

Effect of Ground Rubber Powder and Devulcanizates on the Properties of Natural Rubber Compounds

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ABSTRACT: Ground rubber powder (GRP) and devulcanized rubber (Dev.R) waste through a continuous shear-flow reaction were used as fillers for virgin natural rubber. A Horikx plot and the gel fraction proved that both main-chain scission and crosslink scission occurred during the devulcanization. The cure characteristics, swelling behavior, crosslink density, and mechanical properties were studied. GRP and Dev.R, generated from passenger car and light

truck tires, showed applicable mechanical properties in the new rubber compounds, and the compounds containing Dev.R demonstrated better properties than those containing GRP. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 208–217, 2005

Key words: recycling; rubber; waste

INTRODUCTION

For decades, the rubber industry has faced a major challenge in finding a satisfactory way of dealing with the enormous quantity of rubber goods, particularly tires, that reach the end of their life cycle.^{1,2} Many attempts to recycle waste rubber have been made, for both environmental and economical reasons.^{3,4} New rubber recycling technologies, such as microbial action,^{5,6} grafting reactions,^{7,8} microwave methods,⁹ and ultrasonic methods,^{10,11} have been developed with the goals of shorter reaction times and higher quality. A new material recycling technology for crosslinked rubber has been established with the continuous reactive processing method.^{12–14} In this process of producing devulcanized rubber (Dev.R), the breakage of crosslinking points in the crosslinked rubber occurs selectively under the controls of shear stress, reaction temperature, and internal pressure in a modular screw-type extruder.

According to the published results of numerous examinations in the field of rubber recycling, ground rubber powder (GRP) and Dev.R can be used in tires, profiles, construction articles, mats, and so forth.¹⁵ Besides these applications, Dev.R exhibits some positive effects on processing, such as reduced die swell, reduced mixing times, and lower extrusion temperatures.¹³ Therefore, using Dev.R can reduce not only the cost of the materials but also the price of the total

compound, including the production and further processing. However, the mechanism of the devulcanization and the effect on virgin rubber need to be studied in depth.

The purpose of this research was to investigate the effects of GRP and Dev.R on a natural rubber (NR) matrix with respect to the physical properties and mechanical properties. The mechanism of the devulcanization was also examined discussed, together with the gel fraction and Horikx plot.

EXPERIMENTAL

Materials

The virgin NR (SMR5) used as a matrix in this study was prepared according to ASTM D 3184 (formula 2A). SMR5 was masticated with a 0.2–0.5 phr peptizing agent (Struktol A86, Schill & Seilecher, Paris, France). GRP (ca. 4 mm), generated through ambient grinding from passenger car and light truck tires, was purchased from Genan A/S (Viborg, Denmark), and it contained approximately 30% NR, 40% styrene–butadiene rubber (SBR), 20% butadiene rubber, and 10% butyl and halogenated butyl rubber. Dev.R, supplied by Hauler, Ltd. (Lahti, Finland), was produced from GRP with a continuous shear-flow reaction treatment under optimized process conditions (temperature = 180–230°C, screw speed = 375 rpm, yield = 80–100 kg/h).

Sample preparation

The compound recipes are listed in Table I; the loadings of the waste rubber (i.e., GRP or Dev.R) were 10,

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TABLE I
Compound Recipes

Component	phr
NR	100
Zinc oxide	5
Stearic acid	2
N-220	35
CBS	0.7
Sulfur	2.25
GRP or Dev.R	0, 10, 30, and 50

30, and 50 phr. To improve the mixing quality and to prevent prevulcanization, we used a two-stage mixing process. In the first stage, the virgin NR was premixed at 60–80°C for 1 min in an internal mixer. After the premixing, zinc oxide, stearic acid, carbon black, and waste rubber were added to the mixer gradually. The mixing continued for 5 min, and then *N*-cyclohexyl-2-benzothiazyl sulfenamide (CBS) was added to the mixer for further mixing (<1 min). In the second stage, a two-roll mill was used at 60°C for 1 min to soften the premixture, and then sulfur was added. The mixing was continued for 2.5 min, and then the mixture was cut into sheets and cooled to room temperature. The sheets were molded at 160°C in an electrically heated compression press.

Cure characteristics

A Monsanto 100S oscillating disc rheometer (Haryana, India) was used to obtain the cure characteristics at 160°C according to ISO 3417.

Gel fraction, swelling degree, and crosslink density

The gel fractions of virgin NR, GRP, and Dev.R were measured gravimetrically. First, the samples were immersed in toluene at 25 ± 2°C until equilibrium swelling was reached, and second, the swollen samples were placed in a vacuum chamber for 3 days so that the solvent would vaporize and the dry, insoluble part would be obtained. The gel fraction was determined as follows:

$$\text{Gel fraction(\%)} = \frac{M}{M_i} \times 100\% \quad (1)$$

where M_i is the initial weight of the sample and M is the weight of the dry, insoluble part.

