For NCG, which shows the highest reduction of torque development, the drop in the modulus is the most severe.

As presented in Figure 14, tensile strengths abruptly drop with a small amount of GR, but with an increase of GR, they show little change. However, the variation in the NCG vulcanizates is much larger than that of other sulfur-cured vulcanizates, and peroxide-cured-GR has the most severe effects on the tensile strength.

The elongations at break of GR-filled vulcanizates are depicted in Figure 15. Except for NCG10, which shows the most severe decrease, the variations of
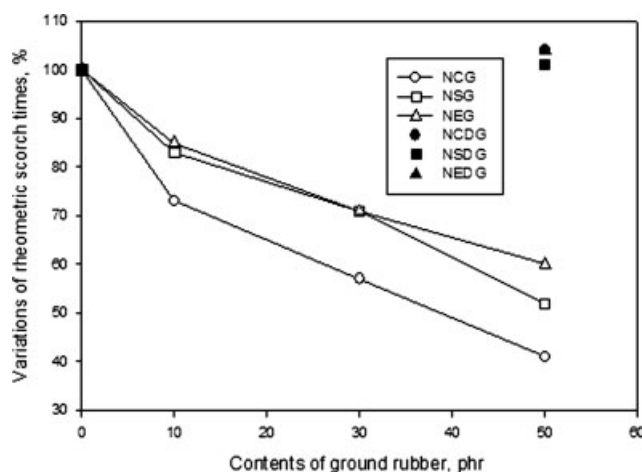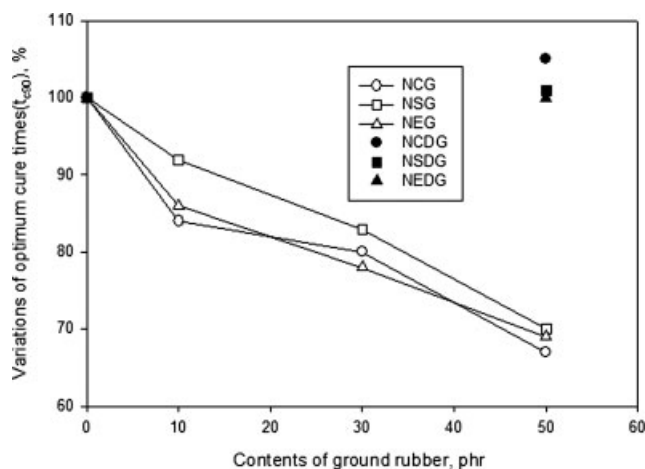

Figure 6 Cure curves of NSG and NSDG compounds.

Figure 8 Variations of the rheometric scorch times of NR compounds.

Figure 9 Variations of the optimum cure times of NR compounds.

Figure 11 Plot of $\ln[1 - (\Delta L_t/\Delta L)]$ versus the curing time.

NCG, NSG, and NEG are insignificant, and with over 30 phr GR, the elongation is in the range of their parent compounds. Similarly to the tensile strength, peroxide-cured GR shows the most adverse effects on the elongation at break.
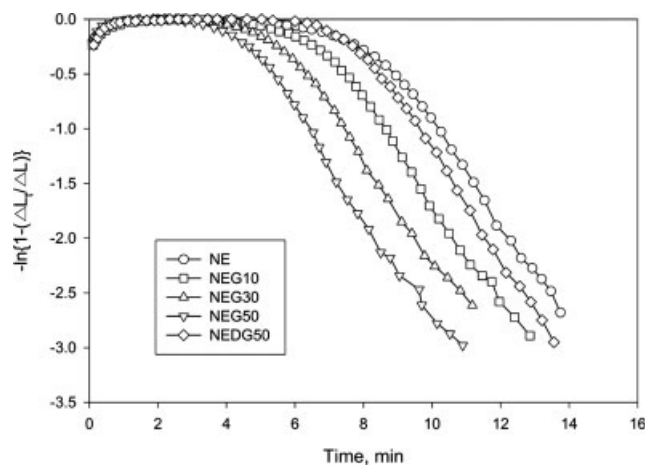
According to previous reports, the decrease in the tensile properties of GR-filled vulcanizates is thought to result from the low surface adhesion between GR and the rubber matrix[13,37] or from the role of GR as a stress-raising flaw in the rubber matrix, even though there is enough adhesion between them.[38]

