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A Novel Approach to Improving the Mechanical Properties in Recycled Vulcanized Natural Rubber and Its Mechanism

Amiya R. Tripathy, Jeremy E. Morin, Drew E. Williams, Stephen J. Eyles, and Richard J. Farris*

Polymer Science & Engineering Department, University of Massachusetts—Amherst, Amherst, Massachusetts 01003

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ABSTRACT: Vulcanized rubbers have three-dimensional chemical networks, and as a result they do not melt or dissolve. The presence of these networks creates a tremendous problem at the end of a product's life (i.e., recycling). Recently, R. J. Farris et al. have rediscovered a technique coined "high-pressure high-temperature sintering" (HPHTS) that fuses/sinters 100% vulcanized rubber powder into a solid mass recovering approximately 35−40% of the original mechanical properties. A method of enhancing the mechanical properties of sintered natural rubber powder by incorporating various organic compounds will be discussed in this paper. Additives of different chemical structures such as dienophiles (maleic acid and maleic anhydride), dipolarophiles (phthalimide), and organic acids (benzoic acid, salicyclic acid, and others) are employed. Attenuated total reflection infrared spectroscopy (ATR-IR) and electron ionization mass spectrometry (EIMS) are used to investigate the mechanisms of sintering and the underlying factors behind the enhancement of the properties that is seen with incorporation of these additives.

Introduction

The recycling and reutilization of cross-linked elastomers are difficult propositions because of the three-dimensional chemical network. This network renders the material insoluble and nonmelting. The global consumption of vulcanized elastomers has grown to a yearly production level of about 17.2 million tons.[1] Approximately 40% of that is natural rubber (around 7 million tons) with the remaining 60% consisting of various synthetic rubbers. Vulcanization is required to give rubber its characteristics such as high elasticity and strength. Unfortunately, once rubbers are cross-linked, they become a serious recycling problem (especially rubber tires due to the vast number employed in society). Many attempts have been undertaken to reuse vulcanized rubber such as reclaiming,[2−5] devulcanization,[6−11] fuel recovery,[12] and others. Most of these techniques, however, yield a nonelastic material, and currently no technique exists that uses 100% scrap rubber to make new rubber products.

Chemically vulcanized diene elastomers contain cyclic and mono-, di-, and polysulfide linkages at the diene sites in a network structure.[13] Therefore, it is logical that a cross-linked rubber can be recycled provided these bonds are cleaved by some means. In 1944, Tobolsky et al.[14,15] realized that the sulfur−sulfur bonds used to chemically cross-link all diene rubbers are among the weakest chemical bonds:[16] bond energies, $D_{\mathrm{C-C}}$ (in cross-link peroxide vulcanization) = 93 kcal/mol, $D_{\mathrm{C-S-C}}$ (in monosulfide cross-link) = 50−60 kcal/mol, $D_{\mathrm{C-S-S-C}}$ (in disulfide cross-link) = 35 kcal/mol, and $D_{\mathrm{C-S-S-S-S}}$ (in polysulfide) = 27 kcal/mol. Employing heat and pressure, the sulfide linkages in vulcanized rubber could eventually be cleaved in situ during molding. Devulcanization by ultrasound[17] and microwave[18] energies has also been reported. Recently, Farris et al.[19,20] (Figure 1) have rediscovered a process called "high-pressure high-temperature sintering" (HPHTS) that converts vulcanized rubber powder into usable rubber products. This technique is typically done at 200 °C temperature and 8.5 MPa pressure in the molding stage without incorporating any virgin rubber or binder. This process works well, and sheets made from recycled natural rubber yield about 35−40% recovery of the original mechanical properties. However, by incorporating a small amount of common organic compounds such as dienophiles, aromatic acids, and anhydrides with the vulcanized rubber powder prior to sintering, greater than 70% of the original properties of the vulcanized elastomer have been recovered. It is worth mentioning here that most of the rubber recycling processes that have been attempted over time have had little success because of the limitations of the resulting mechanical properties.

The present investigation attempts to determine the effect of additives on the mechanical properties of sintered natural rubber powder (*cis*-polyisoprene). Compounds such as benzoic acid, salicylic acid, phthalic acid, phthalic anhydride, phthalimide, maleic acid, maleic anhydride, and others were mixed with the vulcanized natural rubber powder and then sintered. Incorporation of small amounts of these additives was found to yield better properties than nonadditive sintering in several cases.

Tobolsky suggested that, at elevated temperatures when the materials are protected from oxygen and other reactive compounds, the rates of bond scission and re-formation in vulcanized rubber are essentially equal. According to Murakami et al.,[21] degradation occurs at cross-link sites on the secondary carbon atom adjacent to the cross-link moiety (Scheme 1), when *cis*-polyisoprene is heated beyond 200 °C. A mechanism has been proposed for the improvement in mechanical properties from data obtained via attenuated total reflection infrared spectroscopy (ATR-IR), electron ionization mass spectrometry (EIMS), and other relevant observations. The sintering mechanism and the effects of additives on the sintering mechanism are explained later in this paper. In short, it is believed that the additives slow/

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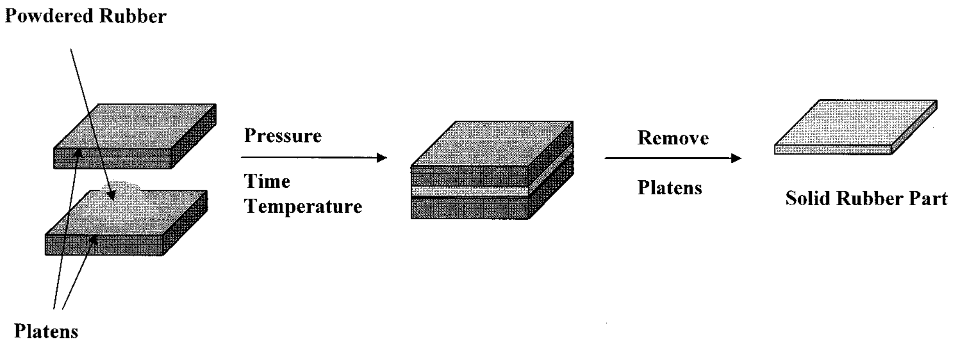


Figure 1. High-pressure high-temperature sintering process.

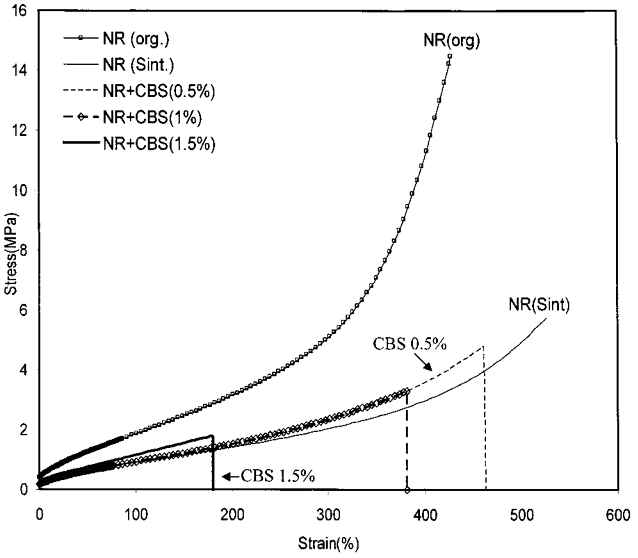


Figure 2. Stress–strain curve of sintered natural rubber powder with the addition of CBS.

stop conjugated diene formation along the rubber backbone, and with this an increase in properties is noticed.

Experimental Section

Materials. Stearic acid (98%, Aldrich), molecular sulfur (Flexsys), zinc oxide (99%, powder, <1 μm, Aldrich), and *N*-cyclohexyl-2-benzothiazole sulfenamide (Santocure CBS, Flexsys) were used without further purification. Dipolarophiles and dienophiles—benzoic acid (99%, Aldrich), salicylic acid (99%, Aldrich), maleic acid (99%, Aldrich), phthalic acid (98%, Aldrich), adipic acid (98%, Aldrich), maleic anhydride (99%, Fluka), phthalic anhydride (99%, Aldrich), phthalimide (99%, Aldrich), *N*-methylphthalimide (98%, Aldrich)—were used as received. Vulcanized white filled natural rubber from McMaster-Carr [hardness 50 ± 2 Shore A, ash content 12% from thermogravimetric analysis (TGA), sulfur cured, tensile strength = 14.5 MPa, elongation at break = 480%] and raw natural rubber, SMR CV(ISO 2000) [ash content 0.5%, volatile matter 0.8%, PRI (plasticity retention index) 60, Mooney viscosity, M(1+4) at 100 °C − 60 ± 5, M_n = 817 000, PDI = 1.7], were also used for this study.

