Continuous Ultrasonic Devulcanization of Unfilled NR Vulcanizates

M. TAPALE, A. I. ISAYEV

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

Received 2 February 1998; accepted 31 March 1998

ABSTRACT: Sulfur-cured unfilled natural rubber (NR) is successfully devulcanized in a continuous extrusion process under the application of high-power ultrasonic energy. The die characteristics and ultrasonic power consumption are measured. A unique correlation is found between the crosslink density and gel fraction of the devulcanized NR. This correlation is independent of the processing parameters, such as barrel temperature, die gap, flow rate, and amplitude of ultrasound. However, these parameters do influence the degree of devulcanization. In most cases, the degree of devulcanization is found to pass through a maximum at an intermediate level of ultrasonic energy. It is hypothesized that simultaneous breakup and reformation of crosslinks occur during the devulcanization of NR, with the relative contribution of each being determined by the process parameters. The cure curves and mechanical properties of the revulcanized NR are studied. The mechanical properties are found to depend on the revulcanization recipe. On optimizing it, tensile strength as high as 14.2 MPa is achieved, which is about 70% of that of the virgin NR vulcanizate. Ultimate elongation as high as 670% is obtained, which is the same as that of the virgin NR vulcanizate. Such stress-strain behavior is an indication that the devulcanized NR maintains the strain-induced crystallization characteristics inherent to the virgin NR vulcanizates. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2007–2019, 1998

Key words: natural rubber; recycling; reclaim rubber; devulcanization; revulcanization; ultrasound; crosslink density; gel fraction; mechanical properties; optimization

INTRODUCTION

Natural rubber (NR) is one of the most widely used elastomers. It supplies about one-third of the world demand for elastomers and is the standard by which the performance of other synthetic rubbers is judged.¹ Along with styrene–butadiene rubber (SBR), NR forms a major component of tire rubber.

The rubber industry faces a major challenge in this decade to find a satisfactory way to deal with the enormous quantity of rubber goods, particularly tires which reach the end of useful life each year and their concomitant stockpiles, all of which pose a major ecological threat to this planet. It is estimated that 240 million used tires are discarded each year in the USA alone. These are added to the already existing stockpiles, which are believed to exceed 2.5 billion scrap tires.²

Recycling of vulcanized elastomers has always intrigued the industry and the scientific community. In order to carry out successful recycling of vulcanized rubber, it is necessary to preferentially break the crosslinks in the three-dimensional network. The practical inability in achieving it was a major deficiency of the existing recycling methods.^{2,3}

Correspondence to: A. I. Isayev.

Contract grant sponsors: National Science Foundation (NSF) and Ohio Environmental Protection (EPA); contract grant number: DMI 9312249 (NSF)

Journal of Applied Polymer Science, Vol. 70, 2007-2019 (1998)

^{© 1998} John Wiley & Sons, Inc. CCC 0021-8995/98/102007-13

Recipe	NR (parts) (SMR CV 60)	Sulfur (phr)	Accelerator CBS (phr)	ZnO (phr)	Stearic Acid (phr)
Recipe 1	100 (virgin)	2	1	5	1
Recipe 2	100 (devulcanized)	2	1	5	1
Recipe 3	100 (virgin)	4	2	10	2
Recipe 4	100 (devulcanized)	2	0	2.5	0.5
Recipe 5	100 (virgin)	4	1	7.5	1.5

Table I Recipes of NR Model Compounds

Recently, Isayev and coworkers^{4,5} have shown that ultrasonic waves of certain levels can, in the presence of heat and pressure, rapidly breakdown the three-dimensional network in vulcanized rubbers. This devulcanized rubber is soft and can be reprocessed very much like the virgin rubber. The process of ultrasonic devulcanization is very fast and occurs on the order of a second or less and leads to the breakage of mono-, di-, and polysulphidic crosslinks, along with carbon—carbon bonds of the main chain. They have successfully carried out devulcanization of ground rubber tire (GRT) and unfilled SBR vulcanizates in a continuous process using an extruder coupled with an ultrasonic horn.

The present article describes the continuous ultrasonic devulcanization of unfilled NR vulcanizates. This study can thus complement our previous studies on SBR and enhance our understanding of the ultrasonic devulcanization of GRT. In addition, the similarities and differences between the devulcanization of SBR vulcanizates studied earlier and NR vulcanizates will be discussed.

