J Mater Sci (2007) 42:7520–7529
DOI 10.1007/s10853-007-1623-9

Ultrasound devulcanization: comparison of synthetic isoprene and natural rubbers

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Received: 1 February 2006 / Accepted: 16 February 2007 / Published online: 18 May 2007
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Abstract Sulfur-cured vulcanizates of unfilled synthetic isoprene rubber (IR) were prepared and successfully devulcanized in a continuous co-axial ultrasonic reactor. Die pressure characteristics and ultrasonic power consumptions were measured. Network structures of the virgin vulcanizates, devulcanizates and revulcanizates were characterized by gel fraction and crosslink density according to the classic swelling method. The molecular characteristics of the sol generated by ultrasound treatment were determined by GPC. Kinetics of revulcanization, rheological properties of the devulcanizates and mechanical properties of the revulcanizates were compared with those of virgin uncured IR and their vulcanizates. In addition, a comparison of the cure behavior, devulcanization characteristics, network structures and the mechanical properties was made between IR and the natural rubber (NR) reported earlier. Simulations on the correlation of the normalized gel fraction and the normalized crosslink density show that these two rubbers have almost equivalent probability of main chain scission and crosslink rupture ratio, which is probably determined by the main chain structure of both rubbers consisting of *cis*-1,4-isoprene.

Introduction

Natural rubber (NR) is primarily utilized in the tire industry and it is produced through the bio-synthesis in *Hevea brasiliensis* Tree [1] naturally. The stress-induced crystallization behavior has made this rubber unique among all the other elastomers as far as its mechanical properties are concerned. NR is usually the standard by which the performance of synthetic rubbers is judged [2]. Synthetic isoprene rubber (IR) is the artificial equivalent of NR since they both share the same basic chemical structural unit—*cis*-1,4-isoprene. The most critical difference between these two rubbers is that NR consists almost exclusively of *cis*-1,4-isoprene unit (~99%) and a small portion of non-rubber component such as protein, sugar, amino acid, fatty acid and other substances [3]; while IR always contains a lower content of *cis*-1,4-isoprene unit than NR and it is a 100% pure chemical product. Different polymerization methods lead to IRs with somewhat different *cis*-1,4-isoprene contents [4]. The slightly different contents of 1,4-isoprene unit could contribute to the large difference in the rate and the degree of crystallization and mechanical properties. Compared with its natural counterpart, IR is inferior in mechanical strength, anti-aging and crystallization. However it exceeds NR in the consistency of product, uniform cure rate, better processing (mixing, extrusion, molding and calendering), purity and particularly it does not undergo storage hardening [3].

Ultrasound devulcanization provides a rapid breakage of three-dimensional rubber network within a time of several seconds. It is a continuous process without the involvement of any chemicals making it unique and attractive to the rubber recycling industry. The rubber treated with powerful ultrasound is soft, moldable, and can be reshaped and revulcanized similarly to the virgin rubbers [5]. Extensive studies regarding the devulcanization of various elastomers such as NR [6, 7], SBR [8, 9], EPDM [10], BR [11] and other rubbers have been conducted and reviewed in [12]. During the extrusion process with ultrasound, both

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devulcanization and revulcanization can happen simultaneously in the materials. The material type and the processing conditions will determine which step is dominant over the other. Research on a wide variety of rubbers shows, that for most rubbers the devulcanization process is prevalent within a large range of processing conditions (such as reactor barrel temperature, flow rate, gap size and ultrasonic amplitude). In contrast, for NR under certain circumstances, with an increase of ultrasonic amplitude from 7.5 to 10 μm, the revulcanization prevails over the devulcanization, which can be revealed by the observation of less power consumption as well as higher gel fraction and crosslink density [6]. The extreme high content of *cis*-1,4-isoprene unit in NR is probably responsible for this unique phenomenon. In addition, the normalized experimental crosslink density and gel fraction for ultrasonically devulcanized rubber can be correlated by a universal master curve. This curve is found to be unique for each type of elastomer due to its unique chemical structure [12].

In this paper the sulfur-cured IR was successfully devulcanized in a continuous ultrasonic co-axial reactor. The devulcanization process characteristics (die pressure and power consumption), revulcanization of the devulcanized rubbers, rheological properties of the devulcanized rubbers and the mechanical properties of the vulcanizates and revulcanizates were investigated. The gel fraction and crosslink density of the vulcanizates and devulcanizates were quantitatively determined by the classic swelling method. A detailed comparative study of IR and NR in the cure and revulcanization behavior, devulcanization characteristics, network structures, and the mechanical properties is presented. The results suggest that these two rubbers share some basic characteristics in ultrasound devulcanization and in the cure behavior. However they also show some clear differences in devulcanization and revulcanization behavior, and mechanical properties.

