

Continuous Ultrasonic Devulcanization of Carbon Black-Filled NR Vulcanizates

CHANG KOOK HONG, A. I. ISAYEV

Institute of Polymer Engineering, The University of Akron, Akron, Ohio 44325-0301

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ABSTRACT: The continuous ultrasonic devulcanization of natural rubber (NR) filled with various concentrations of carbon black (CB) indicated a minimum of crosslink density and gel fraction at an intermediate amplitude, which is independent of CB content. An attempt was made to improve the efficiency of devulcanization by use of various chemicals (1,3 Diphenylguanidine, 2-Mercaptobenzothiazole, Thianaphthene). However, these experiments did not indicate any improvement in comparison with devulcanization without chemicals. An idea of adding fresh CB into devulcanized compound, which has been shown to improve mechanical properties in the case of styrene-butadiene rubber (SBR), was tested in the present study for CB filled NR compound. The obtained result indicated that an addition of fresh CB to devulcanized CB-filled NR did not lead to an improvement in mechanical properties upon revulcanization. The revulcanization recipe was optimized to improve the mechanical properties of revulcanized CB-filled NR vulcanizates. It was found that CB-filled NR upon revulcanization retained its strain-induced crystallizability with the tensile strength and elongation at break at about 50 and 70% level of the virgin vulcanizates. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2340–2348, 2001

Key words: NR; devulcanization; carbon black; vulcanizates; mechanical properties; rheology

INTRODUCTION

The management of waste rubbers has become a growing problem in recent years. Vulcanization of elastomers leads to the formation of a three-dimensional crosslinked network. The presence of this network creates a tremendous problem in rubber recycling. Therefore, the development of a suitable technology to recycle waste rubbers is an important issue facing the rubber industry. A number of methods^{1–3} have been developed to find more effective ways of

rubber recycling. In recent years, Isayev and coworkers^{4–9} have carried out extensive studies on the application of ultrasound to polymer processing. The ultrasonic waves of certain levels, in the presence of pressure and heat, can break down the three-dimensional network in cross-linked rubbers. The devulcanized rubber can be reprocessed in the same way as the virgin rubber. The process of ultrasonic devulcanization is very fast, and occurs in the order of a second, and may lead to the preferential breakage of sulphidic crosslinks in vulcanized rubbers.

Natural rubber (NR) has been widely used in a variety of industrial and engineering applications. The strain-induced crystallization behavior makes NR a unique material among elastomers as far as mechanical properties are concerned. NR

Correspondence to: A. I. Isayev.

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Table I Recipes for NR Compound

Comp.	NR	Sulfur	CBS	ZnO	Stearic Acid	CB
Recipe 1	100 (virgin)	2	1	5	1	0–60
Recipe 2	100 (devulcanized)	2	0	2.5	0.5	0–60
Recipe 3	100 (devulcanized)	2	0.5	2.5	0.5	0–60

Unit: phr

is the standard by which the performance of other synthetic rubbers is judged.¹⁰

The most common substance used for strengthening or reinforcing rubber is carbon black. It inhibits rupture by absorbing and dissipating strain energy at the friction points where the rubber molecules slip across the carbon black surface.^{11,12} The function of the filler depends significantly upon the extent to which the filler affects crosslinking in the course of vulcanization. Due to the interaction between rubber and carbon black, the rubber molecules can be adsorbed onto the filler surface either chemically or physically. This is related to the restriction of the segmental movement of polymer molecules.

In this study, continuous ultrasonic devulcanization of carbon black-filled NR was considered to enhance our understanding of the process. Also, the effect of carbon black on ultrasonic devulcanization was investigated. The similarities and differences between the devulcanization of SBR vulcanizates^{6–8} and unfilled NR vulcanizates⁹ studied earlier will be discussed. In addition, the present study is attempted to improve the efficiency of devulcanization and to improve the mechanical properties upon revulcanization of the devulcanized CB filled NR.

EXPERIMENTAL

Materials

The natural rubber (NR, SMR CV 60) obtained from Akrochem Corp. was used in the present experiments. The other compounding ingredients were sulfur, zinc oxide, stearic acid (Akrochem Corp.), CBS (*N*-cyclohexylbenzothiazole-2-sulfenamide, Monsanto Inc.), and carbon black (HAF N330, Huber Engineered Carbons). The recipes used in this study are given in Table I. The chemicals used to improve the efficiency of devulcanization are summarized in Table II. These chemicals have been shown to promote chain break-

down of NR and to accept radicals during the scission process.¹³ Therefore, these chemicals can be possibly used to minimize recrosslinking during ultrasonic treatment.