Circular test pieces with diameter of 10 mm were cut from the vulcanized sheets (2 mm thick) and dried overnight in a vacuum desiccator. GRP and Dev.R samples (ca. 2 g) were closed in the net for drying and measuring because these samples could be dispersed in the solvent; the other methods were the same as those used for

vulcanized sheets. The specimens were soaked in toluene at room temperature (25 ± 2°C), removed from the solvent, blotted, and weighed quickly at periodic intervals. The weighing continued until equilibrium swelling was reached (ca. 72 h). The rubber swelling in the solvent [$Q(t)$] was defined as the swelling degree and calculated with the following equation:

$$Q(t) = \frac{M_t - M_i}{M_i} \quad (2)$$

where M_t is the weight at time t . The crosslink densities of the gels were calculated with the Flory–Rehner equation.¹⁶ The interaction parameter for the NR–toluene system was 0.39.¹⁷

Mechanical properties

The tensile and tear properties were measured with a Monsanto Tensometer 10 testing machine. The tensile specimens were dumbbell-shaped test pieces according to ISO 37 (type 1), and the tear resistance was determined with trouser test pieces according to ISO 34 (type A). The speed was 500 mm/min for the tensile test and 100 mm/min for the tear strength. The abrasion resistance was determined with a Zwick instrument (Ulm, Germany) according to ISO 4649 with an abrasive run of 40 m and a loading of 10 N. The hardness was tested based on ISO 7619 with a Shore A durometer (Instron, Grove City, PA).

RESULTS AND DISCUSSION

Mechanism of devulcanization

GRP was devulcanized through a continuous shear-flow reaction treatment under optimum process conditions (i.e., the screw configuration, reaction temperature, and screw rotation speed). To obtain a better understanding of the devulcanization behavior, we must know whether main-chain scission, crosslink scission, or both occur. Horikx analyzed the relationship between the soluble fraction after the devulcanization of the network and found that a relative decrease in the crosslink density resulted from either main-chain scission or crosslink scission.^{14,17} When only main-chain scission takes place, the relative decrease in the crosslink density can be obtained as follows:

$$1 - \frac{v_f}{v_i} = 1 - \frac{[1 - (S_i + S_f)^{1/2}]^2}{(1 - S_i^{1/2})^2} \quad (3)$$

where v_i is the crosslink density of the untreated vulcanizates, v_f is the crosslink density of the vulcanizates after treatment, S_i is the soluble fraction of the untreated vulcanizates, and S_f is the soluble fraction after the treatment of the vulcanizate.

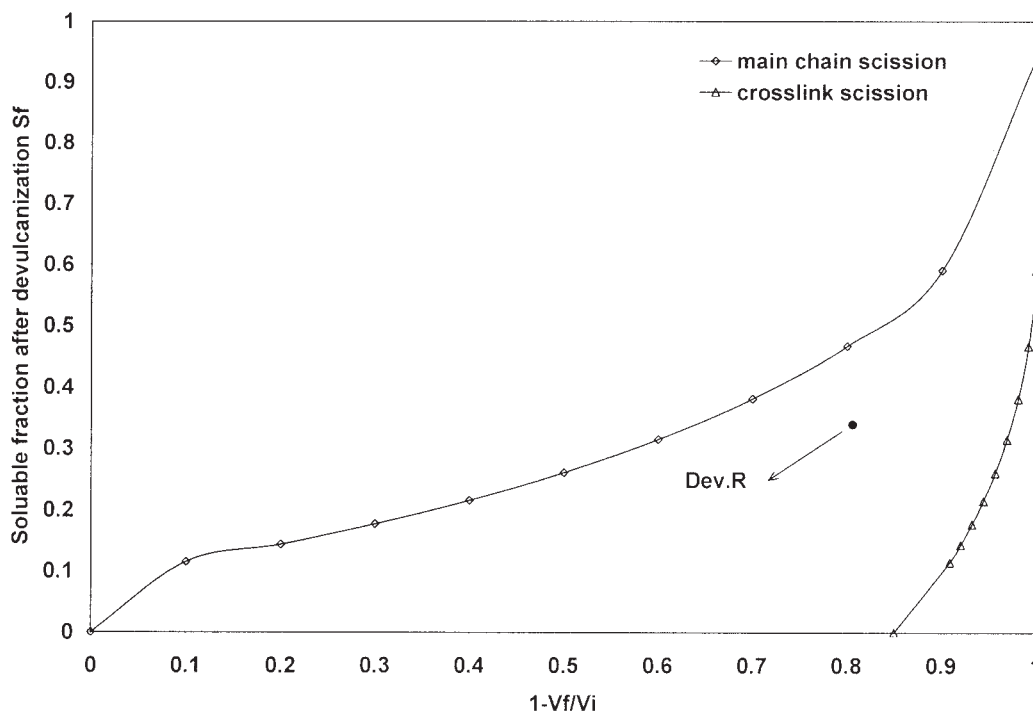


Figure 1 Calculated Horikx plot of waste rubber.