The larger error bars of the tensile test samples with 10 phr GR versus those with 30 or 50 phr GR may result from the nonuniformity of the tensile specimens because the particles of GR used in this study are too large to compose uniform samples with a small amount of GR.

As shown in Figure 16, the changes in the tear strength are marginal, with the exception of NCG. The differences between sulfur- and peroxide-cured GRs

are not so large. The tear strength is known to be affected by the size of the crack tip and the degree of the crack diversion from the dispersed phase, and it is quite possible for these to increase or decrease the tear strength.[38]
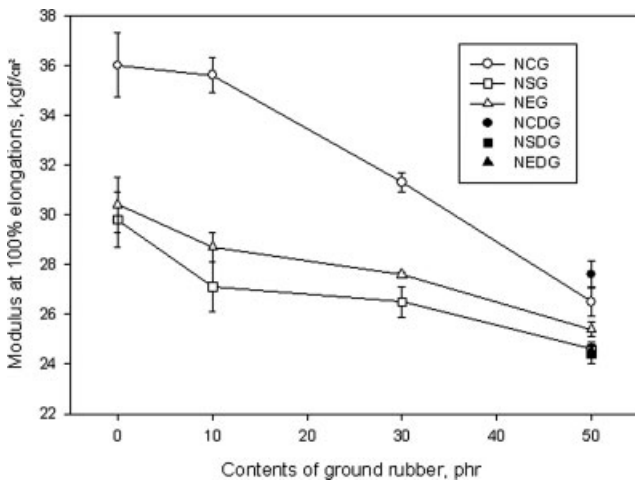
Fractured surfaces

SEM photographs of fractured surfaces of tensile and tear specimens of NR vulcanizates containing 50 phr GR are presented in Figure 17. The tear direction of the test samples is from bottom to top in the photographs.

When the adhesion between GR and the rubber matrix was reported to be low, a very roughly fractured surface was observed, and the surface of GR was distinctive from the rubber matrix.[13,16,29] However, the fractured surfaces of NCG50, NSG50, and NEG50 are relatively smooth, and the interface of the GR and rubber matrix cannot be clearly seen. Moreover, fractures also occurred through the GR, as shown in Figure 18(a–c). Therefore, it can be inferred that the adhesion between the GR and rubber matrix was high enough to resist the external forces during the tensile tests when sulfur-cured GR was used.

However, in the case of NCDG50, NSDG50, and NEDG50, which contain peroxide-cured GR, the frac-

Figure 10 Variations of the differences between T_{max} and T_{min} for NR compounds.

TABLE VI
Crosslinking Rate Constants (min⁻¹)
of GR-Filled Compounds

GR content (phr)	NCG	NCDG	NSG	NSDG	NEG	NEDG
0	0.57		1.20		0.45	
10	0.51		1.08		0.46	
30	0.50		1.00		0.46	
50	0.55	0.55	1.11	1.34	0.47	0.48

