Mechanochemical Surface Activation of Ground Tire Rubber by Solid-State Devulcanization and Grafting

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ABSTRACT: Cured rubber powder was successfully devulcanized under the application of high-energy ball milling. An attempt was made to improve the efficiency of devulcanization with a phenolic antioxidant (2,6-di-*tert*-butyl-4-methyl-phenol). In addition, the grafting of virgin natural rubber to the surface of rubber powder was promoted by milling under an inert atmosphere. The extent of mechanochemical devulcanization was studied by estimation of the sol–gel fractions and crosslink densities. Our findings suggest that the process led to a preferential breakage of sulfur crosslinks. The curing behavior of the compounds and the mechanical properties of the vulcanizates containing treated rubber powder and fresh rubber were investigated. The chemical and mechanical properties depended strongly on the experimental milling conditions, which could consequently be controlled to improve the quality of the reclaimed rubber. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1631–1638, 2003

Key words: elastomers; antioxidants; compounding; curing of polymers; mechanical properties

INTRODUCTION

The environmentally responsible handling of large volumes of scrap tires rubber is an extremely challenging problem faced by communities. More than 300 million tires are discarded every year in European countries, and most of these are presently landfilled. Energy recovery from worn out tires is a viable option; however, on the basis of energy balance, the material recycling of rubber waste may be preferable to any other recovery technique. The reclamation of waste rubber is, therefore, the most desirable approach to solving the disposal problem. Powdered waste rubber can be used as inert filler in a mixture with virgin rubber, whereas devulcanized rubber can be added in new tires up to 10% without a significant drop in the mechanical properties of the final products, as confirmed by actual road tests with truck tires.[1] Nevertheless, the addition of ground rubber (GR) powder in polymeric compounds at higher loading volumes leads to deleterious effects on the physical properties, especially the tensile strength of the finished products. The major problem in the recycling of rubber-like materials such as tires is the crosslinked molecular structure of already vulcanized rubber, which not only prevents the softening and processing of waste rubber particles but also inhibits binding of the powder surface to the virgin material. Several reclamation methods have proposed to overcome these barriers, which have basically followed two main approaches: (1) the devulcanization of cured rubber and (2) the surface modification of waste particles. The devulcanization of rubber causes the cleavage of crosslinks via chemical,[2,3] microbial,[4,5] microwave,[6] or ultrasound[7,8] treatments, which make used rubber suitable to be reformulated and recured into new articles. Surface modification methods treat GR to improve the chemical activity of particles without breaking the crosslinks of the vulcanized material by coating the rubber particles with a bonding agent or by treating them with a caustic gas.[9] None of these methods is dominant in rubber recycling because of the energy intensity, environmental concerns, and severe degradation of rubber involved in the treatment. Despite this, considerable work is still being done on the reclamation of waste GR. Recently, Farris and Morin[10] patented a high-temperature high-pressure sintering process that converts vulcanized rubber powder into a solid mass, recovering 70% of the original mechanical properties. Alternative strategies for recycling discarded tires were investigated by Smith et al.,[11] who suggested cryogenic mechanical alloying as a viable process, through which it is possible to produce highly dispersed blends composed of thermoplastic rubber and GR. A solid-state shear extrusion process was used by

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Bilgili et al.[12] to pulverize rubber granulates without using cryogenic fluid for cooling, enhancing the surface activity, and causing a partial devulcanization of rubber particles.

In a previous article, we provided experimental evidence for the effectiveness of the high-energy ball-milling technique in partially devulcanizing rubber powder at near room temperature.[13] The proposed process, well known in advanced materials technology,[14] might provide an economical and ecologically sound method for recycling waste elastomers, to return the material to same processes and products from which it was originally generated. However, like all other devulcanization methods, the breakage of sulfur crosslinks promoted by the milling action was inevitably coupled to oxidative degradation processes, with a consequent decrease in the mechanical properties of the recycled product. To carry out the successful recycling of vulcanized rubber, it is necessary to preferentially break the crosslinks in the three-dimensional network. To minimize rubber powder degradation during the milling treatment and to obtain a material suitable for revulcanization, several high-energy ball-milling experiments were conceived in this study. In the first milling experiment, the reclaiming action of a phenolic antioxidant [2,6-di-*tert*-butyl-4-methyl-phenol (BHT)] on the vulcanized powder was studied. In the second experiment, grafting between rubber powder surfaces and virgin natural rubber (NR) was induced by milling in the solid state. In the last experiment, carried out for comparative purposes, GR was milled under an inert atmosphere. The obtained samples were then blended with virgin NR to investigate the curing behavior and mechanical properties of vulcanizates before and after accelerated aging. According to an empirical model proposed by Isayev,[15] with chemical tests, we shed light on several aspects of the rubber ball-milling process, such as the extent of degradation and devulcanization of cured GR, which were assessed through measurements of sol content and crosslink density (n_c), respectively.