Compounding and Vulcanization. The compound recipes used are given in Figures 3 and 6.[22] Mixing and compounding were done following the ASTM D 3182 (6.2) method.[23] The vulcanization times, t_{90}, were determined using a linear rheometer, Rheometrics Inc. The vulcanization was performed at 160 °C and 4.5 MPa using a Carver laboratory press, model C.

Cryo-Grinding and Sintering. Vulcanized rubber was ground in liquid nitrogen using a model 6800 cryo-grinder from Spex Certiprep. The resulting particle size of the rubber powder was approximately 300 μm for the cryo-ground vulcanized rubber. Sintering (as per Figure 1) was performed at 200 °C and 8.5 MPa using compression molding in a Carver press for 1 h unless otherwise specified.

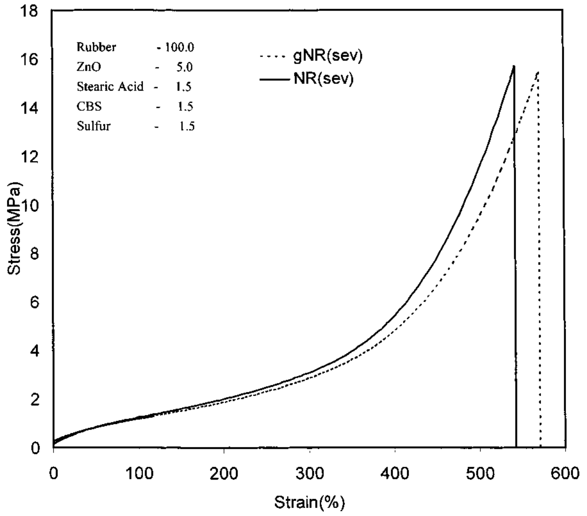


Figure 3. Stress–strain curve of vulcanized raw natural rubber (recipe as above) before and after grinding.

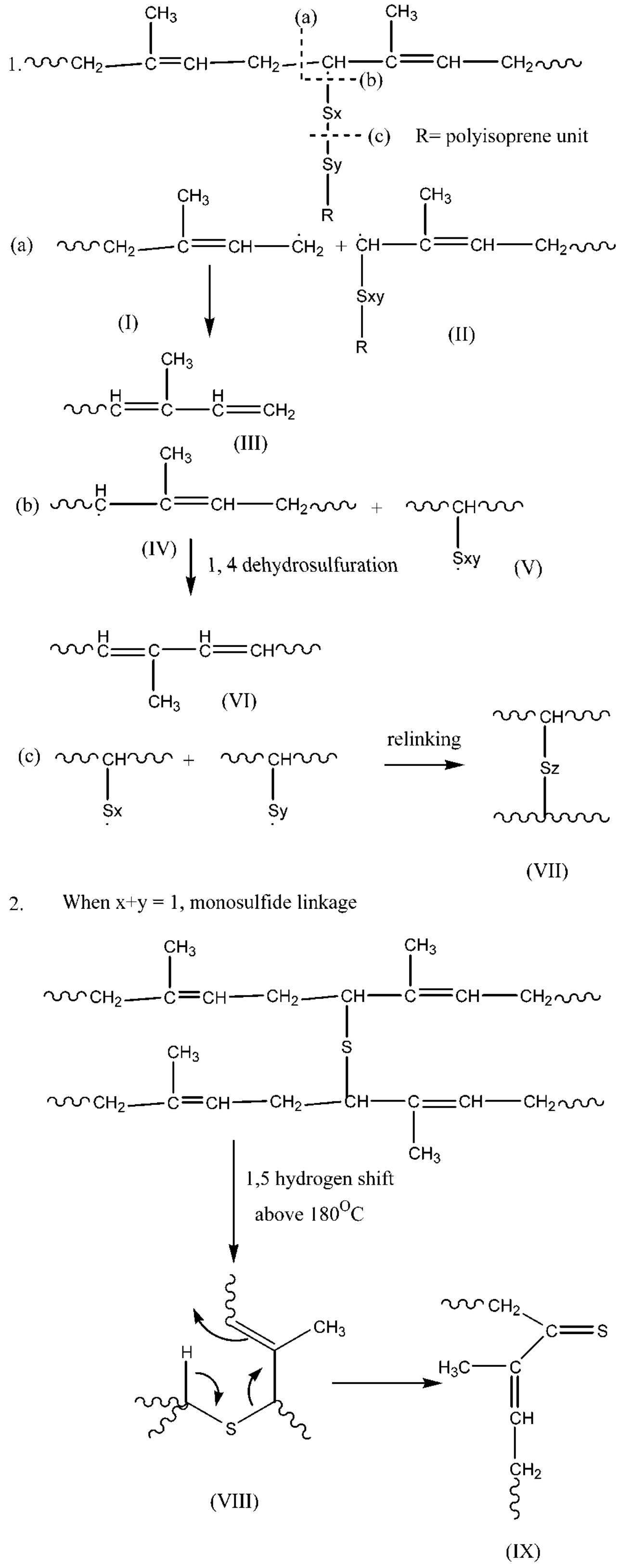
Characterization: Mechanical Properties. The mechanical behavior of the vulcanized and sintered samples was analyzed using an Instron model 5568. The specimen was a circular ring type (ASTM D 412) to avoid sample-gripping problems. The stress–strain curves of samples were obtained at room temperature at a strain rate 10 mm/min. Mechanical tensile data were averaged over at least four specimens.

Gel Permeation Chromatography (GPC). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (M_w/M_n) were obtained using gel permeation chromatogrphy (GPC). The GPC was performed on a modular system comprising a Waters 590 HPLC pump, a Waters 717 autosampler, and an ERMA ERC-7515A refractive index detector (ERMA CR, Inc., Tokyo). The mobile phase used was unstabilized THF (EM Science, Gibbstown) at a flow rate 0.95 mL/min at 30 °C. The molecular weights were calculated using 13 narrow polystyrene standards from 6,300,000 to 580 g/mol (Pressure Chemical Co., Pittsburgh, PA).

Attenuated Total Reflection Infrared Spectroscopy (ATR-IR). Attenuated total reflection infrared spectroscopy (ATR-IR) experiments were done using a Perkin-Elmer 2000 in dry nitrogen atmosphere at room temperature on the sintered samples directly with a 4 cm^{-1} resolution and 128 scans signal average. A KRS 5 (thallium, bromine, iodide) crystal was used. Spectra were taken from 5000 to 400 wavenumbers (cm^{-1}) in the transmission mode using a NB-MCT detector. The ATR-IR data are presented in this paper without any correction or modification.

Electron Ionization Mass Spectrometry (EIMS). Electron ionization mass spectrometry (EIMS) were performed on a JEOL (Peabody, MA) JMS-700 MStation double focusing magnetic sector spectrometer. Samples were introduced via a

Scheme 1. Breaking of Cross-Link on Heating[22]



direct insertion probe and heated in a vacuum at 4 °C/min from 50 to 500 °C. Spectra were acquired with an ionizing energy of 70 eV from 50 to 1600 Da (*m*/*z*). Individual spectra were averaged over the temperature range of interest.

Results and Discussion

Mechanical Properties. The stress−strain curves of virgin vulcanized natural rubber, designated as NR-(org), and sintered vulcanized natural rubber powder, noted as NR(sint), are shown in Figure 2. The sintered property is inferior compared to the vulcanized one. Generally, CBS (cyclohexylbenzothiazole sulfenamide) is a sulfur-donating agent and increases the cross-link density of natural rubber vulcanizates, resulting in high tensile properties. Figure 2 shows the effect increasing the amount of CBS added to the vulcanized rubber powder has on the stress−strain curves. Contrary to our expectation, CBS shows a drastic reduction in the mechanical properties. It was also found that both ZnO and stearic acid decrease the tensile properties as do other typical sulfur accelerators.[20] This is a contradiction to the expected results since all of these materials are used to promote sulfur vulcanization. On the other

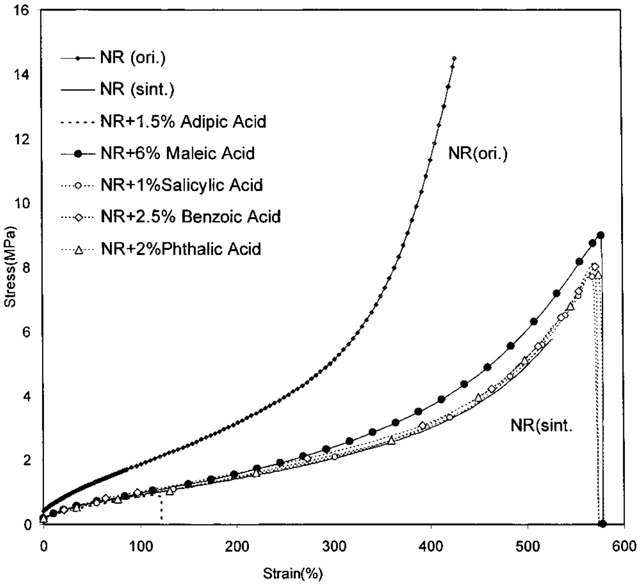


Figure 4. Stress−strain curve of sintered natural rubber powder with the addition of acids.