MATERIALS AND METHODS OF INVESTIGATION

The NR used in the devulcanization experiments is SMR CV60 obtained from Akrochem Corp., Akron, Ohio, and is used for preparing the model compound according to recipe 1, given in Table I. All the other compounding ingredients were also obtained from Akrochem Corp. This recipe was compounded on a laboratory two-roll mill for up to 40 passes, after which it was vulcanized at 160°C for 15 min in a compression molding press into slabs of dimensions $260 \times 260 \times 12 \text{ mm}^3$. The vulcanizates were then ground to a particle size of around 0.5 mm in a Nelmor grinding machine. These particles were charged into the ultrasonic devulcanization reactor (National Feedscrew and Machining, Inc.) described in Tukachinsky et al.⁵ under different combinations of barrel temperatures, die gaps, and flow rates in search of an optimum devulcanization condition. Three sets of barrel temperatures, namely, 60, 120, and 180°C, were employed. The gaps between the flat face of the ultrasonic horn and the die were 1.52, 2.03, and 2.54 mm. The rubber flow rates through the extruder were 0.32, 0.63, 1.26, and 2.52 g/s. The rubber exiting the die was devulcanized by the ultrasonic horn at a frequency of 20 kHz and amplitudes of 5, 7.5, and 10 μ m. The ultrasound power consumption and die entrance pressure were measured at all conditions of devulcanization.

The devulcanized rubber exiting the die was water-quenched. It was then air-dried in an oven at 55°C for 24 h, followed by compounding with curatives on the two-roll mill and then revulcanized. Revulcanization was carried out in the compression-molding press at 160°C up to the optimum curing time (t_{90}) in a mold of internal dimensions $230 \times 114 \times 2 \text{ mm}^3$. As detailed further, different revulcanization recipes (Table I) were used in order to enhance the mechanical properties of the devulcanized samples on revulcanization.

A Monsanto oscillating disc rheometer (ASTM D-2084) was used to obtain the torque time curves for the virgin and devulcanized rubber. The test temperature was 160°C. Gel fraction for the virgin vulcanized, devulcanized, and then revulcanized compounds was measured by a soxhlet extraction apparatus using benzene as a solvent. Crosslink densities were calculated from the Flory–Rehner equation.⁶ The interaction parameter for the NR–benzene system has a value of χ equal to 0.42.⁷

A Monsanto T-1000 tensile-testing machine was used to measure the stress-strain characteristics of vulcanizates of the virgin and devulcanized samples. Dumbbell-shaped specimens of the ASTM D-412, type C, were punched out from



Figure 1 Die pressure as a function of ultrasound amplitude during the devulcanization of NR recipe 1 at various flow rates and at a barrel temperature of 120°C and a die gap of 2.54 mm (a), various die gaps and at a barrel temperature of 120°C and a flow rate of 0.63 g/s (b), and various barrel temperatures and at a die gap of 2.54 mm and a flow rate of 0.63 g/s (c).

the compression-molded sheets and tested at room temperature at an extension rate of 500 mm/min.

RESULTS AND DISCUSSIONS

Ultrasonic Devulcanization of Vulcanized NR

In Figure 1(a)-(c), the die entrance pressure is plotted as a function of ultrasound amplitude for

different flow rates, die gaps, and barrel temperatures, respectively. It is observed that the die pressure decreases substantially with the application of ultrasound and that with increasing amplitude the pressure decreases further. This has been previously explained to be due to the combined effect of softening of rubber due to devulcanization in the die gap and reduction in friction between the particles and the die walls due to ultrasonic vibrations.⁵ As can be seen from Figures 1(a) and (b), the pressure increases with increasing flow rate and decreasing die gap. This is because the die pressure is an inverse function of the average residence time of the rubber in the treatment zone. This average residence time is inversely proportional to the rubber flow rate and directly proportional to the die gap. It is observed from Figure 1(c) that increasing the barrel temperature results in an increased softening of the rubber and more devulcanization, resulting in reduction in the die pressure.

The measured ultrasound power consumption includes the useful power and the losses. It is not possible experimentally to measure the power consumed by devulcanization itself. Also, the power expended on heat dissipation in the material and the power transmitted by the wave traveling through the material cannot be separated. The only measurable loss is the initial power consumption of the acoustic system when the ultrasonic horn vibrates without loading. These losses are subtracted from the total power consumption to give useful power. Figures 2(a)-(c) show the useful ultrasound power consumption as a function of ultrasound amplitude for different die gaps, barrel temperatures, and flow rates, respectively. As shown in Figure 2(a), the useful ultrasound power consumption increases with decreasing die gap. In particular, a decrease in die gap increases the strain amplitude experienced by the rubber at a constant amplitude of ultrasonic waves, leading to the observed increase in the power consumption. Also, Figure 2(b) shows that the power consumption increases with increasing barrel temperature. Possibly, in the rubber treated at 180°C, for the intermolecular bonds in the network, being more receptive to ultrasonic energy by virtue of requiring less energy to overcome the activation energy, less power is expended in heat dissipation, and, therefore, more useful energy is channeled towards devulcanization.