EXPERIMENTAL

Materials

The NR [*cis*-1,4-polyisoprene (PI)] used in this work was a standard 20-grade Malaysian rubber (STR-20). Tire GR (rubber crumb) was kindly supplied by Trelleborg Wheel Systems spa. All the other compounding ingredients used in this work, namely, carbon black N330 grade, zinc oxide, stearic acid, aromatic process oil (DAE type), the antidegradants polymeric trimethyl quinoline and alkyl-phenyl-*p*-phenylene diamine, paraffin wax, the curative sulfur, and the accelerator *N*-Cyclohexyl-benzothiazyl-2-sulfenamide were all standard grades in the rubber indus-

TABLE I
Rubber Compounding Composition with Recycled Material

NR	100 phr
Recycled rubber powder (milled or unmilled)	15 phr
Carbon black N330	50 phr
ZnO	5 phr
Stearic acid	1 phr
DAE oil	10 phr
N-Cyclohexyl-benzo-thiazyl-sulfenamide	1 phr
S	1 phr
Polymeric trimethyl quinidine	1 phr
Alkyl-phenyl-*p*-phenylene diamine	2 phr
Wax	1 phr

try and were obtained by typical world class suppliers of these chemicals. Food-grade BHT was obtained from Great Lakes. The curing recipe used in this study is reported in Table I.

Sample characterization

Before the milling treatment, GR powder was purified by a 5-h reflux extraction with acetone (ASTM D 297) to remove impurities that could interfere with the mechanochemical reactions and physical–chemical characterization of the devulcanized samples. Particle size distribution of the rubber crumb was measured with a Retsch sieve. More than 85% of the particles fell in the range $200-400 \ \mu$m before the milling treatment. Thermogravimetric analysis (TGA) of the GR was performed at a heating rate of $20°C \ \text{min}^{-1}$ under a nitrogen flow on a Linseis apparatus (model L81+DTA). The TGA composition of unprocessed GR was performed according to the method described in ISO/DIS 9225-1 and was as follows: 57.9% rubber, 31.8% carbon black, 7.8% organic nonpolymeric additives, and 2.5% ash. Fourier transform infrared spectra of GR were collected with a Nicolet Avatar equipped with a horizontal attenuated total reflectance device with Ge as crystal material. Sol fractions of both vulcanized and devulcanized samples were measured by Soxhlet extraction with toluene as the solvent. The extraction time was set at 6 h, and the extracted fractions were dried and weighted. The molecular weight of the sol fractions were determined in toluene with a Ubbelohde capillary viscometer at 25°C. The viscosity-average molecular weight (M_v) of the polymer was determined with the following Mark–Houwink parameters:[16] $[\eta] = 50.2 \times 10^{-5} \times (M_v)^{0.667}$. The swelling capacity of the devulcanized samples was measured in toluene by the comparison of the dry gel volume to the swollen gel volume of the material, excluding the carbon black fraction. n_c was calculated from the Flory–Rehner equation:[17]

$$n_c = \frac{-\ln(1 - V_r) + V_r + \chi V_r^2}{V_1(V_r^{1/3} - V_r/2)} \qquad (1)$$

where n_c is the effective number of chains in the network per unit volume, V_1 is the molecular volume of the solvent, χ (0.42)[18] is the interaction parameter value for the toluene–PI system, and V_r is the polymer volume fraction in the swollen network. Soxhlet extraction and swelling measurements were repeated three times, and average values were obtained. Natural PI, with a nitrogen content of 6.8%, was purified by reprecipitation from a 1% w/v toluene solution into methanol. The precipitate was dried *in vacuo*. The nitrogen content after purification was measured with a Carlo Erba EA 1108CHN elemental analyzer and was at a 3.8% level. The molecular weight of NR (M_v = 1.2 × 10^6 g/mol) was determined in toluene with a viscometer at room temperature.