Figure 12 Modulus at 100% elongation for GR-filled NR vulcanizates.
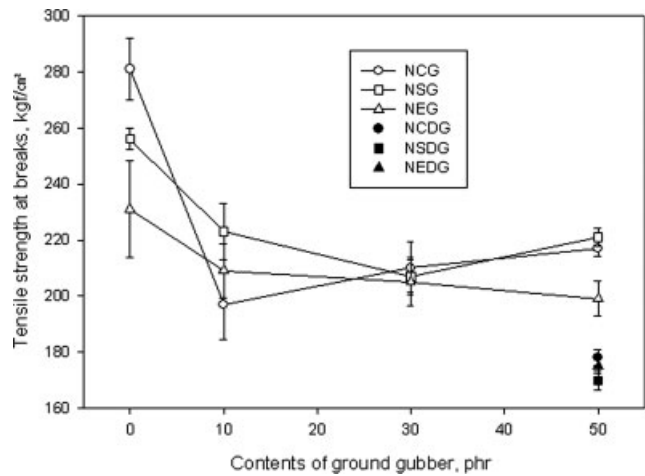
Figure 14 Tensile strength at break for GR-filled NR vulcanizates.

tured surfaces are rougher than those of NCG50, NSG50, and NEG50, as shown in Figure 17, and the smooth surface of GR can be seen on the fractured surfaces shown in Figure 18. Thus, the adhesion between the peroxide-cured GR and sulfur-cured rubber matrix is thought to be low.

According to these results, it can be expected that the adhesion between GR and the rubber matrix will be largely dependent on the curing systems, that is, the crosslink structures of GR and the rubber matrix. This has been further investigated in another study.[39]

The crosslink densities of GR-filled vulcanizates are presented in Figure 19. With the addition of GR, the crosslink densities diminished, but the rate of the decrement from their parent compounds also decreased, as the GR content was increased.

The crosslink density of ND is higher than those of rubber matrices such as NC, NS, and NE, but the crosslink densities of NCDG50, NSDG50, and NEDG50 are

lower than those of the pure rubber matrix. It is inferred that the crosslink density of GR-filled vulcanizates largely depends on that of the rubber matrix rather than that of GR. However, the amount of GR is also thought to affect the crosslink densities of GR-filled vulcanizates because of the decreasing rate of reduction as the amount of GR increases.

The decreasing tendency of crosslink densities, shown in Figure 19, is in good accord with those of the torque developments presented in Figure 10 and the moduli of GR-filled vulcanizates presented in Figures 12 and 13. From this, it has been confirmed that the decrease in the physical properties of GR-filled vulcanizates mainly results from the reduction of the crosslink density of the rubber matrix. For NCG vulcanizates with a CV curing system, the variations of the modulus and crosslink density are higher than those of other cases.

In addition, the adhesion between GR and the rubber matrix also has to be considered to understand the
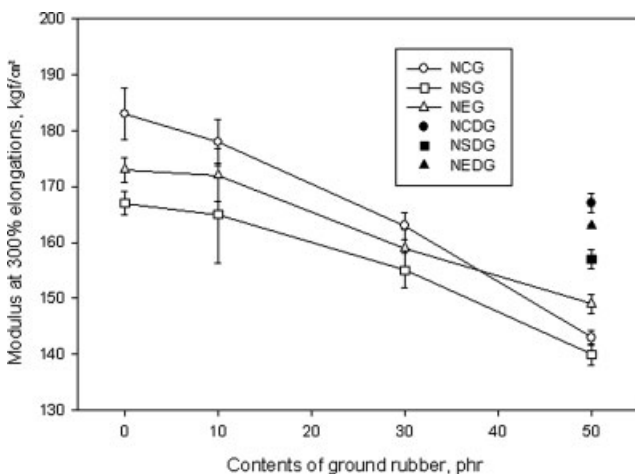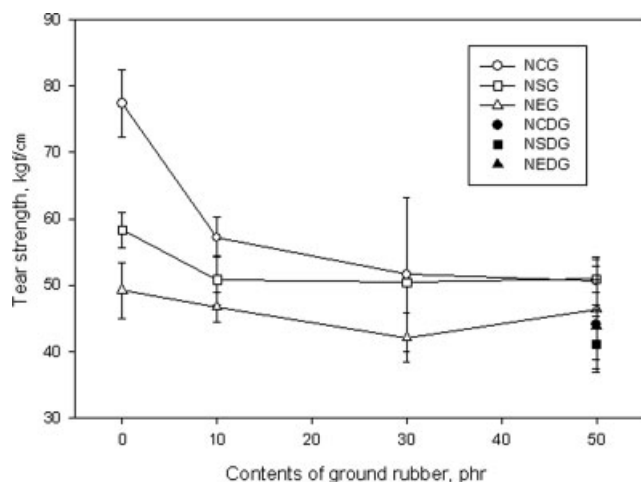