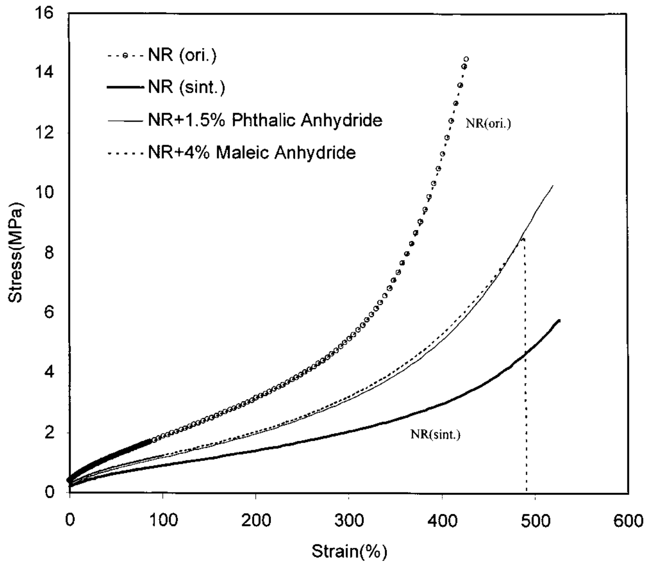


Figure 5. Stress−strain curve of sintered natural rubber powder with the addition of anhydrides.

Table 1. GPC Data of Natural Rubber in THF

GPC	natural rubber	natural rubber (cryo-ground)
M_n	817000	513000
polydispersity index (PDI)	1.7	2.1

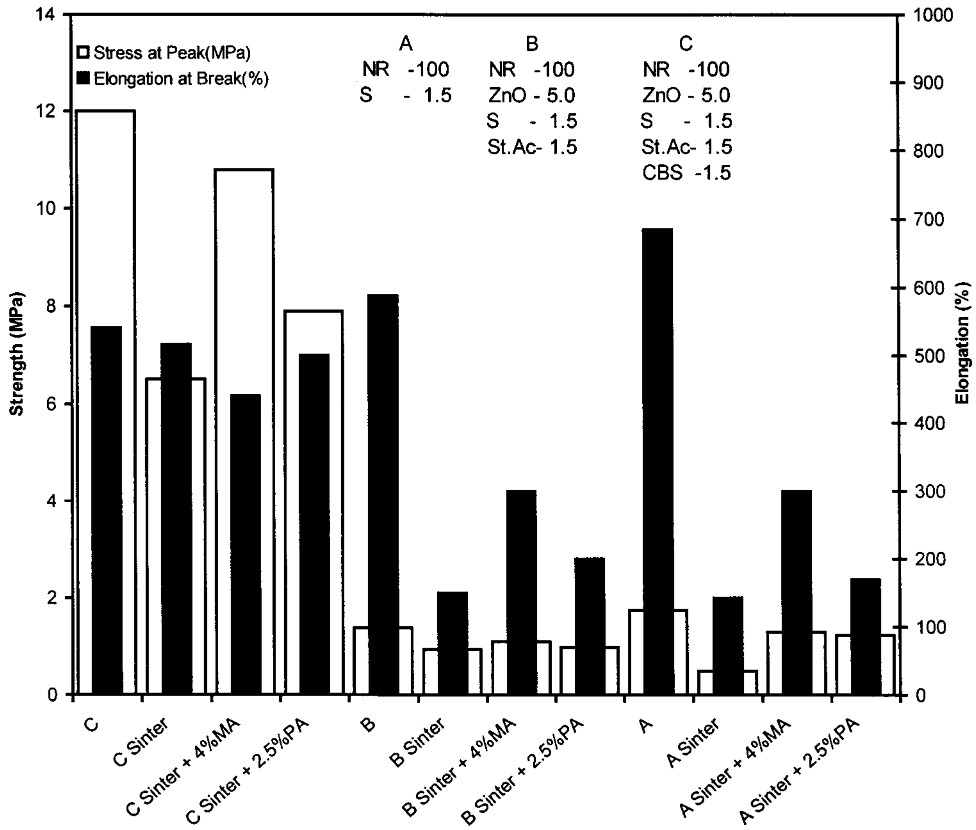


Figure 6. Effect of anhydrides on the mechanical properties of sintered vulcanized natural rubber (recipe as above).

Table 2. Influence of Various Additives on the Tensile Properties of Sintered Natural Rubber

samples	tensile strength (MPa)				100% modulus (MPa)				elongation at break (%)			
NR (original)	12.9				1.8				417			
NR(sintered)	5.3				0.9				516			
% additives	2	4	6	8	2	4	6	8	2	4	6	8
NR + phthalic anhydride	8.9	8.1		2.2	1.1	1.1		0.6	499	500		513
NR + phthalic acid	6.8	4.7		1.2	0.9	0.9		0.8	547	496		210
NR + maleic anhydride	6.4	7.8	8.1	5.6	1.1	1.2	2.8	2.0	471	497	577	501
NR + maleic acid	5.9	6.6	8.3	4.9	1.6	2.5	2.8	2.0	471	497	577	501
NR + phthalimide	6.6	9.6	7.9	7.1	1.0	1.4	1.5	1.7	508	534	463	411
NR + *N*-methylphthalimide	7.4	7.9	7.7		1.1	1.0	1.1		549	550	540	

hand, the addition of sulfur enhances the tensile strength but results in an abnormally low elongation at break.

The sintered rubbers have inferior mechanical properties because of the energetics between void propagation and strain-induced crystallization (SIC). While stretching the rubber sample, the network chains tend to orient themselves in the direction of stretching, and this typically leads to the formation of crystallites. These crystallites tie together a number of neighboring network chains, thereby contributing to the cross-linking network and allow for high tensile strength and elongation. In the case of sintered rubber, it is believed that it takes less energy to propagate a defect/void (due to absence of any chain entanglement) than stretch the backbone chains to allow for SIC. Thus, the samples fail before the SIC can occur, or samples experience a very small extent of SIC formation and therefore have a lower strength and elongation at break.

To understand the effect of grinding, gel permeation chromatography (GPC) has been performed on both raw un-cross-linked natural rubber and cryo-ground un-cross-linked natural rubber (particle size ~350 μm) in tetrahydrofuran (THF) (Table 1). As expected, the number-average molecular weight (M_n) in the ground rubber is less, but the polydispersity index (PDI) is higher than that of the starting rubber (Table 1). Both ground and nonground rubbers were compounded fol-

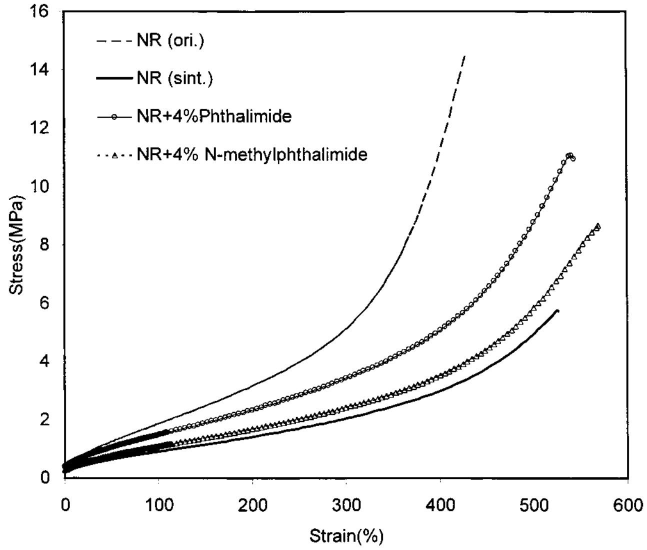


Figure 7. Stress–strain curve of sintered natural rubber powder with the addition of imides.