Mechanochemical treatments

With stainless steel 250-cm³ vials and 12-mm diameter balls placed on a Fritsch Pulverisette 5 apparatus, three different milling experiments were carried out. The first sample to be milled (sample A) was obtained by the addition of 4% (w/w) BHT to GR powder and slight mixing of the powder (i.e., low energy input). The second sample (sample B) was obtained the addition of GTR powder to a toluene–NR solution. The stirring of suspension was maintained during the evaporation of solvent until it was dry. Each starting mixture (6 g of each) was placed in a vial with 120 g of steel balls and then milled at a speed of 320 rpm for intervals up to 15 h to produce a homogeneous powder, which was removed and stored. Rubber powder was also milled as received in the third experiment (sample C). The vials temperature was controlled by a thermocouple and kept at 40°C by the use of an air cooling system. Sample A was milled in an air atmosphere, and samples B and C were milled in an inert environment, with the vials sealed in argon.

Vulcanization tests and mechanical properties

The modified rubber crumb derived from the milling operations was compounded according to the recipe reported in Table I in a two-roll open-mill apparatus. The crumb was incorporated into the NR band after the incorporation of carbon black; then, all of the other ingredients were added with the exclusion of the curatives. The rubber master batches were cooled for 6 h, and then, the curatives were added in the open-mill apparatus. The samples were vulcanized in a steam press at 151°C for 30 min. The physical and mechanical properties were measured on the resulting cured slabs. Each test sample, containing 15 phr of treated material, was compared with a control sample containing 15 phr of untreated GR.

The cure kinetics were studied with a Alpha Technologies moving die rheometer (MDR 2000) according to the procedure described in ASTM D 2240-93. The Mooney viscosity was determined with a Monsanto automatic Mooney viscometer at 120°C according to ASTM D 1646-94. Tensile tests were performed at a crosshead speed of 500 mm min⁻¹ on dumbbell-shaped specimens (ASTM D 412) on an Acquati dynamometer, and hardness was measured with an IRHD apparatus in accordance with ASTM D 2240. The crack growth rate was measured with the De Mattia flex cracking test by the ASTM D 813 test method. The cut length was measured at frequent intervals to determine the cut growth rate. To simulate aging conditions, the vulcanized samples were heated for 3 days at 100°C.