Preparation of Vulcanizates

The carbon black (CB)-filled compounds were mixed using the Banbury mixer (Farrel, Model 86EM9804). To improve the mixing quality and to prevent prevulcanization, a two-stage mixing process was applied. First, the rubber was premixed in the Banbury mixer at 80°C for 1.5 min. After premixing, zinc oxide, stearic acid, and CB were added into the mixer and the mixing was continued for 2.5 min. After the first mixing, a two-roll mill (Dependable Rubber Machinery Co.) was used at 50°C to prevent any scorch problem during this mixing step. Thirty seconds were required to soften the compounds. After softening, sulfur and accelerator were added together. The total mixing time was 3 min. The unfilled compounds were milled with the ingredients on a two-roll mill for 6 min.

The compression molding of slabs (260 × 260 × 12 mm³) was performed at 160°C using an electrically heated compression molding press (Wabash). According to the cure curve, the cure time was determined based on the maximum torque.

After molding, the vulcanized samples were ground using the Nelmor grinding machine. To

Table II Chemicals Used to Improve the Efficiency of Devulcanization

Chemicals	Supplier
1,3 Diphenylguanidine	Aldrich Chemical Company, Inc.
2-Mercaptobenzothiazole	Aldrich Chemical Company, Inc.
Thianaphthene	Aldrich Chemical Company, Inc.

investigate the effect of ultrasonic treatment on virgin-uncured NR, the virgin-uncured NR was cut into pieces about 1 cm³ and fed into the ultrasonic devulcanization reactor.

Ultrasonic Devulcanization

The particles were devulcanized in an extruder with an ultrasonic die attachment^{4,5} developed by National Feedscrew and Machining, Inc. The temperature of the extruder barrel was set at 120°C. The gap between the die plate and the horn was set at 2.54 mm. The flow rate was 0.63 g/s. Devulcanization was carried out at a frequency of 20 kHz and amplitudes of 5, 7.5, 10 μm. The ultrasound power consumption and die entrance pressures were measured at the conditions of devulcanization.

Re vulcanization

The devulcanized NR was compounded with curatives on the two-roll mill. Revulcanization was carried out at 160°C in the compression molding press in a mold (127 × 127 × 2 mm³) with cure time based on the maximum torque. Different revulcanization recipes (recipes 2 and 3) were used to enhance the mechanical properties of the devulcanized NR on revulcanization.

Characterization

A Monsanto oscillating disc rheometer was used to obtain the torque–time curves according to ASTM D2084.

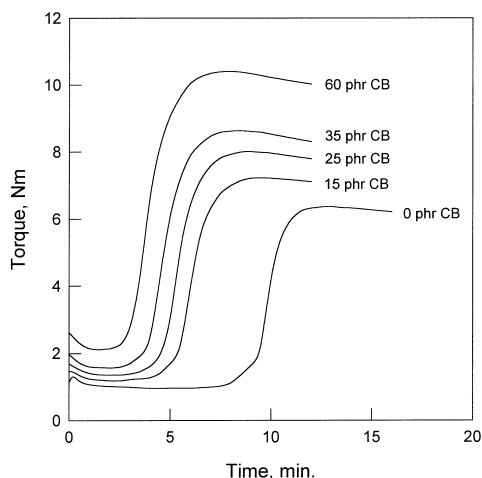


Figure 1 Cure curves of virgin NR compounds using recipe 1 at 160°C.

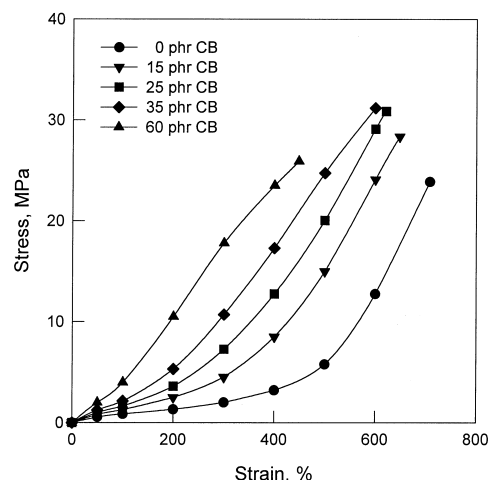


Figure 2 Stress–strain curves for virgin NR compounds using recipe 1.