Figure 13 Modulus at 300% elongation for GR-filled NR vulcanizates.
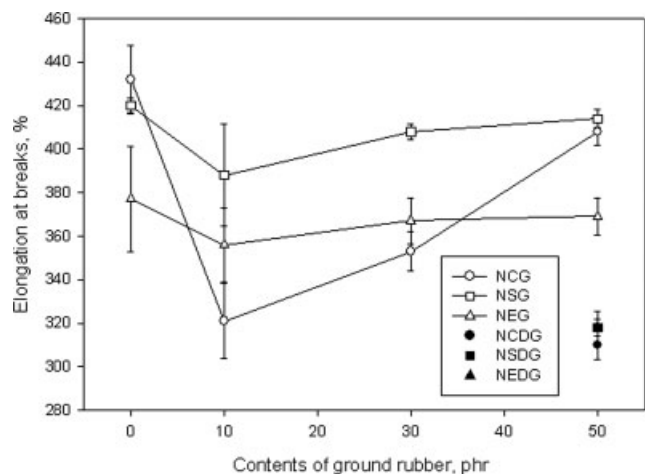
Figure 15 Elongation at break for GR-filled NR vulcanizates.

Figure 16 Tear strengths of GR-filled NR vulcanizates.

Although the large particle size of the GR used in this research, the fractured surfaces of the tensile and tear specimens were unexpectedly smooth, and the interface between GR and the rubber matrix was not easily differentiated. Moreover, it was observed that the fracture was propagated through GR when GR was cured with sulfur and accelerators. It can be inferred that the adhesion between GR and the rubber matrix was sufficient to fracture GR. However, the surface of peroxide-cured GR was observed on the fractured surfaces.

The addition of GR decreased the crosslink densities of GR-filled vulcanizates, and this implies that the crosslink densities of the rubber matrix dominate the cross-

reason for the severe drop in the tensile properties of NR vulcanizates filled with peroxide-cured GR. NR vulcanizates with sulfur-cured GR, which are inferred to have enough interfacial adhesion between GR and the rubber matrix to resist extension, showed higher tensile strength and elongation at break than NR vulcanizates with peroxide-cured GR, which were expected to have little adhesion between them. The adhesion between GR and the rubber matrix has been further investigated, and the results are in good accordance with the aforementioned results.[39]
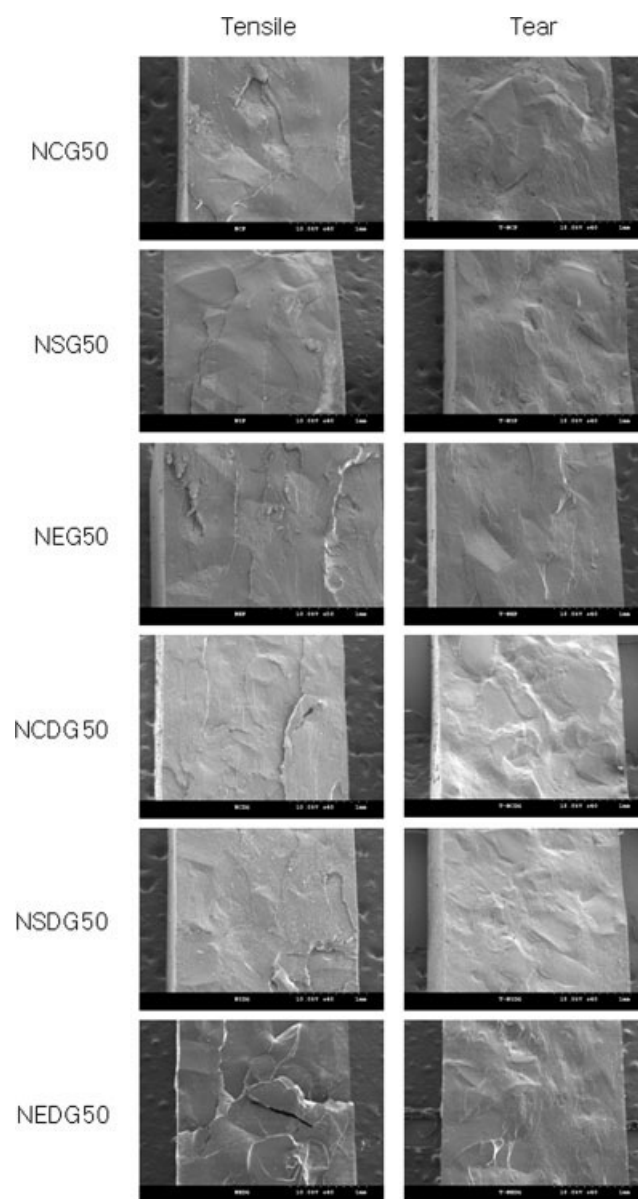
CONCLUSIONS