On increasing amplitude from 5 to 10 μ m, it is observed that the useful power shows a maximum



Figure 2 Ultrasound power as a function of amplitude during the devulcanization of NR recipe 1 at various die gaps and at a barrel temperature of 120°C and a flow rate of 0.63 g/s (a), at various barrel temperatures and a die gap of 2.54 mm and a flow rate of 0.63 g/s (b), and at various flow rates and a barrel temperature of 120°C and a die gap of 2.54 mm (c).

at 7.5 μ m. This was the case in all experiments with different die gaps [Fig. 2(a)] and barrel temperatures [Fig. 2(b)]. It is believed that imposition of ultrasonic waves leads to simultaneous bond breakage and reformation in the material. It is only the relative magnitude of each process that determines the ultimate state of the material. This is controlled by the process parameters. In this case, while devulcanization is dominant in between 5 and 7.5 μ m, some revulcanization occurs with increasing intensity when the ultrasound amplitude is increased from 7.5 to 10 μ m, which accounts for the reduction in power consumption after 7.5 μ m.

Limiting conditions of this competition between devulcanization and revulcanization can be observed by varying the flow rate through the reactor, as is shown in Figure 2(c). At the highest flow rate of 2.52 g/s, no revulcanization occurs, as is seen by the monotonous increase in the power with amplitude in this figure. However, as the flow rate is decreased and, consequently, the residence time is increased, the revulcanization process becomes more dominant with increasing amplitude at any particular flow rate. The power consumption drops from 1428 W at 2.52 g/s and 10 μ m to 465 W at 0.32 g/s and 10 μ m. This is also evident from the behavior of pressure with changing flow rates, as was shown in Figure 1(a). The pressure decreases from 4.38 MPa at 7.5 μ m to 4.02 MPa at 10 μ m for 0.32 g/s rubber flow rate. For 2.52 g/s, which is the highest flow rate, this pressure decreases from 10.58 MPa at 7.5 μ m to 8.14 MPa at 10 μ m. Thus, the pressure differential in between 7.5 and 10 μ m for 0.32 g/s is about 15% of that for 2.52 g/s. This suggests that revulcanization at high amplitude apparently does initiate an increase in die pressure. However, at lower flow rates and a higher amplitude, it is offset by the decreased friction due to ultrasonic vibrations in the die. This behavior is unique to NR and was not observed in the case of SBR. Further studies on the influence of physical and/or chemical structure of NR on its transformation during devulcanization are essential to understand this behavior.

Figures 3 to 6 depict the crosslink density and gel fraction as functions of the ultrasound amplitude for devulcanized and revulcanized samples obtained at different barrel temperatures and rubber flow rates. The filled symbols represent devulcanized samples, and the open symbols represent them after revulcanization using recipe 4. Both the crosslink density and gel fraction decrease substantially during ultrasound treatment. It was observed that their values decrease with increasing barrel temperature (Figs. 3 and 4), decreasing die gap (not shown), and decreasing flow rate (Figs. 5 and 6) at any amplitude of ultrasound. Due to predominant effect of revulcanization from 7.5 to 10 μ m, the crosslink density and gel fraction increase when the amplitude is increased from 7.5 to 10 μ m at any particular barrel temperature (Figs. 3 and 4) or die gap. As can be seen from Figures 5 and 6, respectively, the crosslink density and gel fraction for 2.52 g/s



Figure 3 Crosslink density of devulcanized NR recipe 1 (filled symbols) and revulcanized NR recipe 4 (open symbols) as a function of ultrasound amplitude at various barrel temperatures and at a die gap of 2.54 mm and a flow rate of 0.63 g/s.

at 10 μ m are lower, however, than that at 7.5 μ m, implying that no revulcanization occurs with an increasing amplitude at this flow rate. But on



Figure 5 Crosslink density of devulcanized NR recipe 1 (filled symbols) and revulcanized NR recipe 4 (open symbols) as a function of ultrasound amplitude at various flow rates and at a barrel temperature of 120°C and a die gap of 2.54 mm.

decreasing the flow rate from 2.52 g/s to 0.32 g/s, which is the lowest flow rate, these values are higher at 10 μ m than at 7.5 μ m. This only sub-



100 95 90 Gel fraction, % 85 80 75 Flow rate, g/s 0.32 0 70 **___** 0.63 \wedge 1.26 ۸ 65 2.52 60 2 4 6 8 10 12 0 Amplitude, µm

Figure 4 Gel fraction of devulcanized NR recipe 1 (filled symbols) and revulcanized NR recipe 4 (open symbols) as a function of ultrasound amplitude at various barrel temperatures and at a die gap of 2.54 mm and a flow rate of 0.63 g/s.

Figure 6 Gel fraction of devulcanized NR recipe 1 (filled symbols) and revulcanized NR recipe 4 (open symbols) as a function of ultrasound amplitude at various flow rates and at a barrel temperature of 120°C and a die gap of 2.54 mm.



Figure 7 Normalized gel fraction as a function of normalized crosslink density for devulcanized NR of recipe 1.

stantiates our earlier hypothesis that revulcanization occurs with increasing amplitude in between 7.5 and 10 μ m when the flow rate is decreased from 2.52 to 0.32 g/s.

As has been described before,^{5,8} the crosslink density and gel fraction for ultrasonically devulcanized rubber can be correlated by a universal master curve. This curve is unique for every elastomer due to its unique chemical structure. The same master curve for devulcanized NR is presented in Figure 7.