The gel fractions of NR vulcanizates and devulcanized NR were measured by the soxhlet extraction methods using benzene as a solvent. The crosslink densities were characterized by the swelling method using the Flory-Rehner equation¹⁴ with the Kraus correction.¹⁵

The rheological behaviors of virgin-uncured NR and ultrasonically treated uncured NR were investigated using a Monsanto Processability Tester (MPT) at a temperature of 120°C according to ASTM D5099.

Monsanto Tensiometer (Flexsys T2000) was used for the tensile property measurement according to ASTM D412 (type C). All tests were performed at room temperature with a crosshead speed of 500 mm/min.

RESULTS AND DISCUSSIONS

Characterization of Virgin NR

The cure curves at 160°C for virgin CB filled NR are shown in Figure 1. It is seen that an addition of carbon black to NR caused a progressive increase of the cure rate and maximum torque and a decrease of induction time.

In Figure 2, the strain–stress curves for CB-filled NR are plotted. Because of its stereoregular structure, NR is capable of crystallizing when stretched and, therefore, yields very high tensile strength and ultimate elongation. As indicated in Figure 2, the tensile strength shows the existence of an optimum amount of filler at 35 phr. Above this concentration the reinforcing effect of filler is

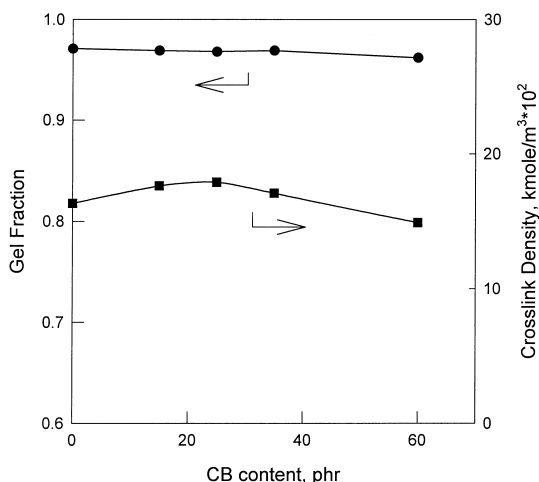


Figure 3 Gel fraction and crosslink density of virgin NR vulcanizates as a function of CB content.

counteracted and dominated by a volume effect of the filler.

Figure 3 shows gel fraction and crosslink density of virgin NR vulcanizates as a function of carbon black content. The gel fraction and crosslink density were little affected by CB content. These results are in agreement with Mori and Koenig,¹⁶ who reported that the total amount of chemical sulfurization reactions occurring in NR was almost independent of the level of carbon black loading.

Ultrasonic Devulcanization

Figure 4 gives a dependence of the die entrance

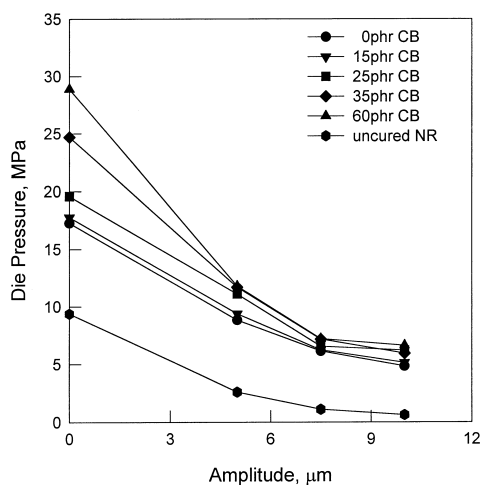


Figure 4 Die pressure as a function of ultrasonic amplitude during the devulcanization at various CB contents.