RESULTS AND DISCUSSION

Mechanochemical devulcanization

Previous experimental evidence[13] suggests that high-energy ball milling has the effect of simultaneous degradation and devulcanization on GR. Although the mechanical action promoted an increase in sol fraction, a slight decrease in n_c was observed when milling was carried out in air for 15 h. The CH_2—CH_2 bond is the weakest bond in the polyisoprenyl chain and is prone to rupture under mechanical stress.[19] Alkenyl radicals generated when these bonds are broken may undergo resonance stabilization and, subsequently, react, depending on the milling conditions. In the absence of oxygen, radicals can recombine to reform the original PI chain or react with an unsaturated bond of another molecule and form a crosslink. In the presence of oxygen, macroradicals react rapidly with O_2 molecules to produce peroxyl radicals, which may subsequently extract hydrogen from the chain usually in allylic position to the double bonds to form hydroperoxides. Mechanically generated macroradicals can be scavenged by a radical trapping agent, thereby preventing the recombination of polymer radicals. Several phenolic antioxidants, such as BHT, have been shown to prevent both the crosslinking and oxidation of γ irradiated polymers.[20] The quenching of reactive oxygen species by BHT has been extensively studied,[21] and it is clear that such an antioxidant reacts efficiently only with strongly oxidizing species. The inhibition of a radical chain reaction by BHT proceeds by a reaction with alkyl peroxyl radicals rather than alkyl radicals. Similarly, in our milling experiments, antioxidants incorporated in the rubber powder worked either by reacting with any peroxides present to form stable end groups or subsequent grafting on a macroperoxyl radical, as is expected of phenoxyl rad-
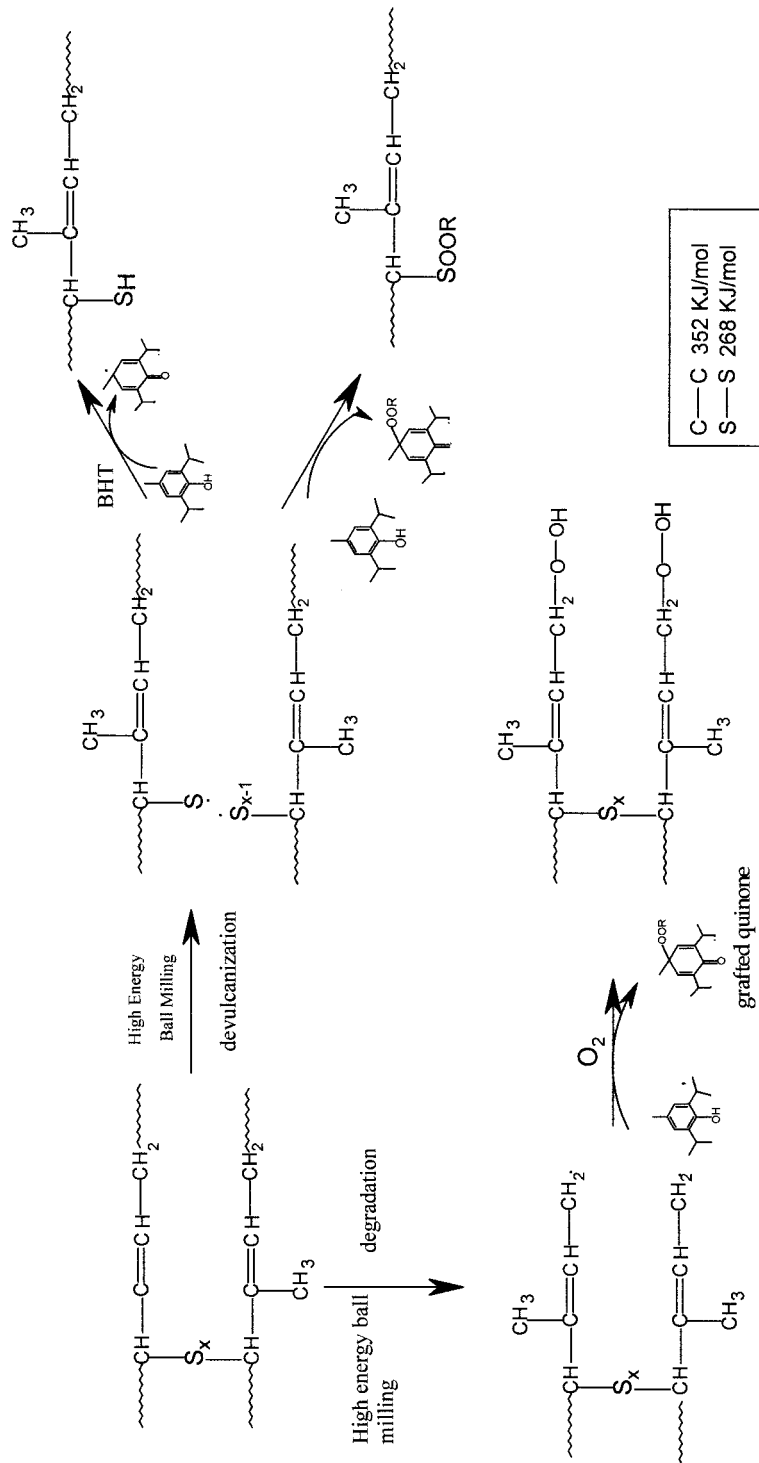
Scheme 1 Mechanical milling in the presence of a phenolic antioxidant.
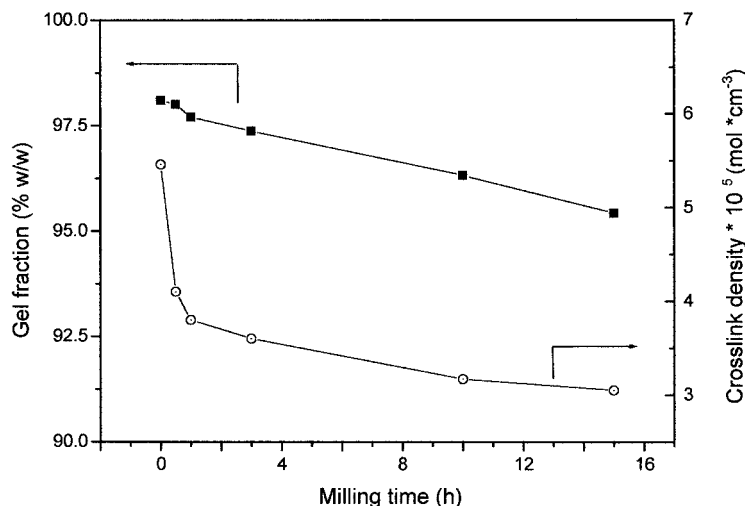
Figure 1 Gel fraction and n_c as a function of milling time.