In previous investigations⁸ on SBR rubber, it was found that the $T_{\rm g}$ of devulcanized rubber depends on the parameters of ultrasound devulcanization; namely, the T_g of devulcanized rubber is higher than that of the virgin rubber. Thus, it is interesting to determine whether this is true in the case of devulcanization of NR. Our experiments indicate that the $T_{\mbox{\scriptsize g}}$ of the devulcanized NR compounds does not exhibit any sensitivity towards the amplitude of devulcanization. But the overall T_g of the devulcanized compound is about -64° C, while that of the virgin gum rubber is -68° C. This increase in the T_g of devulcanized NR is much smaller than that observed in devulcanized SBR. The difference in the chemical structure of these elastomers may be responsible for this difference. It was proposed in previous studies⁸ that this increase in T_g with devulcanization is due to transformation of polysulphidic crosslinks to cyclic sulphidic structures, which

reduce the main chain mobility.⁹ The insensitivity of T_g of devulcanized NR to ultrasonic amplitude explains why the T_g of devulcanized GRT containing NR was found to be close to that of untreated GRT and independent of parameters of devulcanization.⁵

Revulcanization of Ultrasonically Devulcanized NR

The devulcanized NR samples are compounded using recipe 2, that is, with the same amount of curatives as in the original virgin recipe 1 and then revulcanized at the same temperature (160°C) to an optimum cure. Figure 8 presents the crosslink density of NR samples devulcanized at different barrel temperatures as a function of amplitude, as represented by the filled symbols. The open symbols represent their corresponding crosslink densities on revulcanization with recipe 2. In order to investigate the mechanism of revulcanization, the virgin rubber is compounded with recipe 3, that is, with twice the initial amount of curatives as in recipe 1. As is seen in Figure 8, on the crosslink density axis, the crosslink density of recipe 3 (open symbol) is 0.28 kmol/m³, while that of the original recipe 1 (filled symbol) is 0.157 kmol/m³. The difference in the crosslink densities of these 2 recipes is 0.123 kmol/m³. This difference is then added to the crosslink densities of the



Figure 8 Crosslink density of devulcanized NR recipe 1 (filled symbols) and revulcanized NR recipe 2 (open symbols) as a function of ultrasound amplitude at various barrel temperatures and at a die gap of 2.54 mm and a flow rate of 0.63 g/s.



Figure 9 Cure curves for NR recipe 1 ultrasonically devulcanized at different barrel temperatures and amplitudes: a die gap of 2.54 mm and a flow rate of 0.63 g/s and revulcanized with recipe 2 (curves 2–9), cure curves for NR recipe 1 (curve 1), and NR recipe 3 (curve 10).

devulcanized NR samples to give theoretical values of their crosslink densities on revulcanization with recipe 2. It is observed that the actual measured values of the crosslink densities of the revulcanized rubber using recipe 2, as are shown in Figure 8, are higher than their theoretical values, with the percentage of increase over the theoretical values being highest, that is, 33% for the sample devulcanized at 180°C and 5 μ m, and the lowest being 13% for the same temperature and 10 μ m. Since the curative level is the same in all compounds, the devulcanized samples having higher crosslink density have a correspondingly higher crosslink density on revulcanization.

The cure curves for the recipe 2 at 160°C are shown in Figure 9. They are plots of the behavior of the torque as curing proceeds in time. These torque time curves for recipe 2 are completely different from that for the virgin compound, as is seen in Figure 9. The curves for all the revulcanized samples with recipe 2 exhibit similar kinetics of cure. The scorch time is of the order of 1 min or is almost absent, while the time for a 90% cure is about 3 min. As compared to this, the scorch time for recipe 1 is 8 min, and the time for a 90% cure is 10 min. The shortness or complete absence of the induction period indicates that crosslinking reactions may start immediately upon heating.¹⁰ Indeed, faster revulcanization is characteristic of reclaimed rubber.^{11,12} Also, the higher the degree of devulcanization, the lower the minimum torque, as well as the final or maximum torque on the revulcanization curve. It is interesting to note that the maximum torque for the revulcanized compounds is always higher than that for the virgin compound (recipe 1). This is only expected as the crosslink densities of the revulcanized samples (Fig. 8) are also correspondingly higher than that for the virgin recipe 1. This is again reflected in the measurements of modulus at 100% strain for the revulcanized NR samples (recipe 2), which were found to be higher than that for the virgin vulcanizate (recipe 1). This may be because the additional sulphenamide accelerator (CBS) incorporated during revulcanization increases the degree of vulcanization and also reduces the curing time. If the devulcanized samples contained a disproportionate amount of cyclic sulphidic links, the revulcanization temperature is sufficient for these to reform intermolecular crosslinks. This is in addition to those being formed due to the additional sulfur-accelerator system, which may explain the abnormally high crosslink density.