For crosslink scission, the soluble fraction is related to the relative decrease in the crosslink density:

$$1 - \frac{v_f}{v_i} = 1 - \frac{\gamma_f [1 - (S_i + S_j)^{1/2}]^2}{\gamma_i (1 - S_i^{1/2})^2} \quad (4)$$

where the extra parameters γ_i and γ_f are the average numbers of crosslinked units per chain before and after the treatment, respectively. These numbers are calculated from the molecular weight and the crosslink density. The Horikx plot gives the relation between the degree of decrosslinking and the soluble fraction of the network that has been decrosslinked.¹⁸ With a Horikx plot, the ratio of the polymer chain breakage to the rubber network breakage can be described to obtain knowledge of the reaction mechanisms.

The Horikx plot of Dev.R has been calculated and is presented in Figure 1. The point of Dev.R in the Horikx plot is just between the main-chain-scission and crosslink-scission curves. It is evident that the GRP was partially devulcanized and partially depolymerized during the devulcanization¹⁹ (see Fig. 2).

The devulcanization degree of Dev.R was analyzed from the amount of the gel fraction and the soluble fraction.^{11,20} The gel fraction and soluble fraction of Dev.R, NR, and GRP are shown in Table II.

Cure characteristics

The cure characteristics obtained at 160°C are given in Figures 3 and 4.

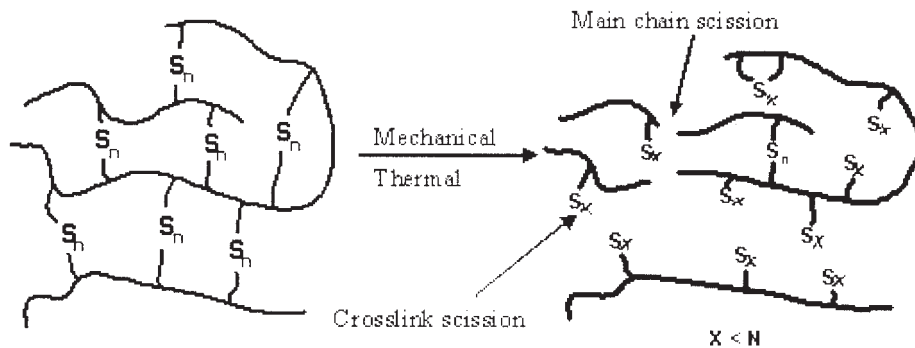


Figure 2 Schematic of the devulcanization reaction.

TABLE II
Gel Fraction and Sol Fraction of the Compounds

	Gel fraction (%)	Sol fraction (%)
NR	98.9	1.1
Dev.R	66	34
GRP	94.5	5.5

The minimum torque increased slightly as the Dev.R concentration increased, but it increased remarkably with the addition of GRP. This indicates that the processing of compounds containing GRP becomes more difficult than that of compounds with Dev.R. The reason for the minimum torque increase could be the agglomeration of waste rubber particles in the NR matrix.²¹ Another possibility is that GRP is already crosslinked and does not easily flow into the matrix, and so an increase in the GRP loading will reduce the flow and consequently increase the torque. It is also believed that the highly aggregated and convoluted structure of waste rubber powder contains voids in which the matrix rubber is trapped, and this increases the effective volume fraction of waste rubber and hence leads to the higher viscosity of the blends.²²

The maximum torque decreased as the Dev.R loading increased but remained stable in the GRP systems. This indicates that the elastic modulus is lower in compounds with Dev.R. The shortest fragments and smaller chains in Dev.R act as plasticizers, reducing

the viscosity and torque of the compounds and increasing their tack. The higher elastic modulus of GRP compounds, in comparison with that of Dev.R compounds, leads to larger maximum torque in GRP systems. The torque reduction with Dev.R compounds can also be explained by the lower sulfur concentration in these blends in comparison with that of virgin NR.

The scorch time of the blends decreased with an increase in both the GRP and Dev.R concentrations (see Fig. 4). Phadke et al.²³ also observed a decrease in the scorch time upon the incorporation of cryo-ground rubber powder into an NR compound. This was due to the presence of crosslinked precursors and an unreacted curative in GRP.^{21,22} The existence of an unreacted accelerator in GRP was reported by Mathew et al.²⁴ Gibala and Hamed²⁵ also observed a decreased scorch time in SBR compounds upon the incorporation of powdered rubber vulcanizates, and it was ascribed to the migration of the accelerator from the ground vulcanizates to the matrix. The same reason can also explain the reduction of the scorch time in the compounds containing Dev.R. The shorter scorch time in the blends indicates that the crosslinking reactions started earlier. Because the scorch time slightly decreased in all blends, the processability did not change remarkably with the waste rubber loading.

The optimum cure time is the vulcanization time needed for obtaining optimum physical properties.