ical, as reported in Scheme 1. The grafting of BHT with the rubber macromolecules was demonstrated by the fact that BHT was not recovered by the acetone extraction of the treated rubber crumb. Figure 1 shows the gel fraction and n_c as a function of milling time. n_c of the unprocessed powder was 5.5×10^{-5} mol/cm^3, whereas all milled samples had lower n_c's. Such a decrease could be attributed to the breakage of sulfur crosslinks (—Sy—) in the vulcanized rubber during the milling process. The gel fraction of the untreated powder was 98%, Figure 1 shows a slight decrease in the measured values with processing time. This could have been due to the breakage of the carbon bonds (—C—C—) at the backbone of the rubber molecules and the generation of the new free chains. Our findings suggest that BHT exerted its reclaiming action by preventing the recombination of sulfur radicals or by scavenging the radical SOO•. The normalized gel fraction (ξ/ξ_0) and the normalized crosslink density ($X/$

X_0) could be correlated according the empirical model first proposed by Isayev et al.[22] or ultrasonically devulcanized GR[15] and recently applied by Bilgili et al. to rubber powder obtained from the pulverization process. The model implies that devulcanization and degradation occur simultaneously at random throughout the rubber network, a condition that is believed to sufficiently be satisfied during high-energy ball milling. However, for a given mechanical stress applied to the rubber powder, the probability of the breakage of sulfur crosslinks (—Sx—), whose strength is 285–251 kJ mol^{-1} [12], is higher than the probability of the breakage of the carbon–carbon (—C—C—) bonds, whose strength is 352 kJ mol^{-1}. In particular, the polysulfidic bonds of the crosslinked rubber are more easily subject to rupture. Isayev's single-parameter model is described by eq. (2):

$$\frac{\xi}{\xi_0} = \left(1 + \zeta \ln\frac{[X]}{[X_0]}\right) H\left\{\frac{[X]}{[X_0]} - \exp\left(-\frac{1}{\zeta}\right)\right\} \quad (2)$$

where H is the Heavi-side unit step function used to make its argument, which ranges from 0–1 because a negative gel fraction has no physical meaning. The parameter ζ scales the relative change in gel fraction with respect to the change in n_c, which should be controlled by the relative breakage probability of the bonds. A fit of the data according to eq. (2), as reported
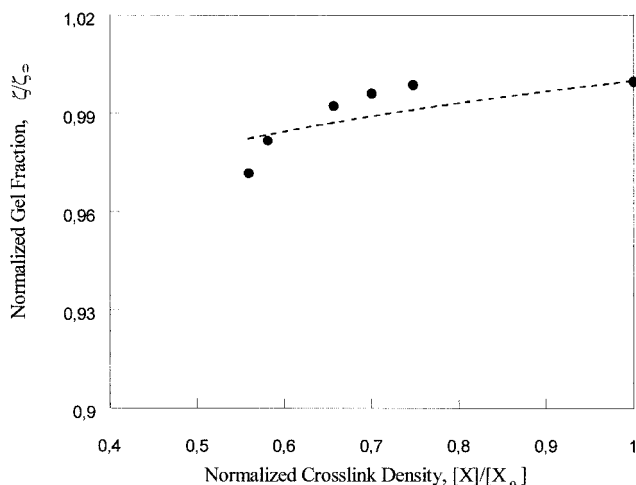

Figure 2 Correlation between ξ/ξ_0 and X/X_0 of sample A and a comparison with Isayev's empirical model..