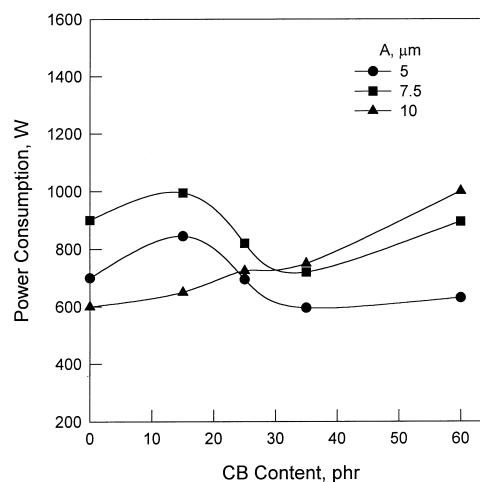


Figure 5 Ultrasonic power consumption as a function of CB content during the devulcanization at various amplitudes.

pressure on ultrasonic amplitude during devulcanization of uncured NR, and unfilled and filled NR vulcanizates. The die pressure decreases as the amplitude of the ultrasound is increased. This has been previously explained as the combined effect of the softening of rubber due to devulcanization in the die gap and reduction in friction between the particles and the die wall due to ultrasonic vibrations.⁵ The die pressure increases with increasing amount of carbon black loading. Also, the die pressures of cured NR are significantly higher than those of uncured unfilled NR. This is caused by an increase of the viscosity of the rubber due to loading of CB and crosslinking.

Figure 5 shows the ultrasonic power consumption as a function of the carbon black loading at various amplitudes. On increasing CB content from 0 to 25 phr, it is observed that, at 5 and 7.5 μm , power consumption shows a maximum at 15 phr. The reason has been explained earlier,⁹ and is due to the competition between bond breakage and reformation during ultrasonic treatment. In this case, while devulcanization is dominant between 5 and 7.5 μm , some revulcanization occurs with increasing ultrasonic amplitude, which accounts for the reduction in power consumption above 7.5 μm . However, as CB content increases, CB may act as a radical acceptor of a special polyfunctional type.¹³ If combination of polymeric radicals and CB occurs, then the reformation of broken bonds can be hindered. The reason for the complicated dependence of ultrasonic power consumption on CB content, seen in Figure 5, is unclear. However, it is clear that higher power

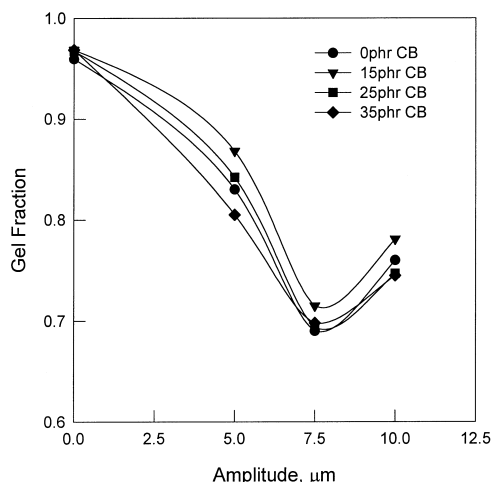


Figure 6 Gel fraction of devulcanized NR as a function of ultrasonic amplitude at various CB contents.

consumption leads to a higher degree of devulcanization, as indicated by Figures 6 and 7, indicating gel fraction and crosslink density of devulcanized unfilled and CB filled NR as a function of ultrasonic amplitude. It is seen that the ultrasonic devulcanization of unfilled and CB-filled NR indicates a minimum of gel fraction and crosslink density at an intermediate amplitude, which is independent of CB content. Due to the predominant effect of reversion from 7.5 to 10 μm , the gel fraction and crosslink density increase when the amplitude is increased from 7.5 to 10 μm . This observation is in accord with the previous study on unfilled NR.⁹ It is also seen that the

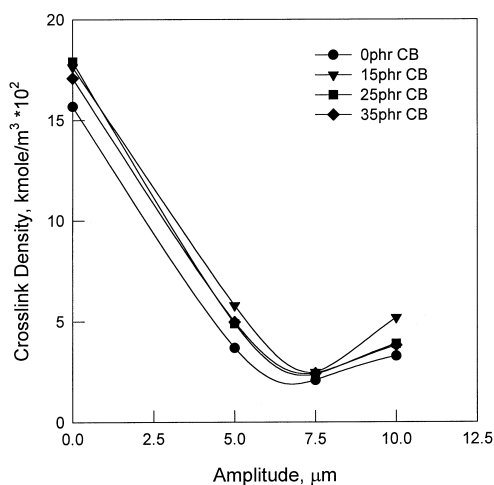


Figure 7 Crosslink density of devulcanized NR as a function of ultrasonic amplitude at various CB contents.