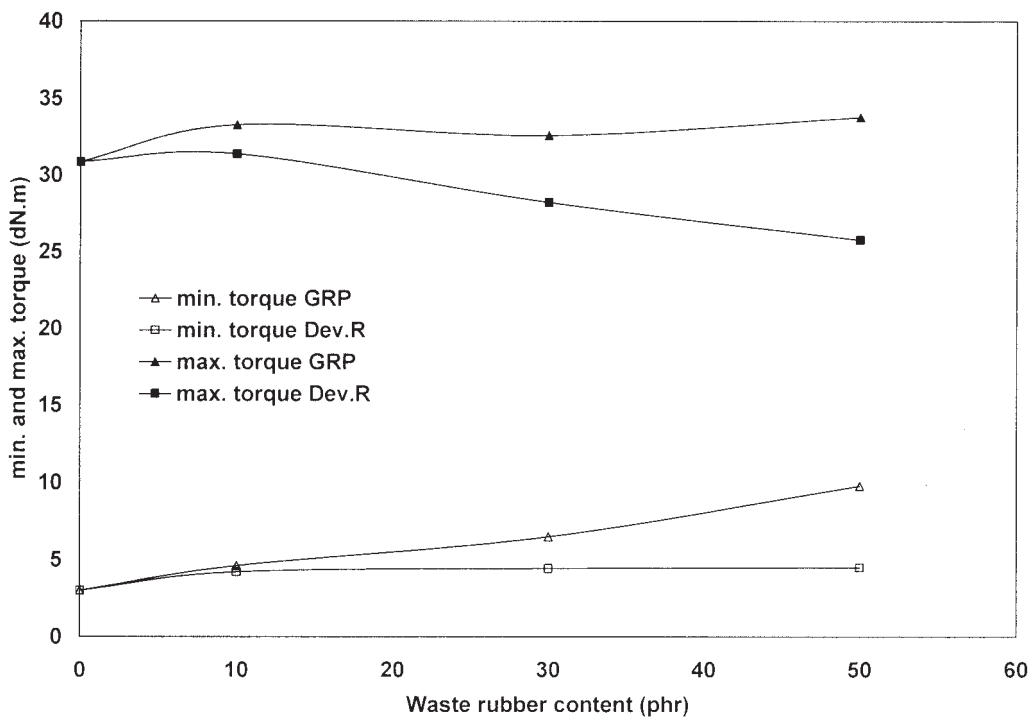


Figure 3 Minimum torque and maximum torque versus the waste rubber concentration in the NR matrix.

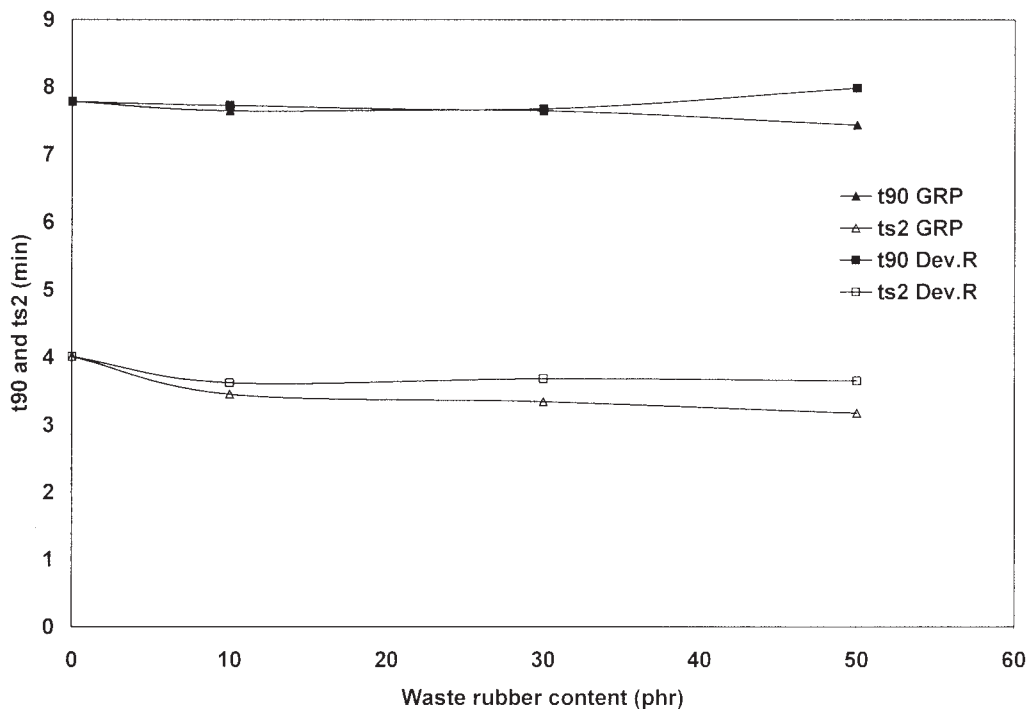


Figure 4 Scorch time (t_{90}) and cure time (t_{s2}) versus the waste rubber concentration in the NR matrix.

Figure 4 shows that the optimum cure time changed slightly with the waste rubber content. We have concluded that the incorporation of waste rubber into a virgin NR matrix does not affect the cure time remarkably.

Swelling behavior and crosslink density

Figure 5 shows the swelling degree of the NR compounds with various waste rubber concentrations in toluene. All the cases showed similar patterns: the rate of the toluene uptake was relatively fast in the initial stage and reached a plateau value of an equilibrium state at the same time. At the equilibrium state, the swelling degree of the compounds rose with an increase in the waste rubber loading. This was due to the void space existing in the compounds containing waste rubber, and more solvent was absorbed.