Because of its stereoregular structure, NR is capable of crystallizing when stretched, therefore yielding very high tensile strengths and ultimate elongations. Hence, as measured in the present study, the virgin vulcanizate (recipe 1) has a tensile strength of 20.12 MPa and an ultimate elongation of 680%. Compared to these high values, typical values obtained for the tensile strengths of recipe 2 were in between 2.76 and 1.42 MPa. In contrast, the tensile strength of recipe 3 is only 4.25 MPa. It is believed that the additional amount of CBS accelerator incorporated in recipe 2 leads to a very high concentration of mono- and disulphidic crosslinks. This is in addition to the residual mono-, di-, and polysulphidic crosslinks already present in the devulcanized rubber. These mono- and disulphidic bonds prevent the stretching and/or slipping of the rubber main chains when subject to tension and therefore inhibit strain-induced crystallization. As a result, a breaking point is attained before the extension is sufficiently high for crystallization to develop.^{13,14}

The modulus at 100% strain is found to be a linear function of crosslink density.¹⁵ It is also true that increased crosslink density decreases ultimate elongation of the vulcanizate, thereby decreasing the degree of crystallinity obtainable by stretching.¹⁶ Here, the highest ultimate elongation for devulcanized NR samples revulcanized



Figure 10 Cure curves for NR recipe 1 ultrasonically devulcanized at a barrel temperature of 120°C, a die gap of 2.54 mm, a flow rate of 0.63 g/s, an amplitude of 5 μ m, and compounded with 2.5 phr ZnO, 0.5 phr stearic acid, and different amounts of sulfur and accelerator (CBS).

using recipe 2 is 288%, which is about 40% of that of recipe 1. A quantitative assessment of the effect of devulcanization conditions on mechanical properties shows that the tensile strength and the ultimate elongation of samples, which were devulcanized at a 120°C barrel temperature, are higher than of those devulcanized at 180 and 60°C. This allows one to infer that rubber treated at 180°C may be considered as overtreated, while that treated at 60°C as undertreated.

Hence, 120°C is chosen as the optimum temperature for devulcanization, and the sample devulcanized at this temperature and 5 μ m amplitude is chosen for its best properties amongst the lot for optimizing the revulcanization recipe in an attempt to improve the mechanical properties.

Optimization of the Revulcanization Recipe

In order to improve the mechanical properties of the devulcanized NR samples revulcanized with recipe 2, an attempt is made to optimize the revulcanization recipe. The amount of sulfur in the revulcanization recipe is kept constant at 2 phr. The amount of accelerator (CBS) is varied from 0 to 1 phr in order to study its effect on the mechanical properties. Also, if a slower, constant rate of cure is desired, less accelerator is required for the reclaim compound. Such savings in accelerator cost represent one of the important commercial advantages of reclaim.¹² ZnO, which is an activator, gives little if any gain in activation function beyond 4 parts. Usually, 3 parts is adequate for most purposes.¹ There is a direct relation between the amount of activator and the fatty acid, which is believed to solubilize the zinc oxide, allowing diffusion into the elastomer.¹⁷ Hence, the amounts of ZnO and stearic acid in the revulcanization recipe were reduced to half of that initially added in recipe 1, that is, 2.5 phr of ZnO and 0.5 phr of stearic acid. This results in recipe 4 in Table I.

As is seen from the cure curves 1, 2, and 3 in Figure 10, reducing the amount of accelerator from 1 to 0 phr reduces the rate of vulcanization by half, as well as the degree of vulcanization. The crosslink density of the vulcanizates reduces from 0.20 to 0.14 kmol/m³. It is clearly evident from Figure 11 that the tensile strength shoots up to 14 from 3.5 MPa when the accelerator concentration is reduced from 1 to 0 phr. The same figure also shows that the ultimate elongation shoots up to 666% when no accelerator is added in the revulcanization recipe. This value is closer to that of the original virgin recipe 1. The modulus at 100%strain decreases, obviously due to the lower degree of vulcanization.

It was shown previously that ultrasonically devulcanized SBR contains about 85% of initially



Figure 11 Mechanical properties of NR recipe 1 devulcanized at a barrel temperature of 120°C, a die gap of 2.54 mm, a flow rate of 0.63 g/s, an amplitude of 5 μ m, and revulcanized with 2 phr sulphur, 2.5 phr ZnO, 0.5 phr stearic acid, and different amounts of accelerator (CBS).



Figure 12 Mechanical properties of NR recipe 1 devulcanized at a barrel temperature of 120°C, a die gap of 2.54 mm, a flow rate of 0.63 g/s, an amplitude of 5 μ m, and revulcanized with 2.5 phr ZnO, 0.5 phr stearic acid, and different amounts of sulfur.

added accelerator.¹⁰ Therefore, it seems possible that there preexists some amount of sulphenamide in the devulcanized sample which is sufficient to catalyze the added sulfur-activator system and give a satisfactory degree of cure, and an additional accelerator only succeeds in giving a very high crosslink density, which inhibits crystallization on stretching. Indeed, it was observed that this new compound exhibits the tensile strength of 14 MPa and an ultimate elongation of 666% due to strain-induced crystallization on stretching during the tensile tests. These results thus confirm that even after ultrasonic devulcanization, the regularity of structure in NR is preserved.