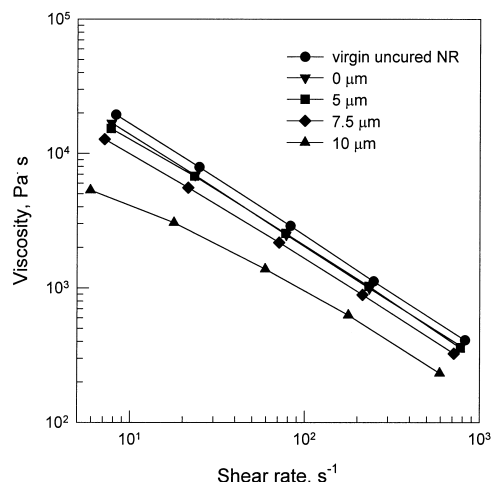


Figure 8 Flow curves of ultrasonically treated uncured NR at 120°C.

increase of the concentration of CB in NR leads to more devulcanization. Therefore, it can be thought that CB increases the probability of bond scission during ultrasonic treatment.

The flow curves of virgin-uncured NR and ultrasonically treated uncured NR are shown in Figure 8. The viscosity of ultrasonically treated virgin-uncured NR decreases with an increase in ultrasonic amplitude. This observation is an indication that the breakup of main chains occurs during extrusion with the imposition of ultrasonic waves. Therefore, during devulcanization of NR vulcanizates along with the breakup of crosslinks, a possibility exists for breakup of main chains. Some difference in viscosity between virgin-uncured NR and NR extruded without the imposition of ultrasonic waves (curve at 0 μm), seen in Figure 8, is due to a mastication effect during extrusion.

Reversion of Ultrasonically Devulcanized NR

The cure curves for the virgin 35 phr CB filled NR (recipe 1) and the devulcanized NR (recipe 2) at 160°C are shown in Figure 9. Recipe 2, which consists of 2 phr sulfur, no accelerator, 2.5 phr ZnO, and 0.5 phr stearic acid added to 100 parts of devulcanized rubber, is the optimized recipe for reversion of devulcanized unfilled NR.⁹ These torque–time curves show that the cure behavior of virgin and devulcanized rubber is significantly different. The scorch time is very short or is almost absent. The shortness or complete absence of the induction period indicates that crosslinking reactions may start immediately

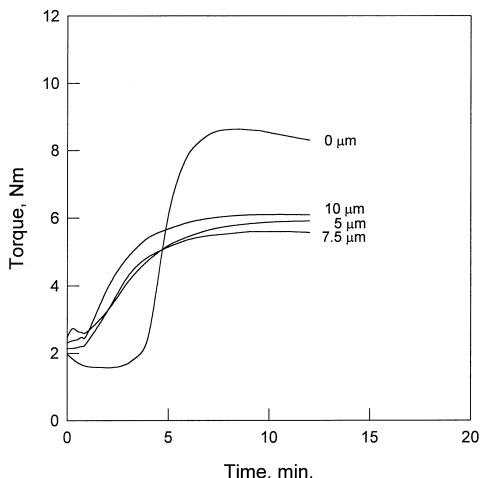


Figure 9 Cure curves of virgin and devulcanized NR containing 35 phr CB using recipe 2.

upon heating.⁷ It is reported that sulfenamides (thiazole derivatives, CBS, and TBBS) first decompose to form an amine and benzothiazole disulfide, which then dissociates to form benzothiazoles (MBT).¹⁷ Crosslinking can occur only after MBT formation. Sulfenamides are delayed action accelerators because the reactions, which produce MBT, require time. Thus, the crosslinking reactions of the devulcanized rubber start immediately upon heating due to the presence of MBT and crosslink precursors in the devulcanized rubber. The final torque of the devulcanized CB-filled NR during curing is lower than that of the virgin NR. This may be explained by the breakup of main chains during the devulcanization.

The stress-strain curves for the virgin 35 phr CB-filled NR and the revulcanized NR (recipe 2) are presented in Figure 10. The tensile strength of revulcanized NR is reduced significantly in comparison with that of the virgin NR. This result is possibly due to breakup of main chains during ultrasonic treatment. In addition, in CB-filled rubber, bound rubber is formed by rubber molecules partially incorporated into CB particles.¹¹ The mobility of such rubber chains is considerably restricted at the surface of the filler particle. This means that filled rubber may exhibit increasing probability of the breakup of the bound chains by ultrasonic treatment. Therefore, the inferior properties of revulcanized CB-filled NR may also be explained by the breakup of the bound chains during ultrasonic treatment. Recipe 2, the optimized recipe for revulcanization of devulcanized unfilled NR, was not suitable for CB-filled NR.