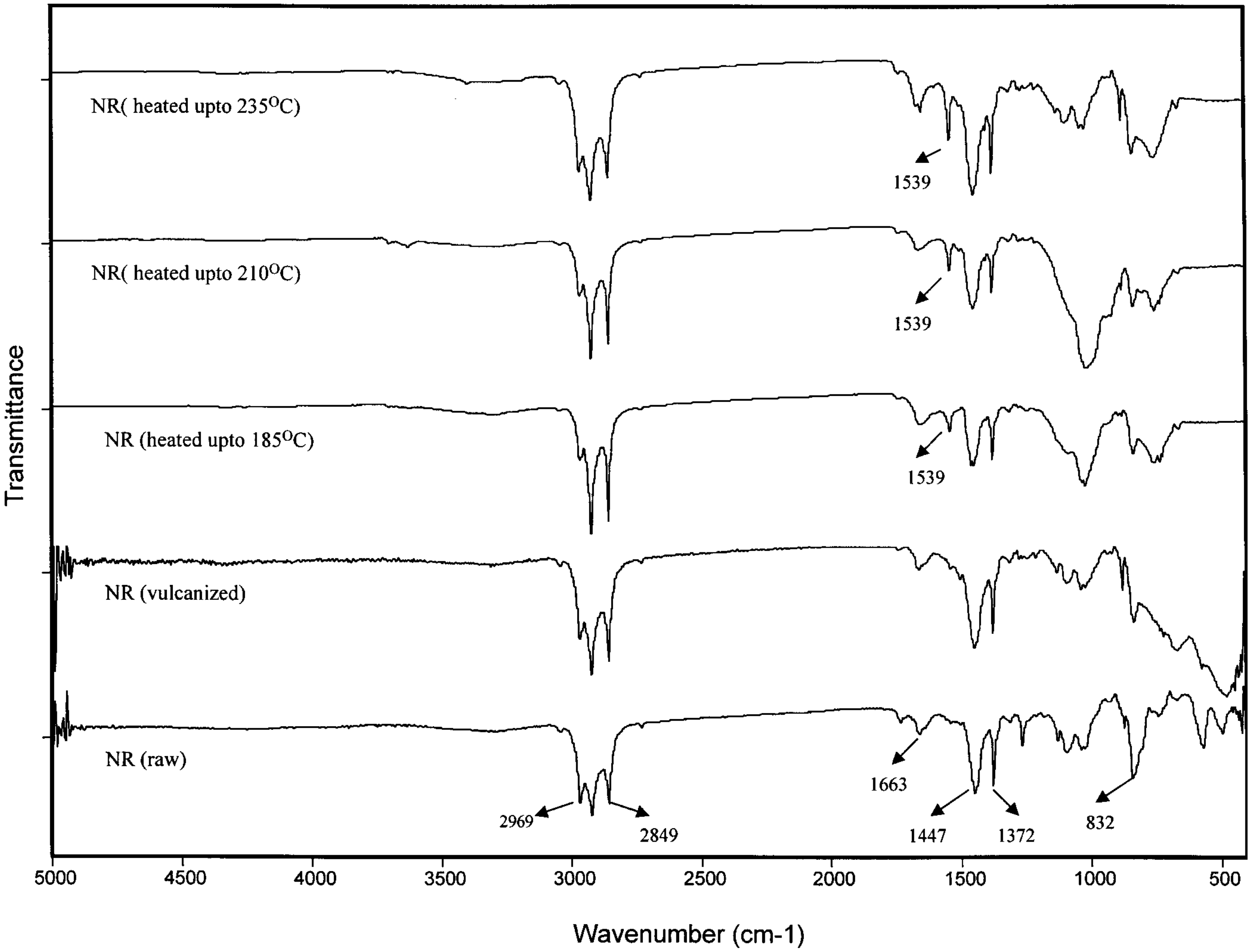


Figure 8. ATR-IR of heat-treated natural rubber sheets at various temperatures.

lowing the recipe shown in Figure 3 and cured as per optimum cure time. There is no major difference in the stress–strain curve of both natural rubber samples, except for the small increase in elongation at break for the ground natural rubber sample. Therefore, it seems that the starting molecular weight has hardly any effect on mechanical properties of vulcanized natural rubber, although there will likely be a difference between grinding prior to vulcanization and grinding after vulcanization.

Typical rubber accelerators show a decrease in the mechanical properties as noted in Figure 2. Therefore, it is believed that the mechanical properties of sintered rubbers can be improved by scavenging Zn–accelerator complexes[24,25] or free accelerator present in vulcanized rubber. Organic acids and their anhydrides are known as potential vulcanization inhibitors and are typically used to increase the induction time or scorch safety in rubber compounds.[26] Figure 4 exhibits the best stress–strain curve for the various compounds (Table 2). In all cases (except adipic acid), the tensile strength and elongation at break are slightly increased compared to the control (purely sintered rubber). The 100% modulus of the rubbers with additives is the same as the sintered rubber, and both are lower than the starting rubber. Generally, sulfur vulcanization is driven by alkaline media,[27,28] and therefore acids typically slow rubber vulcanization by reacting with the rubber accelerators.[29] It is to be noted here that generally whenever tensile strength has been increased, the elongation at break has also been enhanced. The next logical step was to attempt a similar study with anhydrides of the corresponding acids. Anhydrides were used to reduce the acidity of the additive. Astonishingly, a further improvement in the mechanical properties has been noted (Figure 5, Table 2). Phthalic anhydride around 5 wt % in powdered vulcanized rubber has been able to recover almost 70% of the original properties (Figures 5, Table 2). The 100% modulus of these materials is also greater than the sintered rubber but still less than the starting material. Furthermore, substituting an electron-withdrawing group, e.g., nitro group (+I, +R effects), chloride (+I, −R effects), for a hydrogen on the benzene ring of the phthalic group decreases the tensile properties (figure not shown). Figure 6 shows the effects of phthalic and maleic anhydrides on the mechanical properties of the sintered rubbers (known recipes shown in Figure 6). In all cases the mechanical properties have been improved with the addition of the maleic and phthalic anhydrides. Replacing anhydrides by imides (further reducing the acidity of the additive) in the vulcanized natural rubber powder equates to almost 75% recovery of the original mechanical properties (Figure 7, Table 2). By additionally increasing the alkaline effect of the additive (methyl substitution of phthalimide {*N*-methylphthalimide}), there was a decrease in the mechanical properties shown in Figure 7. Excess electron density on nitrogen or steric hindrance around the nitrogen in phthalimide

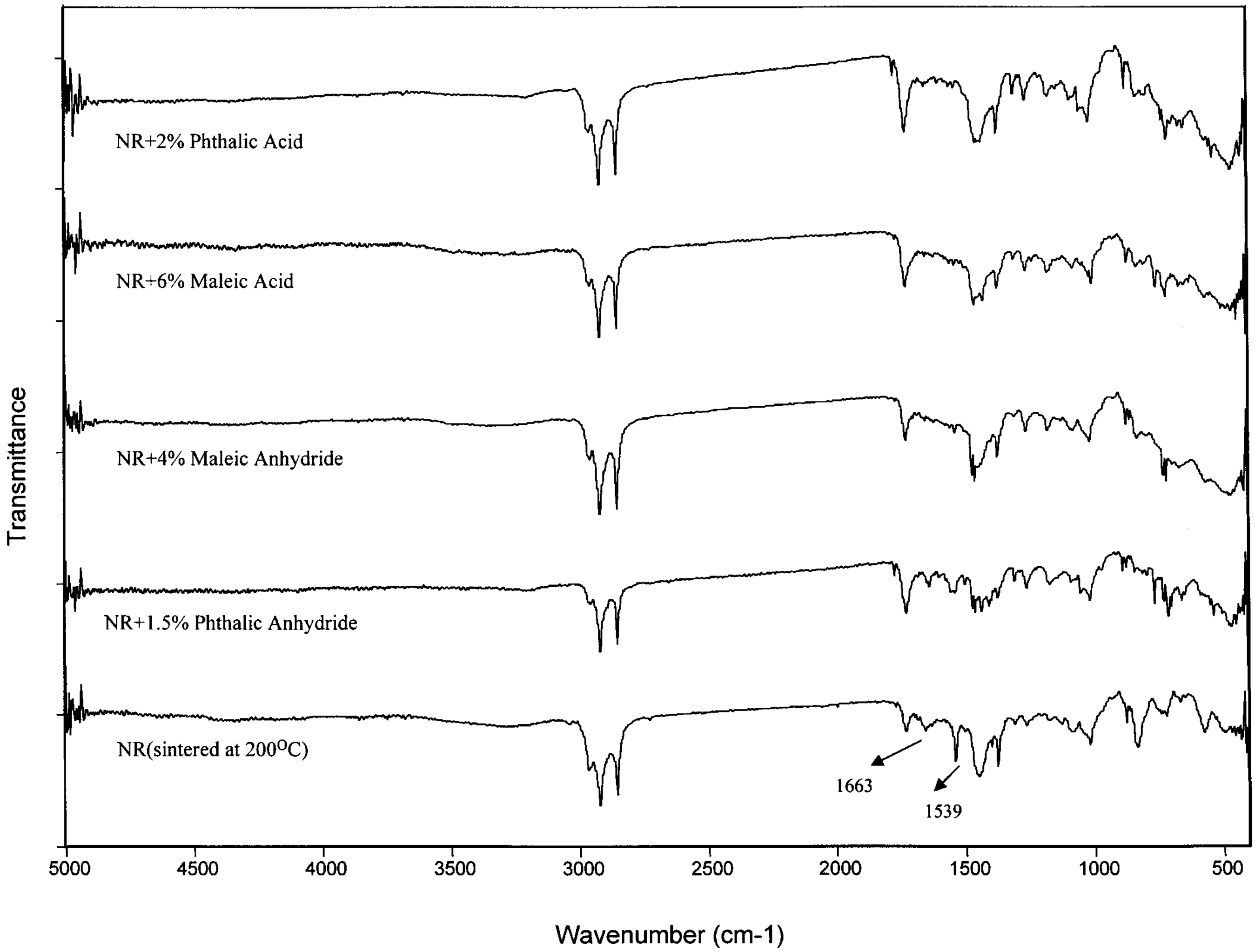


Figure 9. ATR-IR of sintered natural rubber with the addition of acids and anhydrides.