As can be seen from the cure curves 1, 4, and 5 in Figure 10, varying the amount of sulfur from 1 to 3 phr with no accelerator, but with 2.5 phr ZnO and 0.5 phr stearic acid in the revulcanization recipe, does not bring about any substantial change in the cure rate; only the degree of vulcanization increases with the amount of sulfur. Figure 12 shows the effect of varying the amount of sulfur from 1 to 3 phr on the mechanical properties of the revulcanized NR samples. The tensile strength and ultimate elongation show a maxima at 2 phr sulfur, while the modulus at 100% strain increases monotonously with the sulfur content. The increase in modulus is consistent with the increasing level of cure. The tensile strength and ultimate elongation are directly related to the degree of crystallinity of the stretched samples. It is suggested that the reason for initial increase in

the crystallizability is that the larger number of crosslinks causes greater alignment of the chains and thus suppresses flow.^{18,19} Beyond a certain degree of crosslinking, progressively larger portions of the chain will be incapable of taking part in crystallization.

Hence, recipe 4, 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 chosen as the optimized recipe because it has the best mechanical properties amongst all the other revulcanization recipes. It should be kept in mind, however, that this optimum recipe corresponds to only 1 chosen degree of devulcanization. Evidently, it can be optimized for different degrees of devulcanization.

Revulcanization with the Optimized Cure Recipe

The crosslink density and gel fraction of the NR samples revulcanized with recipe 4 are shown by the open symbols in Figures 3 to 6. On revulcanization with this new recipe 4, the crosslink density and the gel fraction follow the same qualitative trend as that observed during devulcanization at different barrel temperatures (Figs. 3 and 4), die gaps (not shown), and flow rates (Figs. 5 and 6), and which were discussed earlier. The samples, which presumably underwent some revulcanization in between 7.5 and 10 μ m during the devulcanization process, show higher crosslink density and gel fraction on revulcanization. In fact, the higher the degree of devulcanization, the lower the crosslink density and gel fraction of the devulcanized, as well as the revulcanized, compounds.

On the basis of mechanical properties, as well as the crosslink densities, it can be inferred that the devulcanized rubber having a crosslink density below 0.016 kmol/m³ and a gel fraction below 60.5% is overtreated, while that having a crosslink density above 0.057 kmol/m³ and a gel fraction above 92% is undertreated. Overtreatment probably results in significant backbone chain degradation, hence, the lower crosslink density and gel fraction. Undertreatment indicates insufficient exposure to ultrasound; as a result, it cannot be compounded on a two-roll mill.

In order to understand the mechanism of revulcanization, the virgin rubber is compounded with recipe 5. This recipe consists of the original amount of curatives, as in recipe 1, plus those required for revulcanization, as in recipe 4. The crosslink density of recipe 5 is represented by the



Figure 13 Cure curves for NR recipe 1 ultrasonically devulcanized at different barrel temperatures and amplitudes, a die gap of 2.54 mm, a flow rate of 0.63 g/s, and revulcanized with recipe 4 (curves 2–9) and cure curves for NR recipe 1 (curve 1) and NR recipe 5 (curve 10).

open symbol on the Y-axis of Figures 3 and 5 and its value is 0.24 kmol/m³. The difference in between the crosslink densities of recipes 1 and 5 is 0.083 kmol/m³. This difference is then added to the crosslink densities of all the NR samples devulcanized under different combinations of devulcanization conditions, as detailed before and represented in Figures 3 and 5 by filled symbols. This yields the theoretical values of their crosslink densities on revulcanization with recipe 4 (not shown). It is observed that the experimental values match reasonably with the calculated ones, except when the samples are overtreated; the revulcanized crosslink densities are lower than the calculated values. In the case of those samples treated at flow rates of 1.26 and 2.52 g/s, the actual values of crosslink density and gel fraction, as shown in Figures 5 and 6, respectively, are higher than their theoretical values, in particular, those for the crosslink density being, on an average, 19% higher. It may be of interest to note that the crosslink density and the gel fraction of recipe 4 never exceed the values for the original virgin recipe 1, except in the case of the rubber treated at 1.26 and 2.52 g/s.

Figure 13 is a plot of the cure curves for NR samples revulcanized with recipe 4 at 160°C after being treated with ultrasonics at different barrel temperatures as well as those for recipe 1 and recipe 5. The torque time curves for all the revulcanized samples with recipe 4 exhibit similar ki-

netics of cure. The induction time is reduced or conspicuous by absence here, as is expected during revulcanization. Significantly, the rate of vulcanization of virgin recipe 1, which is represented by curve 1 in Figure 13, is 0.2 s^{-1} , while that of revulcanization with recipe 4 is about 0.12 s^{-1} , which is 41% lower. This rate of cure for recipe 4 is lower than that observed previously for recipe 2 in Figure 9, in which the same amount of curatives, as in the original virgin recipe 1, were added to the samples ultrasonically devulcanized at different barrel temperatures. Possibly, this may be due to the absence of the additional sulphenamide accelerator in recipe 4 but which was incorporated in recipe 2.