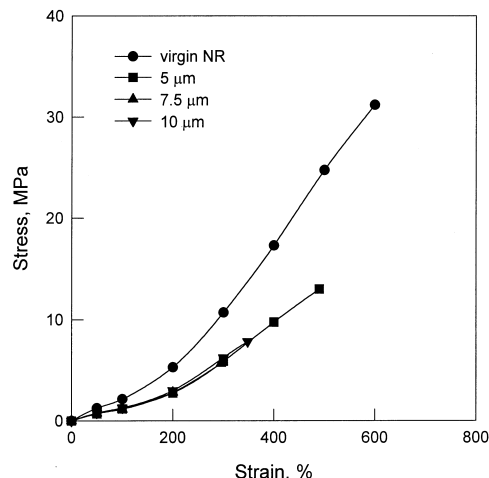


Figure 10 Stress-strain curves of virgin and devulcanized NR containing 35 phr CB using recipe 2.

However, in the case of unfilled NR,⁹ mechanical properties were as good as virgin rubber due to a lesser probability of main-chain breakup. Figure 11 shows the effect of CB loading on tensile properties of revulcanized CB-filled NR using recipe 2. Devulcanized NR was obtained at the ultrasonic amplitude of 5 μm . Dependence of tensile strength of revulcanized NR on CB loading was the same as for virgin CB filled NR with a maximum of 35 phr.

Optimization of Revulcanization Recipe

The revulcanization recipe was optimized to improve the mechanical properties of revulcanized

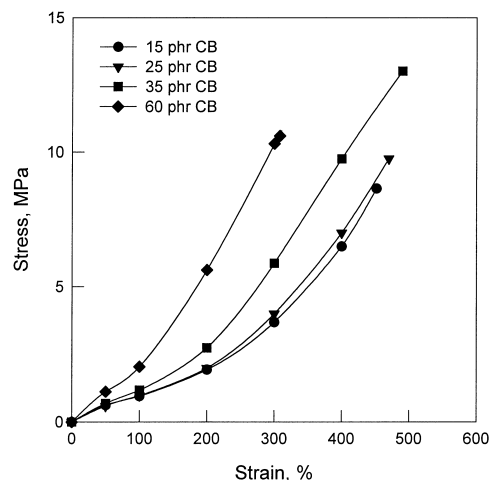


Figure 11 Stress-strain curves of devulcanized NR using recipe 2 at various CB contents.

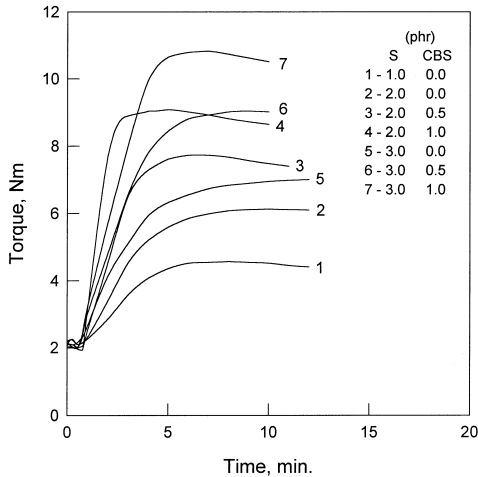


Figure 12 Cure curves for 35 phr CB filled NR ultrasonically devulcanized at an amplitude of 5 μm , and compounded with 2.5 phr ZnO, 0.5 phr stearic acid, and different amounts of sulfur and CBS.

CB-filled NR vulcanizates. The amounts of zinc oxide and stearic acid in the revulcanized recipe were kept at 2.5 and 0.5 phr. As seen from the cure curves in Figure 12, increasing the amount of accelerator increases the rate of revulcanization, and increasing the amount of sulfur increases the degree of revulcanization.