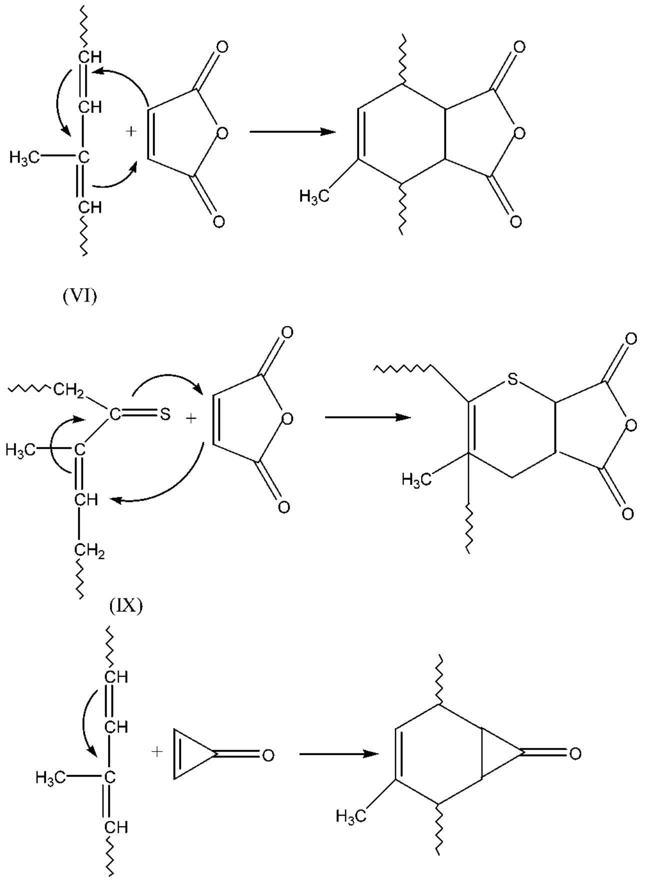
reduces the probability of it reacting with a particular species in the sintering process. This effect is further illustrated by chloro (−Cl) or nitro (−NO_2) substitution of the phthalic anhydride. These materials also show a decrease in the mechanical properties compared to phthalimide. Nonetheless, these results (Table 2) clearly show that, by varying the chemical nature of organic additives, the mechanical properties can be improved in sintered vulcanized natural rubber. Details of the proposed mechanisms will be discussed in the following sections.

Mechanism. To elucidate the mechanisms behind the increase in the mechanical properties in the presence of organic compounds in the vulcanized natural rubber, attenuated total reflection infrared spectroscopy (ATR-IR) and electron ionization mass spectrometry (EIMS) techniques have been used for the assignment of the details of the chemical reactions.

ATR-IR. ATR-IR spectra of various vulcanized natural rubber sheets are shown in Figure 8. The vulcanized natural rubber sheets have been heated to 185, 210, and 235 °C under 8.5 MPa pressure in a compression mold for 1 h each. All the usual peaks are present for *cis*-polyisoprene (natural rubber) [1663 cm^{-1} (for $\nu_{\mathrm{C=C-}}$), 1447 and 1372 cm^{-1} (for $\delta_{\mathrm{CH_2}}$ deformation), 832 cm^{-1} ($\gamma_{\mathrm{C-H}}$ bending), and peaks from 2969 to 2849 cm^{-1} for ($\nu_{\mathrm{C-H}}$ saturated, stretching)]. There is a new peak that appears for the heat-treated samples at 1539 cm^{-1}. The transmittance intensity of this peak increases as the temperature increases. The new peak at 1539 cm^{-1} is assigned as the stretching frequency of a methyl-assisted conjugated double bond [$\nu_{-(\mathrm{CH=CH})_n-}$, when $n > 6$].[30−33] It is well-known that as the conjugated double (Scheme 1) bond forms (due to reversion), the mechanical properties of the rubber decrease. With the addition of maleic acid and maleic anhydride, followed by sintering, the peak at 1663 cm^{-1} has completely disappeared, and the transmittance intensity of the peak at 1539 cm^{-1} has diminished substantially (Figure 9). This suggests that these materials are reacting with the carbon−carbon double bonds (Scheme 2) and therefore slowing the reversion reaction (stops rearrangement at the double bond site, Scheme 3). Therefore, by slowing/stopping the formation of the conjugated double bond, there is an improvement in mechanical properties. There is a similar effect with both phthalic anhydride and phthalic acid (1.5 wt %) as shown in Figures 5 and 6 although it is likely that these additives do not follow the same mechanism.

On the other hand, incorporation of potential vulcanization retarders (like benzoic and salicylic acids) in rubber powder yields ATR-IR spectra that maintain both the 1663 and 1539 cm^{-1} peaks (although they are diminished) along with other usual peaks of *cis*-polyisoprene and few weak peaks in 1600 cm^{-1} region (Figure 9). This is likely why there is not a substantial improvement in the mechanical properties for these additives. On the other hand, Figure 9 also shows that

Scheme 2. Diels Alder Reaction and Thionyl Cycloaddition

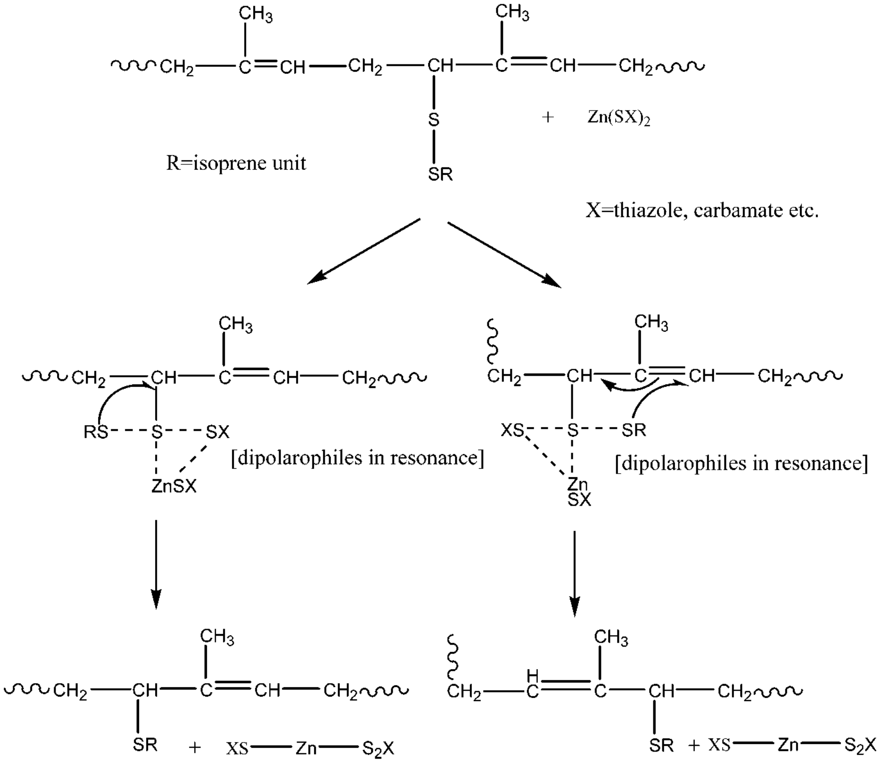


maleic anhydride and phthalic anhydride yield a diminished 1663 and 1539 cm^{-1} peak. Finally, Figure 10 shows how both the phthalimide and *N*-methylphthalimide affect the ATR-IR spectra. There is a complete absence of both 1663 and 1539 cm^{-1}.

From the above ATR-IR spectra analysis, it is evident that a new peak at 1539 cm^{-1} emerges from our sintering conditions. This peak shows up along with the usual $-$C=C$-$ stretching (unsaturation) for *cis*-polyisoprene. As the temperature of sintering is increased, the intensity of the 1539 cm^{-1} is enhanced. This can be further confirmed if the 1539 cm^{-1} peak is normalized by the 1447 cm^{-1} peak (deformation peak of methylene ($-CH_2-$), which remains unaltered (Figure 8)). It appears that there are three different types of reactions that occur after incorporation of various additives in vulcanized natural rubber powder. Complete absence of the 1663 cm^{-1} peak (due to the double bond present in *cis*-polyisoprene*)* with the addition of maleic acid and maleic anhydride suggests the reaction of a dienophile at the conjugated double bonds, following a Diels–Alder reaction (Scheme 2).[24,25,29] There are two types of cycloaddition: a Diels–Alder reaction at the conjugated diene and cycloaddition at the thionyl species (Scheme 2). The improvement in mechanical properties is due to the reduction of the conjugated double-bond concentration. Dipolarophiles might have reacted with the Zn complex such that the detrimental effect of reversion has been suppressed by the acidic nature of the benzoic and salicylic acids. The presence of both 1663 and 1539 cm^{-1} peaks in the case of benzoic acid and salicylic acid indicates that neither the Diels–Alder reaction nor the reaction at the conjugated double bond occurs. Complete absence of peak at 1539 cm^{-1} in the case of phthalimide and *N*-methylphthalimide (Figures 10) indicates that these dipolarophiles (Scheme 3)[34] either inhibit the formation of the conjugated double bond or react completely, if it is formed during sintering.