Figure 6 shows the variations of the crosslink density of the systems as a function of the waste rubber concentration. The crosslink density decreased with an increase in the waste rubber loading; this was due to the obstruction of the sulfur's migration by the waste rubber particles.²⁶ There were new active crosslinking sites in Dev.R, which continued to form crosslinks during revulcanization; the greater the Dev.R concentration was, the more active crosslinking sites there were. However, with more Dev.R loading, the concentration of sul-

fur was lower, and the crosslink density still decreased for whole systems.

Mechanical properties

The tensile strength, elongation at break, tear strength, abrasion resistance, and hardness were used to evaluate the mechanical properties of the systems. Generally, materials tend to become weak and brittle with increasing concentrations of GRP and Dev.R.^{12,21,27} Despite the general decrease in the mechanical properties with increasing waste rubber loading, the retention values of the properties ranged from good to excellent at a 10 phr loading.

The effect of the waste rubber concentration on the tensile strength and the elongation at break are shown in Figures 7 and 8. The tensile strength and the elongation at break deteriorated with the loading of both GRP and Dev.R. The reason was probably the uncontinuous and imperfect structure in the blends. However, the compounds containing Dev.R had much better properties than the compounds with GRP because of the treatment of the waste rubber powder. We assumed that the devulcanization only occurred on the surface of GRP because the size of the ground rubber particle was approximately 4 mm. However, better compatibility between Dev.R and the NR matrix was achieved, and better properties were obtained. Up to a 10 phr loading of Dev.R, the compound still retained 87% of its original strength and 91% of its elongation at break.

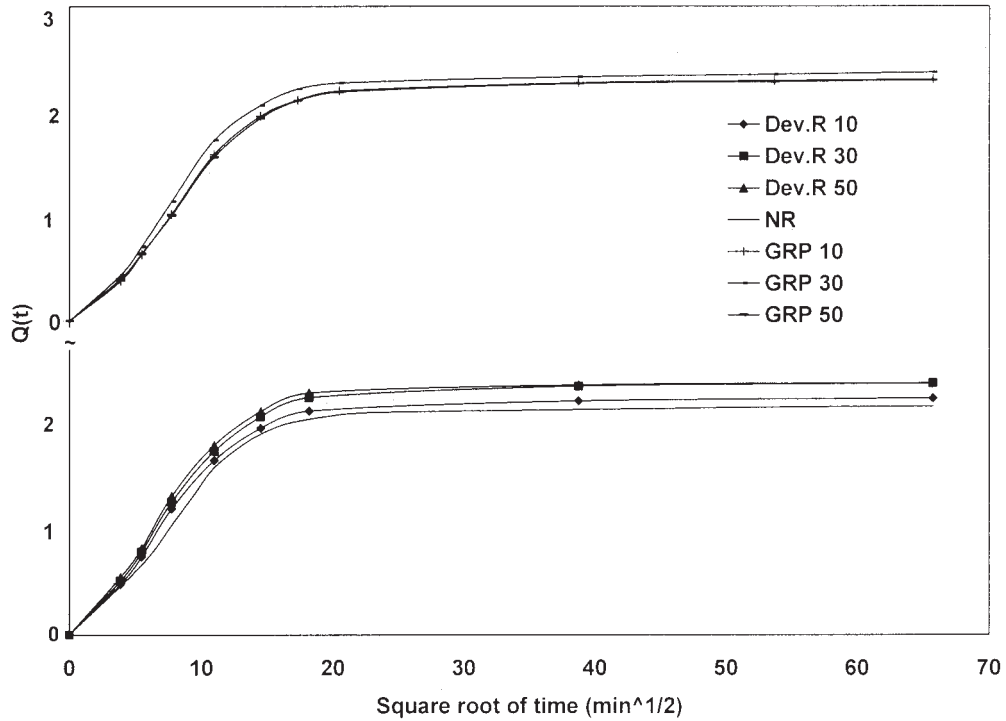


Figure 5 $Q(t)$ versus the square root of time for the compounds containing waste rubber.

The effect of the waste rubber concentration on the tear strength is shown in Figure 9. An improvement was made in tear resistance by the addition of waste rubber fillers to the NR matrix. The tear strength with

10% GRP or Dev.R was twice that of the NR matrix. The higher the waste rubber loading was, the higher the tear strength was. Especially in the compounds containing Dev.R, the tear strength was dramatically