TABLE II
Sol Fraction and n_c of GR Powder Milled for 15 h at Different Experimental Conditions

Sample	Sol fraction (%)	n_c (mol/cm^3)
A	2.0	3.4×10^{-5}
B	1.2	—
C	2.0	13.4×10^{-5}

TABLE III
Curing Properties of Treated Rubber Powder-Filled NR Compound at 151 °C

Parameter	Control	Sample A	Control	Sample B
Torque minimum, M_L (Nm)	2.8	2.6	2.6	2.5
Torque maximum, M_H (Nm)	13.1	12.5	12.9	12.8
Scorch time (min)	5.4	5.2	6.1	5.6
Cure time (90 min)	11.2	10.8	12.7	12.0
Mooney viscosity	50.3	46.8	50.4	49.3

in Figure 2, yielded a ζ value of 0.04 indicating that the extent of devulcanization was much higher than that of degradation for the high-energy ball milling of GR. We conclude that the ball-milling process of GR degraded the network by detaching molecular fragments of short molecular weight at the surface but leaving copious amounts of devulcanized material still involved in the network fragments of the chain (unextractable materials) The picture was also confirmed by the low molecular weight measured for the extracted sol fraction ($M_v = 2500$).

Surface activation by the NR coating of GR

Previous studies[23] on the effect of high-energy ball milling carried out under Ar on PI has demonstrated that this homopolymer undergoes chemical crosslinking during cryomilling. An increase in the n_c of GR to a value of $13.4\ 10^{-5}$ mol/cm^3 was observed when the powder was milled under argon at room temperature, as shown in Table II. This observation was an indication that the mechanochemically induced crosslinking of fresh NR to the surface of waste rubber powder may provide a feasible method for the improvement of the adhesion of rubber particles and the compatibility of the polymeric

components of compounds. In blends with virgin NR, chemically active surfaces of waste rubber allow crosslinking and an homogeneous incorporation of cured rubber powder within the network. Surface activation is obtained by the exploitation of the reaction of macroradicals produced during milling in inert atmosphere by the transfer of impact mechanical energy with an unsaturated bond of another molecule to form a new crosslink. In this experiment, grafting was proven by the very low soluble fraction recovered from the solvent extraction of the mechanochemically coated milled rubber powder. In fact, as shown in Table II, the sol fraction extracted from sample B was 1.2%, whereas almost all of the added NR should have been extracted by toluene in the absence of chemical interactions. In our case, after the milling treatment, the quantity of the extracted phase not only did not correspond to the added virgin polymer but was also lower than the quantity extracted from the argon-milled GR (sample C). It appears that mechanochemical treatment of GR in the presence of NR promoted fresh polymer grafting to the GR powder.

Mechanical properties of the revulcanizates

The suitability of reclaimed rubber in making new products was studied by the mixture of mechanically treated samples with fresh rubber and by investigation of the curing kinetics of compounds and the mechanical properties of the vulcanized products. The aging performance of the vulcanized products containing reclaimed rubber was also tested. The rheometric parameters of compounds containing both devulcanized (sample A) and NR-coated (sample B) GR are reported in Table III. Reclaimed rubber powder added in rubber compounds did not affect the kinetics of vulcanization. Higher curing rates have usually been observed in similar studies,[24] probably because of the presence of unreacted accelerator in the rubber

TABLE IV
Mechanical Properties of NR Compounded with Treated Rubber Powder (15 phr)

Parameter		Sample A		Sample B	
		As obtained	Aged	As obtained	Aged
Hardness IRHD	Test	65.1	66.7	65.5	79.5
	Control	65.1	65.0	63.3	77.6
Tensile strength (MPa)	Test	13.8	9.56	12.7	9.4
	Control	12.5	6.91	12.4	8.7
Elongation at break (%)	Test	491	307	513	301
	Control	493	263	500	300
Modulus at 50% (MPa)	Test	0.9	1.4	0.87	1.5
	Control	0.9	1.5	0.87	1.4
Modulus at 100% (MPa)	Test	1.5	2.7	1.41	2.6
	Control	1.5	2.8	1.41	2.5
Modulus at 200% (MPa)	Test				
	Control				
Modulus at 300% (MPa)	Test	7.8	—	6.9	—
	Control	7.2	—	6.8	—