According to reported literature,[24,27,28] when cross-linked *cis*-polyisoprene is heated, it undergoes a breakdown of cross-linking as in Scheme 1. There is no doubt that desulfurization of vulcanized natural rubber powder occurs at the sintering condition, resulting in

Scheme 3. Reversion Reaction in the Presence of Zn(II) Complex



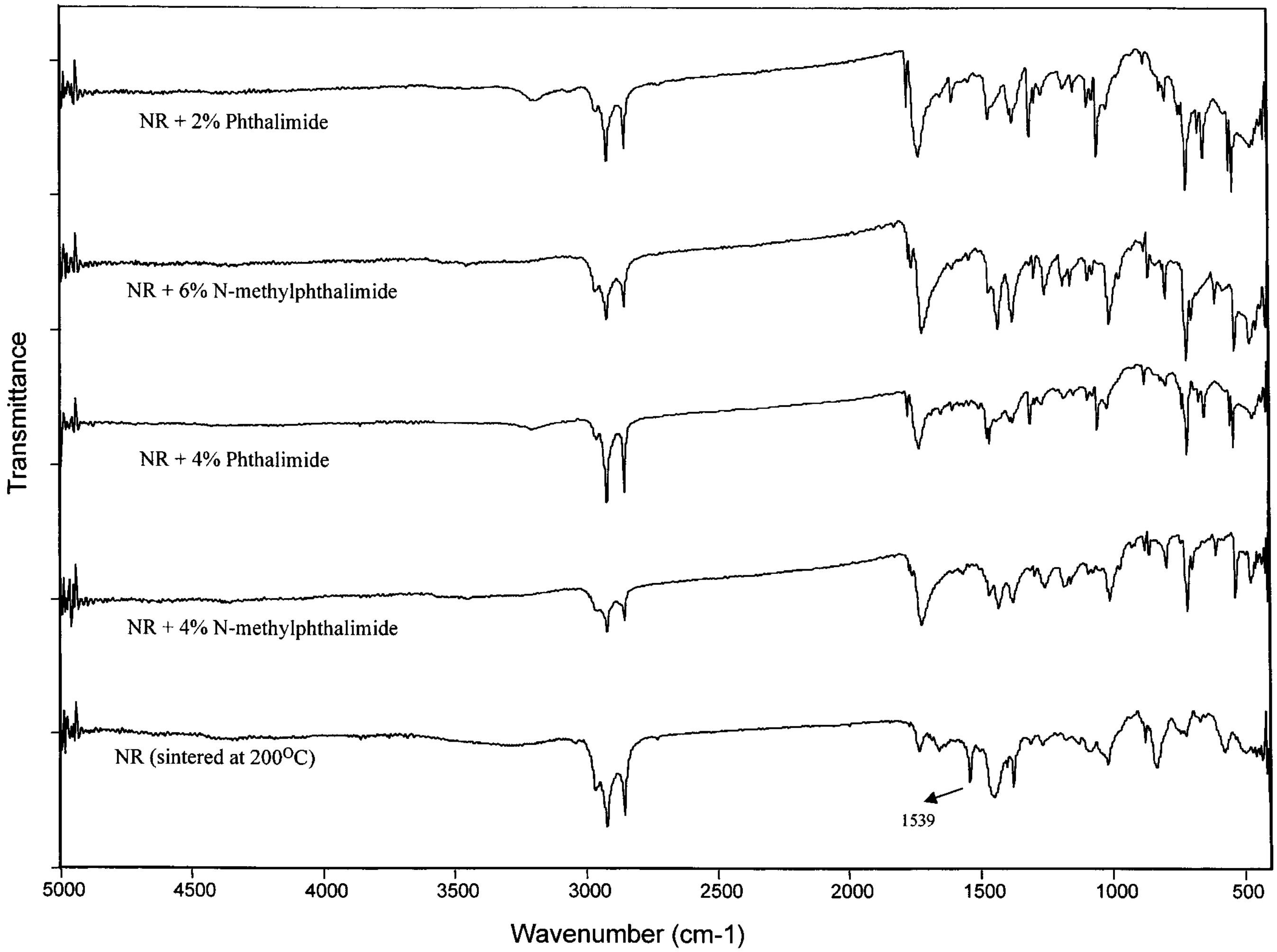


Figure 10. ATR-IR of sintered natural rubber with the addition of imides.

products (**VI**), conjugated alkene (**V**), alkylthianyl radical, the terminal double bond by the main chain breakdown, as well as products (**I**) and (**III**). Elastomers like natural rubber have an inclination to undergo reversion[24] even at temperatures of curing (around 160 °C). The presence of zinc complexes, remaining in the form of bis(mercaptobenzthiazole)zinc(II) and bis(dimethyldithiocarbamato)zinc(II), further promotes reversion.[25,35] During reversion, sulfur cross-links degrade at the molecular level, and at the macro-physical level this results in a reduction of elasticity and strength. Bateman et al.[25] proposed Zn(II)-mediated desulfuration, involving an adduct formation of a di- or polysulfide cross-link and complex (Scheme 3). Although ATR-IR data do not confirm all of these products, terminal double bonds, main chain breakdown, and inferior mechanical properties (from Table 2) have been confirmed. Effort[36] has been made to deactivate these Zn complexes by suitable complexing agents, mainly nitrogen-containing ligands. Therefore, phthalimide and *N*-methylphthalimide (having strong affinity to Zn(II) coordination) may reduce reversion reactions. It seems that nitrogen-containing ligands or even benzoic acid, phthalic acid, and salicylic acid (potential ligands, too) make complexes with Zn(II), such that the detrimental effect of sulfide degradation is minimized. As C−S bond degradation is difficult, on cooling, relinking may be a possible option through S−S type interchange reactions (Scheme 1, path c).

EIMS. EIMS analysis of the sintered samples has been undertaken (400−500 °C) at temperatures where the cross-linked structure or polymer backbone can be cleaved. At lower temperatures (50−400 °C) mass peaks correspond to low molecular weight volatile compounds used to vulcanize the rubber (i.e., MBT [$(m/z) = 135$], ZnO [$(m/z) = 81$], alkyl fragment [$(m/z) = 69$], stearic acid [$(m/z) = 129, 284$], etc.) and in all cases have been observed (not shown). At the higher temperatures (400−500 °C, Figure 11) major peaks[37] correspond to primarily the series of oligomers of the polyisoprene unit [$(m/z) = 68$n] and a series of oligomers with sulfur [$(m/z) = 68n + 32$] in vulcanized natural rubber. Figure 12 shows peaks corresponding to [$(m/z) = 68n$, $n = 1, 4{-}14$], due to oligomers of the polyisoprene unit and $(m/z) = 68n + 32$ in the sintered materials. This result is very interesting since monosulfide linkages are stable even at high temperature in the sintered rubber. There is also evidence of a series of both di- and polysulfides links [$(m/z) = 68n + 32m$] {396; $n = 3$, $m = 6$, 882; $n = 12$ $m = 2$, 1012; $n = 13$ $m = 4$, 1078; $n = 14$ $m = 4$, etc., not shown}. On the basis of these mass spectra peaks, one can conclude that there is chain scission at (a), (b), and (c), as shown in Scheme 1. With the addition of maleic anhydride in the vulcanized natural rubber powder, the EIMS (Figure 13) is completely different from the sintered sheet without any additives (Figure 12). The high-temperature range (400−500 °C) provides some interesting peaks: high-intensity peaks corresponding