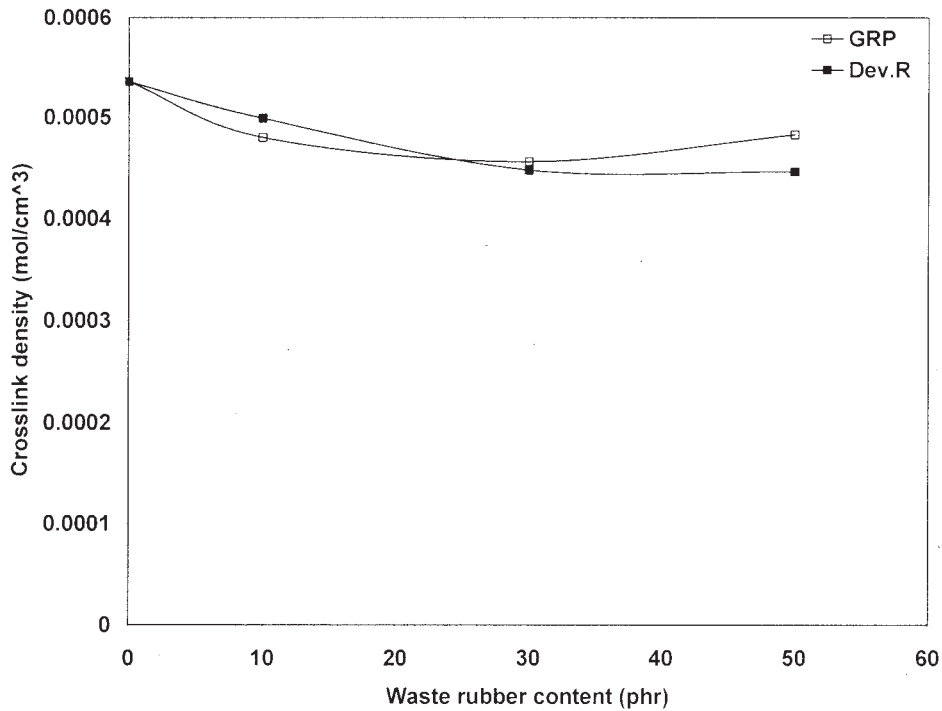


Figure 6 Crosslink density versus the waste rubber concentration in the NR matrix.

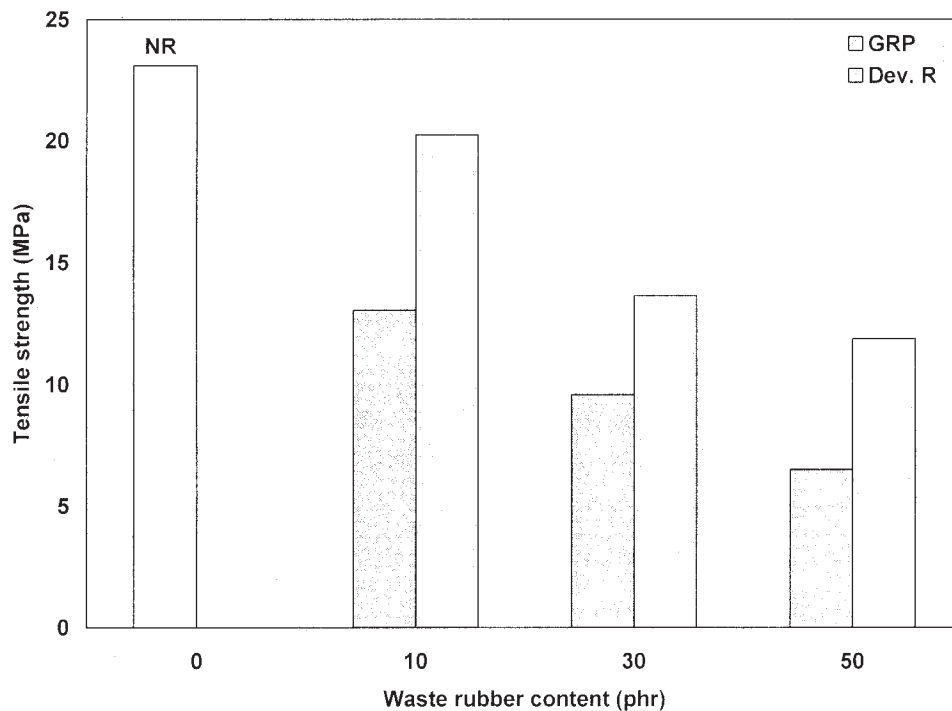


Figure 7 Tensile strength versus the waste rubber concentration in the NR matrix.

higher with an increase in the Dev.R loading. There were double bonds left in the vulcanizates, and even more active crosslinking sites existed after devulcanization. An interpenetrating-network-like structure

might exist in such blends after revulcanization; a further study will be carried out in our laboratory.

The abrasion resistance variation with the waste rubber concentration is presented in Figure 10. The