This study investigated the effects on the cure behaviors and physical properties of the curing system of GR and the rubber matrix. GR slightly increased Mooney viscosities. The addition of GR, cured with sulfur and accelerators, decreased Mooney and rheometric scorch times, optimum cure times, and torque development during vulcanization. In particular, compounds with GR and rubber matrix having a CV curing system showed the largest changes. However, peroxide-cured GR did not show great effects on those properties, except for torque development. The cure rate for the compounds with CV and semi-EV curing systems decreased and then increased a little when GR was added, but compounds having EV curing systems showed a little increment.

The moduli of GR-filled vulcanizates decreased as the amount of GR was increased. The tensile strength, tear strength, and elongation at break abruptly dropped with a small amount of GR, but the elongation at break increased with the increase in the GR contents. The largest decrease in the physical properties was observed for peroxide-cured-GR-filled vulcanizates.

Figure 17 SEM photographs of fractured surfaces of tensile and tear specimens of NR vulcanizates containing 50 phr GR(40×).
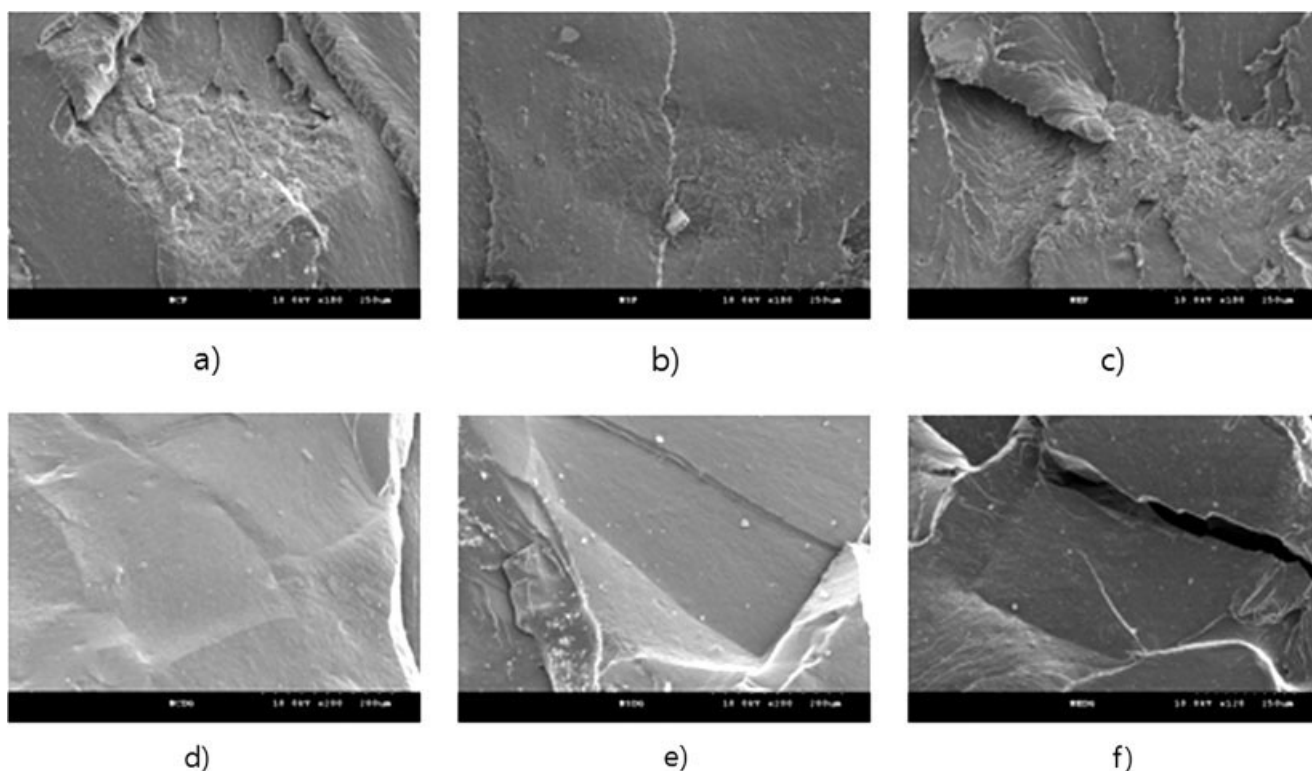