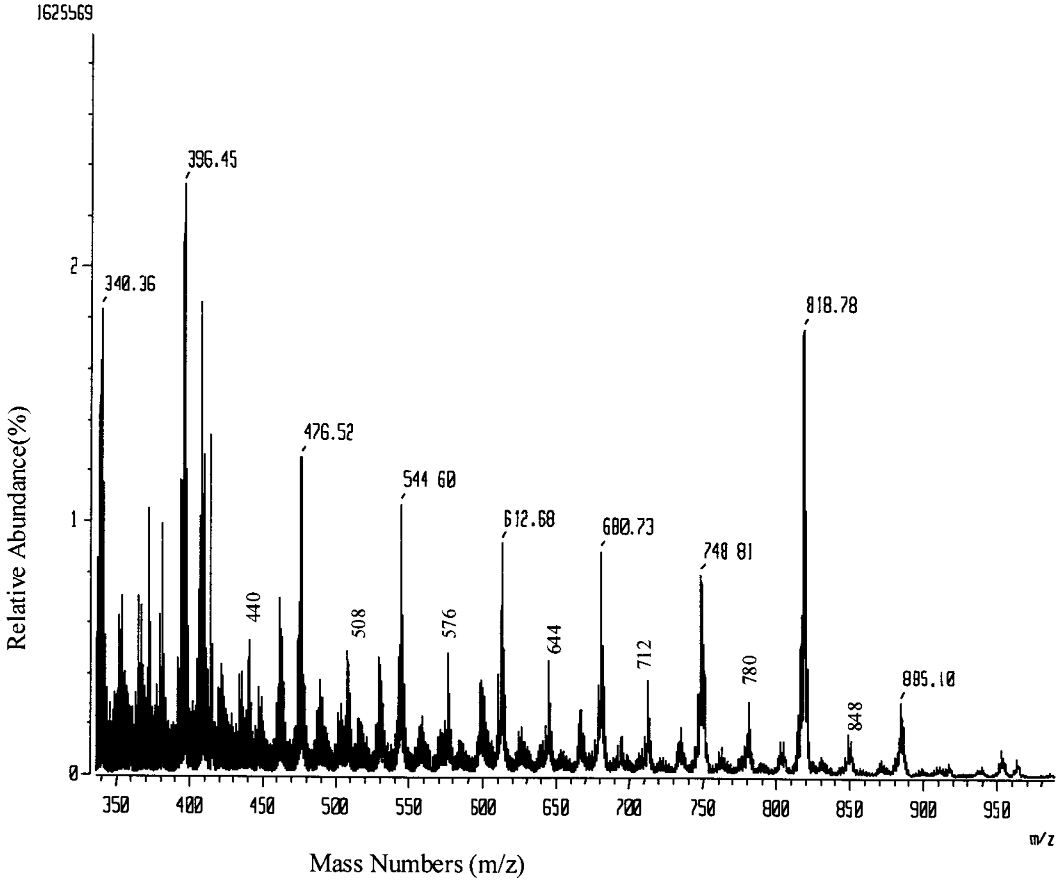


Figure 11. EIMS of sulfur vulcanized natural rubber at 400−500 °C.

to (m/z) at $66n$ (conjugated diene, Scheme 1, path b) are shown. The EIMS of maleic anhydride (from 50 to 500 °C temperature, Figure 13 at 400−500 °C) provides a series of peaks that match (m/z) = $66n + 54$ [(m/z) = 318; 66*4 + 54, 384; 66*5 + 54, 450; 66*6 + 54, 514; 66*6 + 54 + 2*32, 580; 66*7 + 54 + 2*32, 646; 514 + 66, 712; 646 + 66, and (m/z) = 778; 712 + 67, 845; 778 + 67, 912; 845 + 67, 979; 912 + 67, etc. (Scheme 1, path a)] or few peaks at (m/z) = $68n \pm 2 + 98$ (maleic anhydride). Maleic anhydride undergoes a reaction to transform into cyclopropanone (m/z) = [45(cyclonpropanone) + 44(CO_2)].[38,39] Both maleic anhydride and cyclopropanone can undergo a Diels−Alder reaction as shown in Scheme 2. This reaction seems to slow the reversion of natural rubber, and therefore the mechanical properties of treated rubbers are higher than ones not treated. Chain breaking as shown in Scheme 1 is also confirmed, through the addition reaction of maleic anhydride to the rubber backbone.

With the addition of phthalimide into vulcanized natural rubber, the spectrogram pattern has been changed (Figure 14) in comparison to the maleic anhydride treated materials. The EIMS of the phthalimide sample shows almost 99% in relative abundance of (m/z) = 147, along with (m/z) = 104 (M − −NHCO) and (m/z) = 76, corresponding to the breakdown product, benzyne. The low-temperature (below 400 °C) EIMS of the phthalimide treated natural rubber sample shows the expected low molecular weight volatiles like stearic acid (m/z) = 57, 284; phthalimide, (m/z) = 147, and so on, as mentioned above. The high-temperature mass spectra shown in Figure 14 has the characteristic (m/z) of $68n$, $68n + 1$, and probably few peaks related to $68n + 103$ (fragmented phthalimide) or 147 (phthalimide).[40] This is in contrast to the maleic anhydride case because it appears that phthalimide does not react with the rubber backbone. Nonetheless, large improvements in the mechanical properties are achieved. It is believed that the phthalimide reacts with Zn complexes, thus slowing down the zinc-mediated reversion (Scheme 3) of natural rubber, which is primarily responsible for the chain breakdown and formation of conjugated dienes (Scheme 1).

From the EIMS analysis, it is evident that there is a certain change after sintering. There are the expected peaks corresponding to isoprene oligomers (m/z) = $68n \pm 2$ and oligomers with sulfur for the vulcanized cases (m/z) = $68n + 32$ in the vulcanized natural rubber (Figure 11) and the sintered rubber (Figure 12). However, addition of maleic anhydride to the vulcanized ground rubber leads to the addition of the maleic anhydride to the conjugated diene with and without sulfur cross-links (Figure 13). This addition of maleic anhydride slows the reversion of natural rubber, allowing for an improvement in mechanical properties. The situation is somehow different in the phthalimide-treated sample. Phthalimde shows an improvement in mechanical properties without bonding to the rubber backbone, and it is believed that it reacts with Zn complexes to stop/slow reversion.

The absence of the 1539 cm^{-1} peak in ATR-IR (Figures 9 and 10) and (m/z) corresponding to $68n \pm 2$ in the EIMS of the phthalimide added sample (Figure 14) clearly indicates that there is no conjugated double bond formation in phthalimide-treated vulcanized natural rubber sintered sheets. On the other hand, maleic anhydride reacts at the double bond through a Diels−Alder reaction as shown in Scheme 2. This correlates

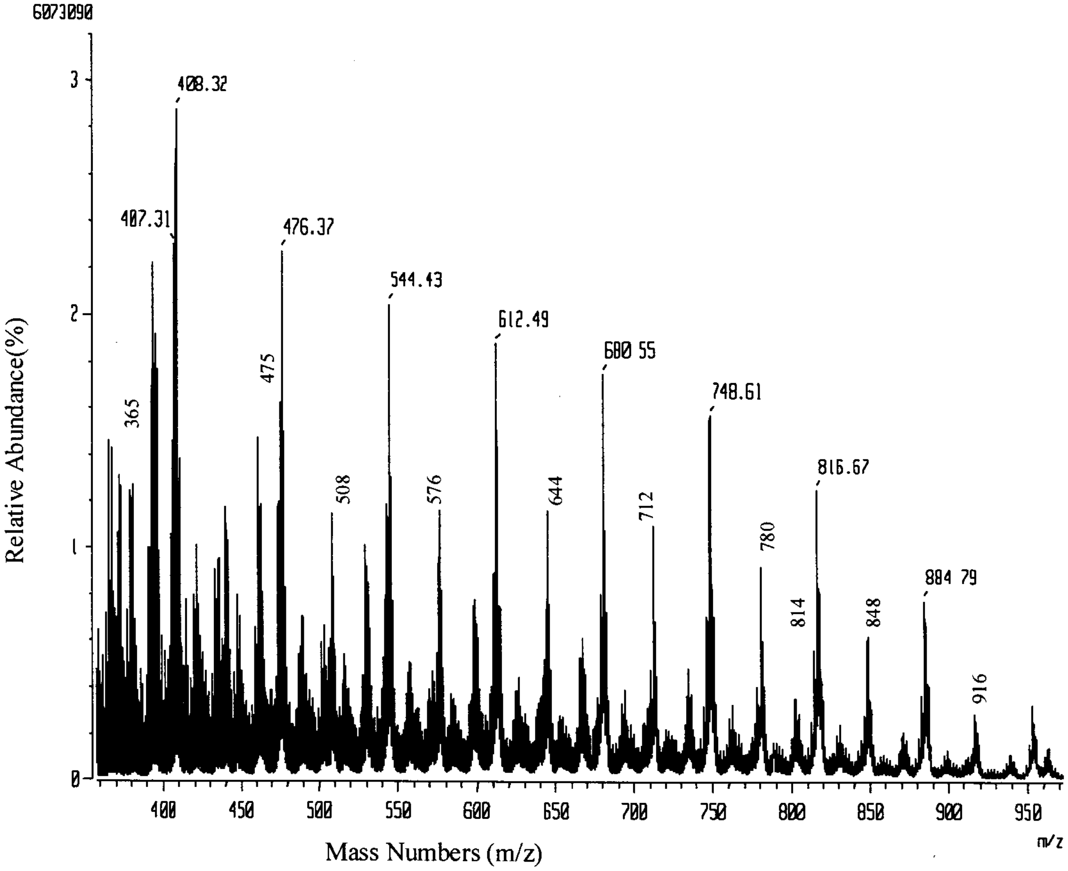


Figure 12. EIMS of sintered natural rubber at 400−500 °C.