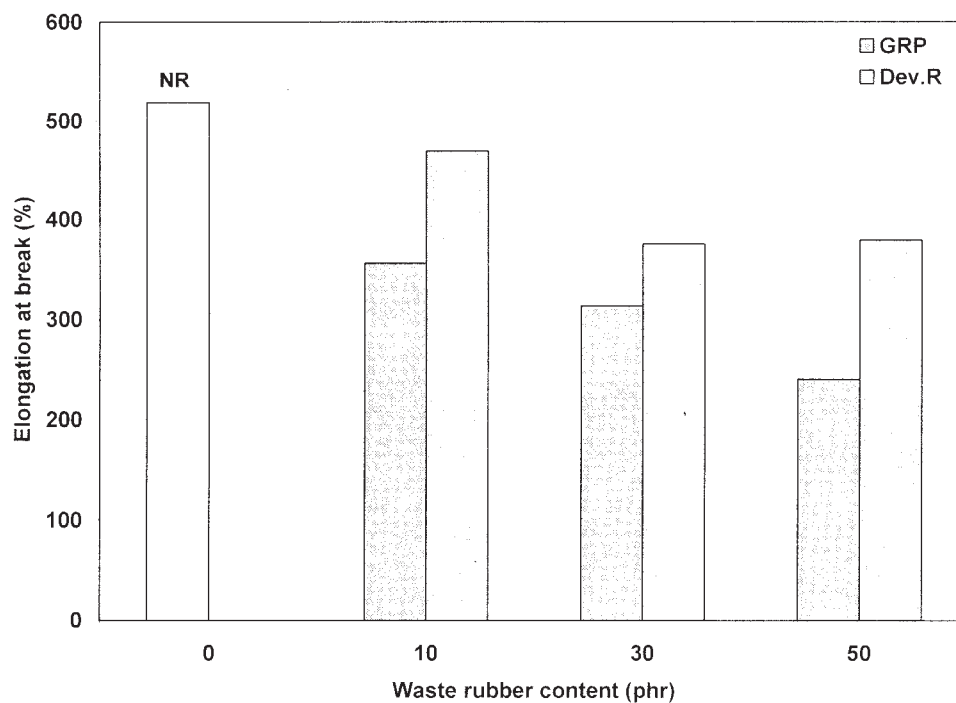


Figure 8 Elongation at break versus the waste rubber concentration in the NR matrix.

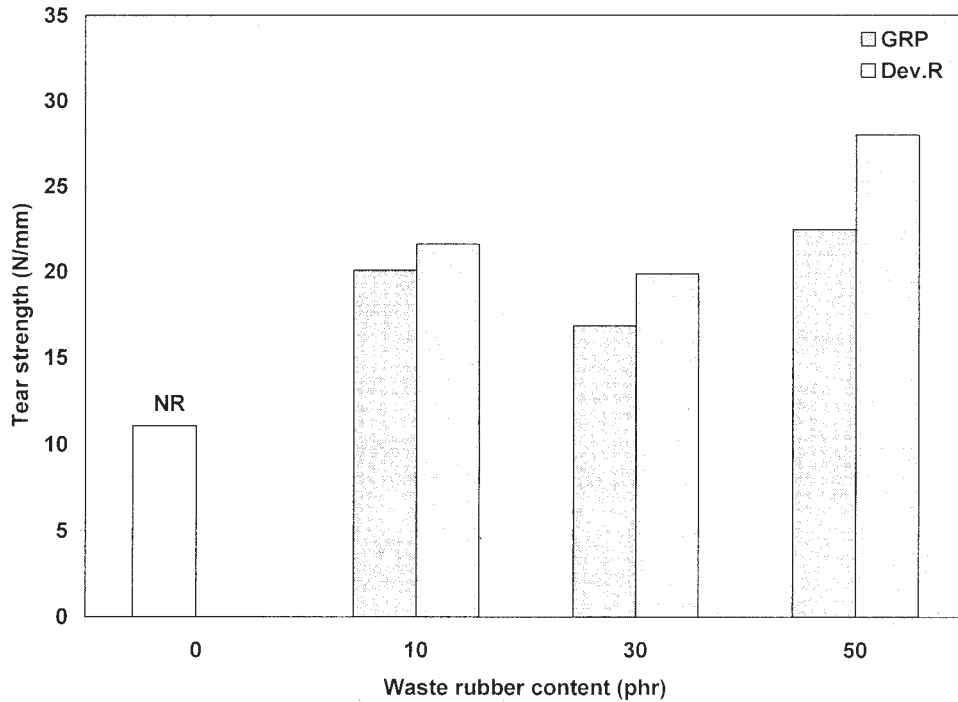


Figure 9 Tear strength versus the waste rubber concentration in the NR matrix.

abrasion resistance was improved with the GRP loading but impaired with the Dev.R loading. GRP consisted of vulcanized particles containing higher modulus and led to better abrasion resistance for the compounds. However, the abrasion resistance dete-

riorated because of the shorter fragments and smaller chains of Dev.R, and so the higher the Dev.R loading was, the worse the abrasion resistance was.

A plot of the hardness versus the waste rubber concentration is shown in Figure 11. The hardness