Figure 13 shows the effect of variation of the amount of sulfur and accelerator on the mechanical properties of the revulcanized CB-filled NR. Because it has the best mechanical properties

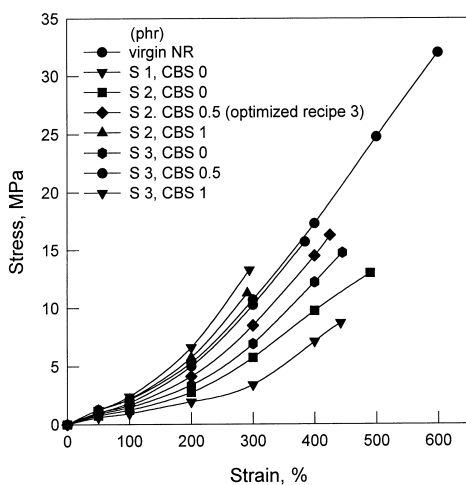


Figure 13 Stress-strain curves of 35 phr CB-filled NR ultrasonically devulcanized at an amplitude 5 μm , and compounded with 2.5 phr ZnO, 0.5 phr stearic acid, and different amounts of sulfur and CBS.

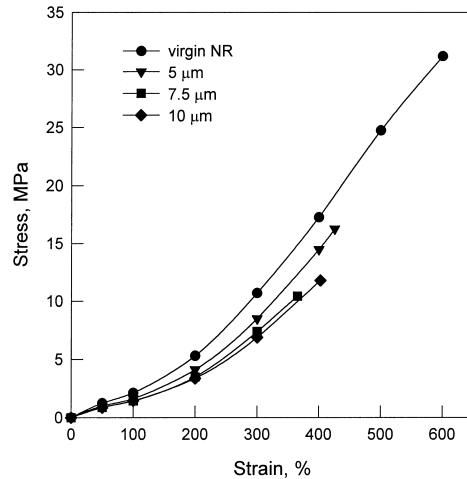


Figure 14 Stress-strain curves for virgin and revulcanized NR vulcanizates containing 35 phr CB using the optimized recipe 3.

among all the other revulcanization recipes, recipe 3, which consists of 2 phr sulfur and 0.5 phr CBS, is chosen as the optimized recipe for devulcanization. In comparison with unfilled NR, the difference in the optimized recipe is the amount of the accelerator. It seems possible that some amount of sulphenamides that preexisted in devulcanized rubber can be absorbed into the voids in CB.

Figure 14 gives the stress-strain curves for revulcanized 35 phr CB-filled NR using optimized recipe 3. It was found that CB-filled NR upon revulcanization retained its strain-induced crystallizability with the tensile strength and elongation at break at about the 50 and 70% level of the virgin vulcanizates.

Effect of Various Chemicals on Devulcanization

An attempt was made to improve the efficiency of devulcanization by the use of various chemicals (1,3 Diphenylguanidine, 2-Mercaptobenzothiazole, Thianaphthene). These chemicals have been shown to promote chain breakdown of NR and to accept radicals during the scission process.¹³ The cure curves for 35 phr CB-filled NR devulcanized with 3 phr of the chemicals are shown in Figure 15. The cure behavior of devulcanized rubber with 1,3 Diphenylguanidine and Thianaphthene was not different from that of the devulcanized sample without chemicals. However, the maximum torque for the compound with 2-Mercaptobenzothiazole was higher because the chemical may act as an accelerator during revulcanization.

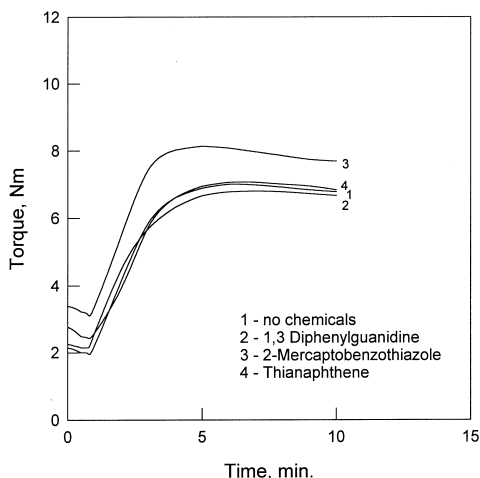


Figure 15 Cure curves for devulcanized NR containing 35 phr CB using recipe 3, NR ultrasonically devulcanized at an amplitude of 5 μm with 3 phr of various chemicals.