The higher the degree of devulcanization, that is, the lower the crosslink density and the gel fraction, the lower the degree of revulcanization, that is, the maximum torque in the torque time curves. The maximum torque during revulcanization with recipe 4 for all devulcanized NR samples is always lower than that for virgin recipe 1. This is true except for the undertreated ones mentioned before. This is confirmed from Figures 3 and 5 in which the crosslink densities for recipe 4 are lower than that for recipe 1. Similarly, it can be seen from Figure 14 that the modulus at 100% strain for recipe 4 is always lower than that for recipe 1, represented by the filled symbol on the



Figure 14 The effect of ultrasound amplitude on the modulus at 100% strain of NR recipe 1 devulcanized at different barrel temperatures, a die gap of 2.54 mm, a flow rate of 0.63 g/s, and revulcanized with recipe 4.



Figure 15 The stress-strain curves for NR recipe 1 ultrasonically devulcanized at different barrel temperatures and amplitudes, a die gap of 2.54 mm, a flow rate of 0.63 g/s, and revulcanized with recipe 4 and for NR recipe 1 (curve 1) and NR recipe 5 (curve 2).

Y-axis. The only exception is the NR sample treated at 60°C and 10 μ m, which has a higher crosslink density (Fig. 3) and, therefore, a higher modulus at 100% strain (Fig. 14) on revulcanization with recipe 4. Evidently, the modulus at 100% strain for recipe 4 has a linear relationship with crosslink density.

The stress-strain curves for NR vulcanizates, which were ultrasonically devulcanized at different barrel temperatures and then revulcanized with the optimized recipe 4, are shown in Figure 15. Strain-induced crystallization is observed in all the revulcanized samples. Thus, this is definitely an improvement over recipe 2, in which strain-induced crystallization was conspicuous by absence. The tensile strength and ultimate elongation of the NR vulcanizates obtained using this optimized revulcanization recipe 4 are plotted as a function of ultrasound amplitude for different barrel temperatures in Figure 16. The filled symbols on the Y-axis represent the tensile strength and ultimate elongation of original virgin recipe 1, and the open symbols represent those of recipe 5. As a result of strain-induced crystallization, the values obtained for recipe 4 show a tremendous improvement over the values obtained previously for recipe 2. The tensile strengths for recipe 4 lie in between 14.2 MPa (Fig. 16) for the revulcanized NR sample having crosslink density

 0.16 kmol/m^3 (Fig. 3) and 2.3 MPa (not shown) for the revulcanized NR sample having the lowest crosslink density 0.063 kmol/m^3 . The latter is the most devulcanized compound.

The highest ultimate elongation is 670% (Fig. 16), obtained for the revulcanized NR sample with crosslink density 0.14 kmol/m³ (Fig. 3). Conditions of devulcanization for this sample were Q = 0.63 g/s, $\delta = 2.54$ mm, $T_b = 120$ °C, and $A = 5 \ \mu$ m. This ultimate elongation is close to the value of 680% for the original virgin recipe 1. The lowest value is 440% (not shown) for the overtreated sample, which has crosslink density 0.063 kmol/m³ on revulcanization. Conditions of devulcanization for this sample were Q = 0.63 g/s, $\delta = 1.52$ mm, $T_b = 120$ °C, and $A = 7.5 \ \mu$ m. It obviously also has the lowest tensile strength, as was reported before.

A study of the variation of mechanical properties of revulcanized NR compounds with the amplitude of ultrasound shows that they exhibit a minima at 7.5 μ m, indicating that the properties deteriorate with increasing degree of devulcanization from 5 to 7.5 μ m. It was hypothesized earlier in the study that during the ultrasound devulcanization of virgin NR vulcanizates, some revulcanization occurs with increasing intensity when the ultrasound amplitude is increased from 7.5 to 10 μ m. Possibly, as a result of the net decrease in the degree of devulcanization from 7.5 to 10 μ m, we observe an improvement in the



Figure 16 The effect of ultrasound amplitude on tensile strength (filled symbols) and ultimate elongation (open symbols) of NR recipe 1 devulcanized at various barrel temperatures, a die gap of 2.54 mm, a flow rate of 0.63 g/s, and revulcanized with recipe 4.

mechanical properties of the revulcanized NR samples, which were devulcanized at 10 μ m over those devulcanized at 7.5 μ m.

A qualitative assessment of the effect of devulcanization conditions on the mechanical properties of revulcanized samples shows that a decrease in the barrel temperature from 180 to 60°C, and an increase in the die gap from 1.52 to 2.54 mm, that is, a decrease in the degree of devulcanization up to a certain limit, improves their mechanical properties.