Figure 18 SEM photographs of fractured surfaces of tensile specimens of GR-filled NR vulcanizates: (a) NCG50 (180×), (b) NSG50 (180×), (c) NEG50 (180×), (d) NCDG50 (200×), (e) NSDG50 (200×), and (f) NEDG50 (120×).

link densities and physical properties of GR-filled vulcanizates. The decrease in the crosslink densities of the CV curing system was much larger than that of the semi-EV and EV systems, and this is in accordance with the differences between T_{max} and T_{min} of the cure curves and the moduli of GR-filled vulcanizates.

From these results, it can be inferred that the curing systems of GR and the rubber matrix have a great effect on the cure characteristics and physical properties of GR-filled vulcanizates and that the reduction of the crosslink density of a rubber matrix is the main reason for the decrease in the physical properties of GR-filled vulcanizates. The large variations in the physical properties of peroxide-cured-GR-filled vulcanizates are likely caused by the low adhesion between GR and the rubber matrix and the decrease in the crosslink densities of the rubber matrix.

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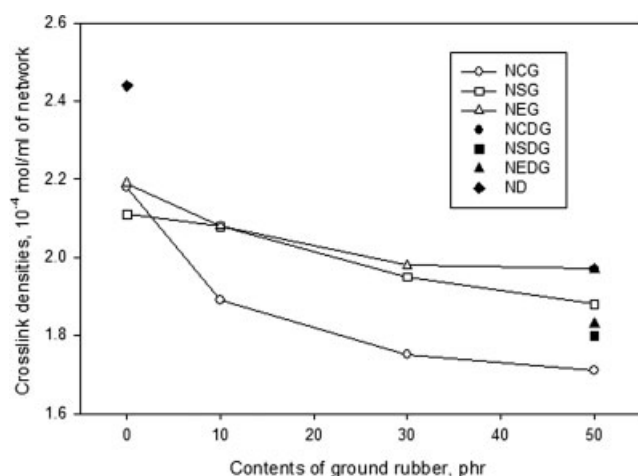
Figure 19 Crosslink densities of NR compounds with respect to the GR content.

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