powder. The addition of devulcanized rubber powder led to a lower minimum torque and, consequently, to a lower Mooney viscosity of compounds compared with control formulations. Mooney viscosity is evaluated as a measure of the devulcanization, as a higher plasticity of a rubber compound indicates a lower crosslinking degree of the treated powder. As shown in Table IV, milled powder loading led to a decrease in the tensile strength and elongation at break. The retention of the tensile strength for milled powder loading was estimated to be 90 and 72% after aging treatment, whereas the hardness and moduli were not affected. Early deterioration of the tensile properties was ascribed to oxidative degradation promoted by milled powder inside the elastomeric matrix. Despite the addition of antioxidant (BHT) to the rubber powder, some peroxyl radicals escaped being scavenged by reaction with phenol, especially for prolonged milling times, which gave rise to a partial degradation of the matrix. During the aging treatment, the reaction of free radicals, formed by the decomposition of hydroperoxides, led to an increase in n_c, which was responsible for the deterioration in the tensile strength of the samples. As shown in Figure 3, the loading of devulcanized powder significantly reduced the crack growth resistance of the specimen in comparison to the control sample. It appears that the partial decrosslinking of particles caused a loss in its ability to stop the growth of the cracks. In an activated powder–NR mixture, the retention of tensile strength was 98 and 93% after aging treatment, as shown in Table IV. The application of rubbers with a higher molecular weight yielded a stronger bond between the activated rubber particles and the surrounding rubber matrix, which improved the mechanical properties and aging characteristics. As clearly shown in Figure 4, the sample containing surface-activated GR exhibited a higher
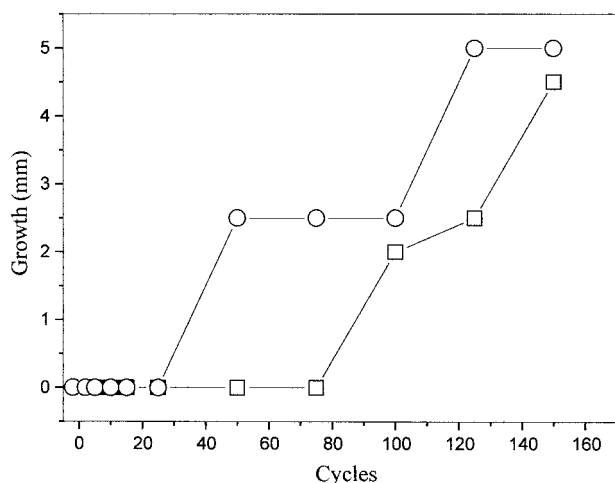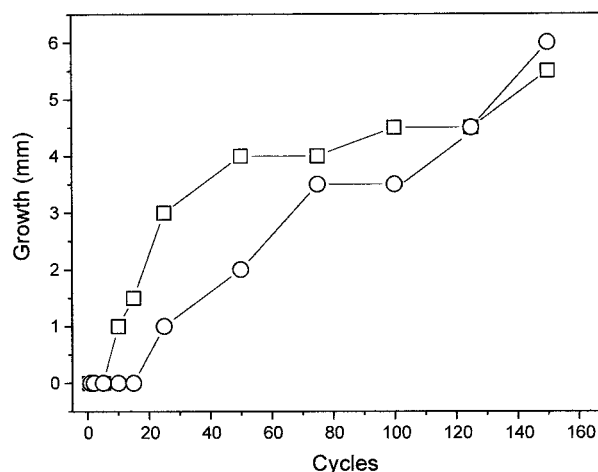

Figure 4 Crack growth resistance as a function of cycle number for (○) test and (□) control samples.

crack growth resistance compared with the control one. Such behavior could be rationalized when one considers that surface-activated particles not only kept their high n_c but also participated in the rubber network by means of the high-molecular-weight NR.

CONCLUSIONS

This work provided a method for the activation of GR by the mechanochemical devulcanization and grafting of cured rubber particles with nonvulcanized NR. Chemical and physical characterization of samples high-energy milled in the presence of a reclaiming agent, BHT, suggested the breakage of both the sulfur crosslinks (devulcanization) and carbon bonds of the rubber chain segments (degradation). However, the relative extent of the partial devulcanization with respect to the partial degradation was mostly determined by the relative strengths of the chemical bond present in the rubber network. Loading 15 phr of devulcanized GR in the standard NR compound increased its plasticity compared to the control because of a lower n_c of the particles. The corresponding vulcanized sample fairly retained its mechanical properties but exhibited poor aging characteristics because of the oxidative degradation of the matrix induced by milled rubber powder. Up to 10% of activated GR could be added to the NR compound without compromising the tensile strength and elongation at break, which further improved its crack-growth-resistance properties. Therefore, the loading of mechanochemically activated powder into compounds was preferred on the basis of mechanical property retention and a more delayed crack growth, which should encourage higher GR content formulations in tire manufacturing.

Figure 3 Crack growth resistance as a function of cycle number for (□) test and (○) control samples.

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