In order to compare the mechanical properties of the revulcanized and virgin NR samples containing the same amount of curatives, the virgin rubber is vulcanized with recipe 5. This recipe consists of the original amount of curatives in recipe 1 plus those required for revulcanization with recipe 4. The modulus at 100% strain for recipe 5 is represented by the open symbol on the Y-axis of Figure 14. The tensile strength and ultimate elongation obtained for recipe 5 is 17 MPa and 490%, respectively, and is represented on the Y-axis of Figure 16. Thus, as is evident from Figure 16, while the best tensile strengths of NR samples revulcanized with recipe 4 are lower than the tensile strength of recipe 5, almost all of them have higher ultimate elongation than that of recipe 5, as is seen in Figure 16, except those subjected to a very high degree of devulcanization. Interestingly, the mechanical properties of the NR samples revulcanized with recipe 4 show a linear relationship with their corresponding crosslink densities and gel fractions. Thus, it can be inferred that the higher the gel fraction and the crosslink density on revulcanization, that is, lower the degree of ultrasound treatment, the better the mechanical properties of the reclaim.

CONCLUSIONS

The effect of ultrasound on vulcanized unfilled NR is studied. There is a substantial decrease in the crosslink density and gel fraction on ultrasound treatment, indicating that NR is subject to devulcanization. Increasing the barrel temperature, decreasing the die gap, and decreasing the flow rate result in an increasing degree of devulcanization. An observed phenomenon unique to NR was that an increasing amplitude of ultrasound resulted in an initial increase in the degree of devulcanization, followed by a decrease in the degree of devulcanization at higher amplitudes. It is suggested that ultrasound has an effect of simultaneous devulcanization and revulcanization on NR. The relative magnitude of each process is controlled by experimental conditions that determine the ultimate state of the material. The crosslink density and gel fraction can be correlated by a universal curve independent of the process parameters but unique to the material.

It is possible to optimize the revulcanization recipe for any condition of devulcanization, thereby improving the mechanical properties on revulcanization. On revulcanization with the optimized recipe, strain-induced crystallization is preserved in the NR samples. The torque time curves for revulcanization differ from those for the virgin compound in that the former exhibits a much shorter or a complete absence of induction period and a slower cure rate. Significantly, the crosslink densities and the gel fractions for the revulcanized compounds never exceeded those for the virgin compound. During revulcanization, no incorporation of additional sulphenamide accelerator gave the best mechanical properties, suggesting the presence of a substantial amount of accelerator in the devulcanized rubber.

This work is supported by a grant DMI 9312249 from the National Science Foundation and by a grant from the Ohio EPA.

REFERENCES

- F. W. Barlow, Rubber Compounding. Principles, Materials and Techniques, 2nd Ed., Marcel Dekker, New York, 1993, Chaps. 2 and 9.
- 2. J. R. Dunn, paper presented at Recycle '93, Davos International Forum, Davos, Mar. 1993.
- 3. W. C. Warner, Rubber Chem. Technol., 67, 55 (1994).
- A. I. Isayev, J. Chen, and A. Tukachinsky, *Rubber Chem. Technol.*, 68, 267 (1995).
- 5. A. Tukachinsky, T. Schworm, and A. I. Isayev, *Rubber Chem. Technol.*, **69**, 92 (1996).
- P. J. Flory and J. Rehner Jr., J. Chem. Phys., 18, 108 (1950).
- A. Barton, CRC Handbook of Polymer Liquid Interaction Parameters and Solubility Parameters, CRC Press, Boston, 1990, Chap. 32.
- V. Yu. Levin, S. H. Kim, A. I. Isayev, J. Massey, and E. vonMeerwall, *Rubber Chem. Technol.*, 69, 104 (1996).
- 9. N. Bekkedahl, Adv. Colloid Sci., 11, 8 (1946).

- V. Yu. Levin, S. H. Kim, and A. I. Isayev, *Rubber Chem. Technol.*, **70**, 120 (1997).
- V. M. Makarov and V. F. Drozdovski, *Reprocessing* of *Tires and Rubber Wastes*, Ellis Howard, New York, 1991, Chap. 2.
- J. M. Ball, Manual of Reclaimed Rubber, Rubber Reclaimers Assoc., New York, 1956, Chap. 4.
- 13. G. Gee, J. Polym. Sci., 2, 451 (1947).
- P. J. Flory, N. Rabjohn, and M. C. Schaffer, J. Polym. Sci., 4, 435 (1949).
- 15. J. Janacek, Rubber Chem. Technol., 35, 572 (1962).

- F. S. Conant, in *Vulcanization of Elastomers*, G. Alliger and I. J. Sjothum, Eds., Huntington, New York, 1978, Chap. 3.
- 17. A. Y. Coran, Rubber Chem. Technol., **37**, 679 (1964).
- H. W. Greensmith, L. Mullins, and A. G. Thomas, in *Chemistry and Physics of Rubber Like Sub*stances, L. Bateman, Ed., Maclaren & Sons Ltd., London, 1963, Chap. 10.
- S. H. Morrell and J. Stern, Trans. Inst. Rubber Ind., 28, 269 (1952).