Figure 16 gives the stress–strain curves for 35 phr CB-filled NR devulcanized with 3 phr of the chemicals. It is seen that the tensile properties of the revulcanized CB-filled NR were not improved by using the chemicals during devulcanization. Therefore, the use of the chemicals during ultrasonic devulcanization of CB-filled NR did not improve the efficiency of the process in comparison with devulcanization without chemicals.

Effect of Fresh CB on Mechanical Properties upon Revulcanization

During ultrasonic treatment, rubber chains bound to carbon black can be broken due to the

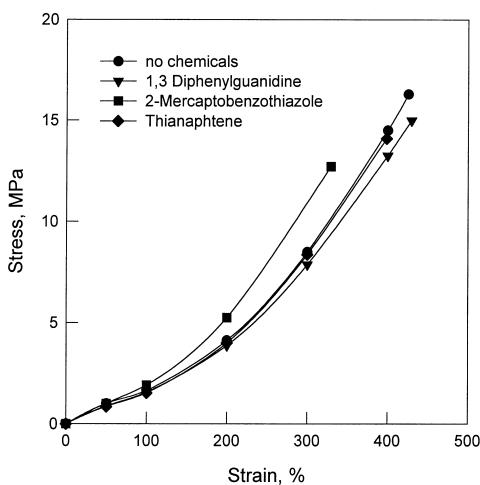


Figure 16 Stress–strain curves for revulcanized NR vulcanizates containing 35 phr CB using recipe 3. NR ultrasonically devulcanized at an amplitude of 5 μm with 3 phr of various chemicals.

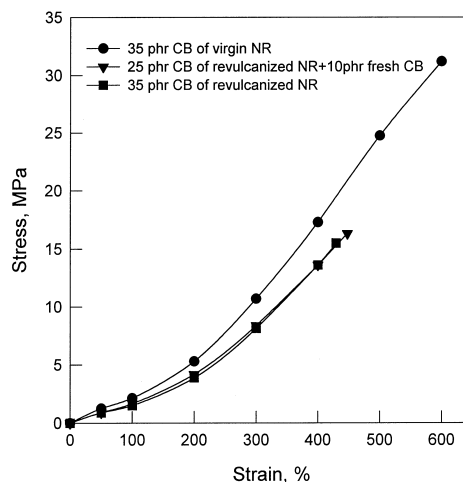


Figure 17 Stress–strain curves of revulcanized NR using recipe 3 with and without the addition of fresh CB. NR ultrasonically devulcanized at an amplitude of 5 μm .

restricted mobility. The broken chains may still occupy active surface and voids of the filler leading to the deactivation of the filler. Due to the deactivation of the filler, the tensile properties of revulcanized-filled rubber would be reduced. Adding fresh CB into devulcanized compound, which has been shown to improve mechanical properties in the case of styrene–butadiene rubber,⁶ was tested on the revulcanization of CB-filled NR compound. Figure 17 shows the stress–strain curves for the virgin 35 phr CB-filled NR, revulcanized 35 phr CB-filled NR, and revulcanized 25 phr filled NR with the addition of 10 phr fresh CB. In contrast to our expectation, the obtained result indicated that an addition of the fresh CB to devulcanized CB-filled NR did not lead to an improvement in mechanical properties upon revulcanization.

CONCLUSIONS

In this study, the continuous ultrasonic devulcanization of carbon black-filled NR was investigated. The devulcanized CB-filled NR indicated a minimum of crosslink density and gel fraction at an intermediate amplitude due to the competition between crosslink breakage and reformation during ultrasonic treatment. CB-filled NR cured using the optimized revulcanization recipe still retained its strain-induced crystallizability with the tensile strength and elongation at break at about

50 and 70% level of the virgin vulcanizates. The reduction in the mechanical properties of revulcanized CB-filled NR can be explained by main-chain breakage during ultrasonic devulcanization and severing of bonds near the filler surface, due to the restricted mobility of bound rubber.

An attempt was made to improve the efficiency of devulcanization of CB-filled NR by the use of various chemicals. However, these experiments did not indicate any improvement in the efficiency of devulcanization in comparison with devulcanization without chemicals.

An idea of adding fresh CB into the devulcanized compound, which has been shown to improve mechanical properties in the case of SBR, with the devulcanized CB-filled NR did not lead to an improvement in mechanical properties upon revulcanization.

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