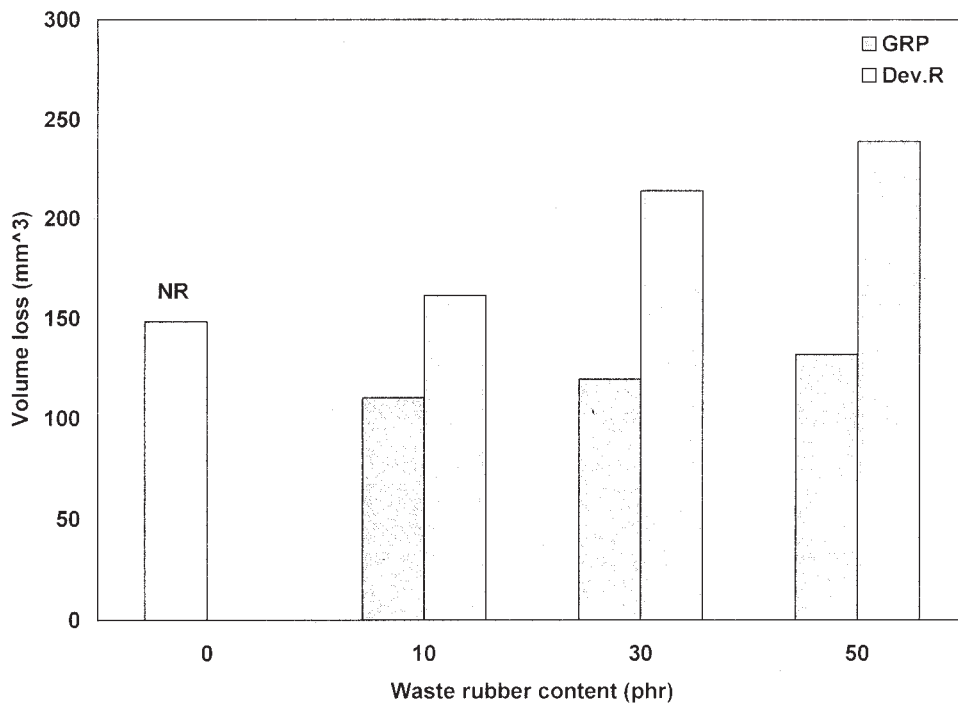


Figure 10 Abrasion resistance versus the waste rubber concentration in the NR matrix.

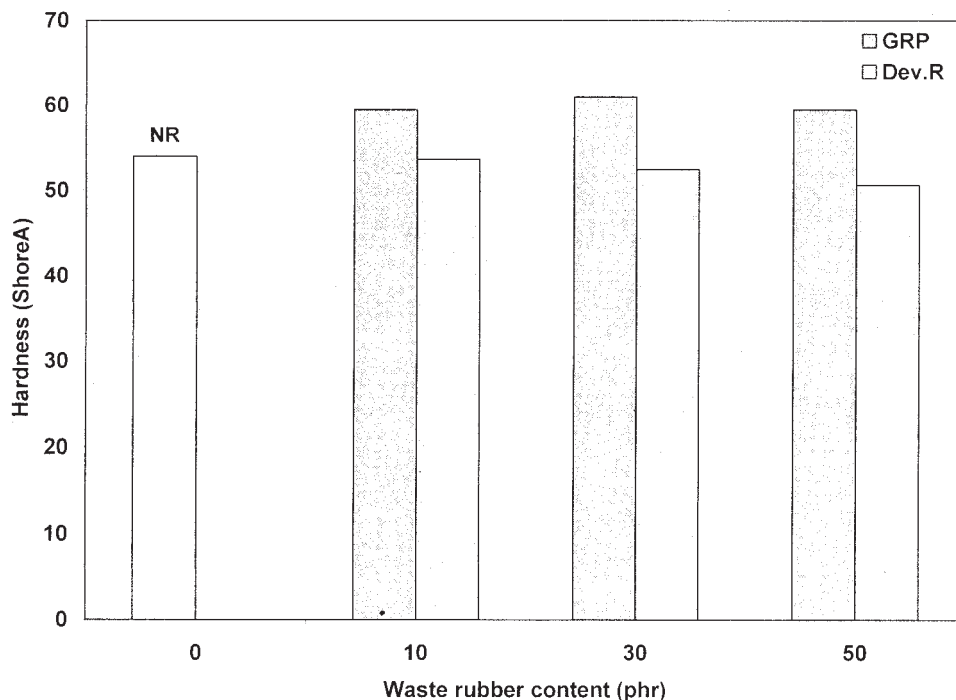


Figure 11 Hardness versus the waste rubber concentration in the NR matrix.

drop in the compounds was slight with an increase in the Dev.R loading. The value with 10 phr Dev.R was the same as that of the NR matrix, and the hardness with a 50 phr Dev.R loading was 93% of that of the virgin NR. The shortest fragments in Dev.R reduced the hardness and mechanical properties. In comparison, the systems with GRP had better hardness because of the higher modulus.

CONCLUSIONS

GRP and Dev.R, produced with continuous shear-flow reaction technology, were mixed with virgin NR rubber. Dev.R was proved to be partially devulcanized with main-chain scission and crosslink scission, as shown by Horikx plot calculations and gel fraction measurements. Cure characteristics such as the scorch time and cure time of the NR compounds decreased slightly with an increase in the waste rubber loading but showed a slight increase in the minimum torque. The processability of the systems evidently did not change remarkably with the waste rubber loading. The swelling resistance decreased with an increase in the waste rubber loading in the NR compounds. When the waste rubber was added to the virgin rubber, a decrease in the crosslink density was observed. Both the tensile strength and elongation at break decreased, and the abrasion resistance was improved with the GRP waste rubber loading but reduced with Dev.R. The tear strength increased remarkably when increasing amounts of

both waste rubber types. The hardness of the compounds remained the same with various waste rubber loadings. The incorporation of Dev.R up to 10 phr in NR did not reduce the performance remarkably. The compounds with Dev.R demonstrated better properties than those with GRP.

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