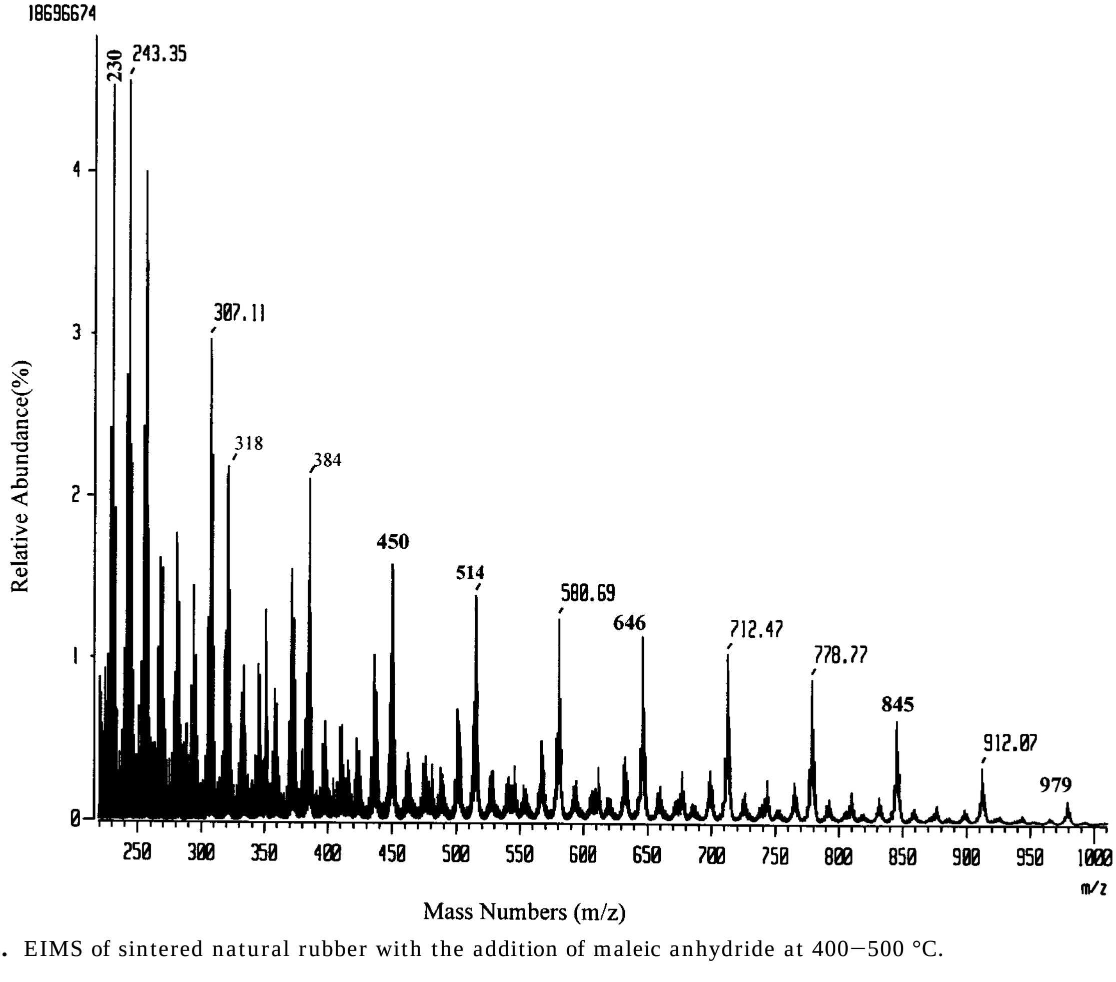


Figure 13. EIMS of sintered natural rubber with the addition of maleic anhydride at 400−500 °C.

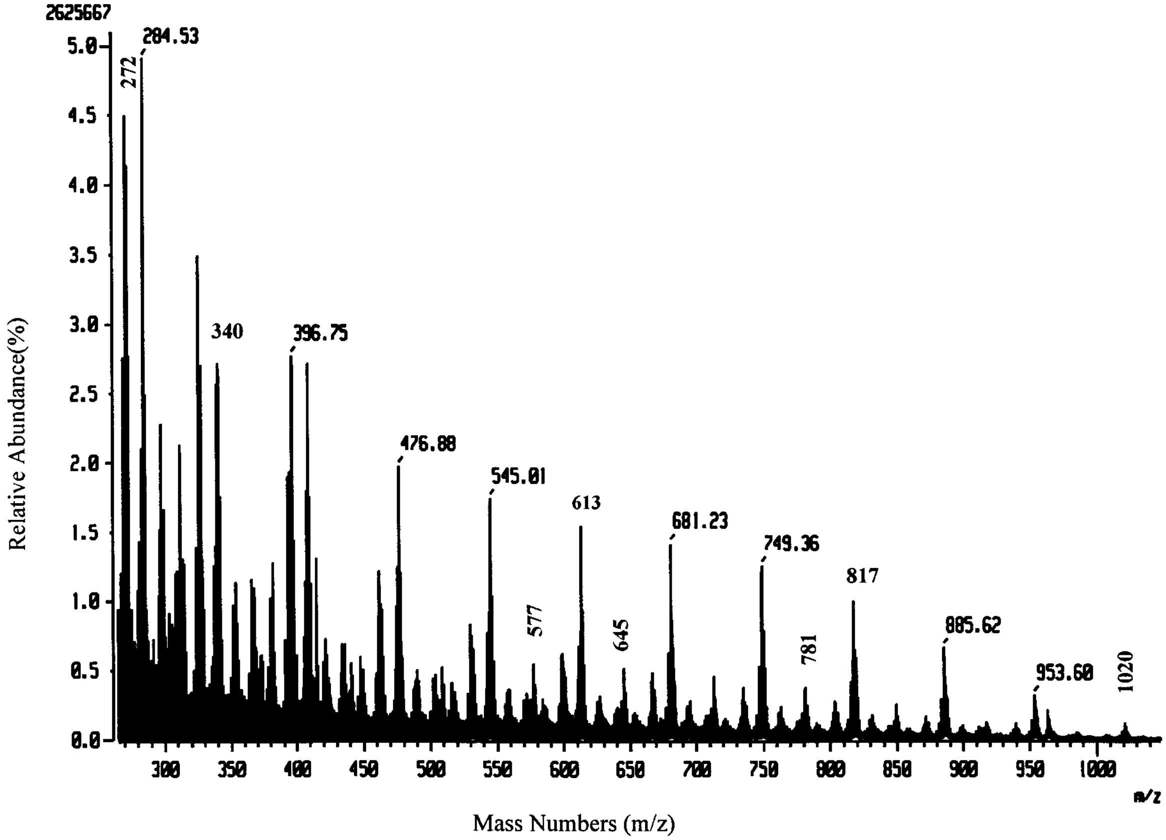


Figure 14. EIMS of sintered natural rubber with the addition of phthalimide at 400−500 °C.

to both a reduction of the double bond peak intensity shown by ATR-IR (Figure 9) and the diene fraction observed via EIMS (Figure 13). Maleic anhydride scavenges the double bond, formed due to cross-link breakdown, and results in an increase in the physical properties. Phthalimide or *N*-methylphthalimide inhibits the zinc-mediated reversion or diene formation. Moreover, it retards in the oxidation at the double bond, if any, at high temperature, thereby increasing in the mechanical properties in the phthalimide-treated samples. Work with a model compound may highlight the details of the reaction of phthalimide with natural rubber in the "high-pressure high-temperature sintering" (HPHTS) process and is currently under way.

Conclusions

Recycling of vulcanized natural rubber (sulfur vulcanized) through the "high-pressure high-temperature sintering" process is possible. The mechanical properties of sintered materials can be improved by incorporating small amounts of dienophiles or dipolar organic additives. With incorporation of phthalimide it was possible to recover 75% of the original vulcanized rubber properties. By controlling the acidity of the additive, it is possible to control the amount of improvement. The mechanism behind the improvement of mechanical properties in vulcanized natural rubber in the sintering process shows that reversion is the key factor in deciding the properties. Reversion has also been shown to be accelerated by the presence of Zn−accelerator complexes. From ATR-IR, we now understand that the additives either react directly with the zinc complex or to the rubber backbone to slow the reversion reaction and the formation of conjugated dienes. The EIMS also confirmed the idea of a Diels−Alder or addition type reaction of additives with either the diene or conjugated diene. Finally, it seems that vulcanized natural rubber is recyclable, and the mechanical properties can be improved with a proper choice of recycling ingredients.

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