Experimental

Materials

IR (NATSYN2200, *cis*-1,4-isoprene: 98.0%) was obtained from Goodyear Tire and Rubber Company with the number-average molecular weight $M_n = 810{,}000$ and the weight-average molecular weight $M_w = 2{,}490{,}000$ (provided by Goodyear and measured by Thermal Field Flow Fractionation—ThFFF). The compounding ingredients sulfur, *N*-cyclohexylbenzothiazole-2-sulphenamide (CBS), zinc oxide (ZnO) and stearic acid are all obtained from Akrochem Corp. The cure recipes applied in this research are shown in Table 1. It should be noted that 100 phr of the devulcanized rubber used in Recipe 2 corresponds to the total amount of rubber and ingredients of Recipe 1. Benzene and tetrahydrofuran (THF) used for extraction experiments is obtained from Aldrich Chemical Co.

Ultrasound devulcanization reactor

The coaxial devulcanization reactor consisting of a 38.1 mm rubber extruder with the single screw of L/D = 11 and a coaxial ultrasonic die attachment was used in the experiment. The cone-tipped ultrasound horn of 76.2 mm diameter was mounted coaxially to the extruder die. The schematic drawing of the reactor was given in [5]. The barrel has three temperature controlling zones equipped with electrical heaters and fans. The ultrasound unit is composed of a 3.0 kW ultrasonic power supply, an acoustic converter and a 1:1 booster. The water-cooled horn vibrates longitudinally with a frequency of 20 kHz and varying amplitudes ranging from 5 to 10 μm. The rubber particles from the extruder flow into the gap between the horn and the die plate where the rubber was subjected to the longitudinal (compressive) wave perpendicular to the flow direction. A flush-mounted thermocouple and a pressure gauge were inserted into the barrel to measure the temperature and the pressure of the rubber at the entrance of the die. The ground rubber particles are fed into the extruder by a conveyor belt feeder with an adjustable output. Starve feeding to the barrel is applied so that the flow rate of the rubber particles is controlled by the rate of feeding. The ultrasonic energy consumed during the experiment is measured by a wattmeter attached to the ultrasound unit.

Procedures

Compounding, molding and grounding

Preparation of the rubber vulcanizates is achieved by compression molding for 20 min at 160 °C in a mold of internal dimensions 260 × 260 × 12 mm^3 after the two-roll mill compounding. Then the vulcanizate is put into the freezer for 24 h and then ground into the particles with a 5 mm sieve in a Nelmor grinding machine.

Cure kinetics

APA 2000 (Alpha Technologies) is used for the study of vulcanization and revulcanization kinetics of IR. The strain amplitude, frequency and temperature used are 4.2%, 10.5 rad/s and 160 °C, respectively.

Devulcanization

The ground rubber was fed into the coaxial ultrasonic reactor at 120 °C and the feeding rates used were varied

Table 1 Cure recipes for IR compounds

Recipe	IR (phr)	Sulfur (phr)	Accelerator CBS (phr)	ZnO (phr)	Stearic acid (phr)
Recipe 1	100 (virgin)	2	1	5	1
Recipe 2	100 (devulcanized)	2	0	2.5	0.5

from 0.47 to 2.55 g/s. The ultrasound power consumption and the die entrance pressure were recorded during the extrusion process.

Characterization

Gel fraction of the vulcanized, devulcanized and revulcanized samples was measured by washing out of the sol part of these rubbers in the Soxhlet extraction apparatus for 24 h using benzene as a solvent. Crosslink density of the vulcanized, devulcanized and revulcanized samples was measured by the swelling technique and calculated using the Flory–Rehner equation [13]. The dynamic rheological behavior of the devulcanizates and IR was investigated using APA 2000 with the strain amplitude of 4.2%, a frequency sweep range between 0.02 and 209 rad/s and a temperature of 120 °C. An Instron T-5567 tensile testing machine was used to measure the stress–strain characteristics of the vulcanizates and revulcanizates. Dumbbell-shaped specimens of the ASTM D-412 Type C were punched out of the compression molded sheets and tested at room temperature with an extension rate of 500 mm/min. The cure time of the compression molded sheets for the tensile test is taken as the time when their individual maximum torque is reached. This choice of cure time is due to the presence of reversion on cure curves of both IR and NR. The molecular weight of the sol from the devulcanized rubber is characterized by GPC. The Soxhlet extraction for the preparation of the sol was done by using THF as the solvent. The extraction time is 96 h.

Results and discussion

Cure kinetics

Vulcanization and revulcanization

Different rheometers were used to measure cure kinetics of IR in the present study and NR in earlier study [6]. Namely, APA 2000 (Alpha Technologies) was used for IR and a Monsanto oscillating disc rheometer (ODR) was used for NR,since only the ODR rheometer was available in our laboratory at the time when NR studies were performed. Although these two rheometers typically show different levels of torques but general cure behavior would not be affected. Thus, a qualitative comparison of the cure curves can be made. Figure 1 shows the vulcanization and revulcanization curves for both rubbers. First, it is evident that both rubbers share some similarity in the vulcanization (recipe 1) and also in revulcanization (recipe 2). Particularly, both virgin rubbers have a comparative induction time of nearly 8 min and both of them also show a clear reversion at the later stage of curing which is due to the irreversible destruction of the polysulfidic crosslinks [14, 15]. Furthermore, in the revulcanization process, the induction period completely disappeared because of the existence of accelerator residue in the system [16, 17]. This

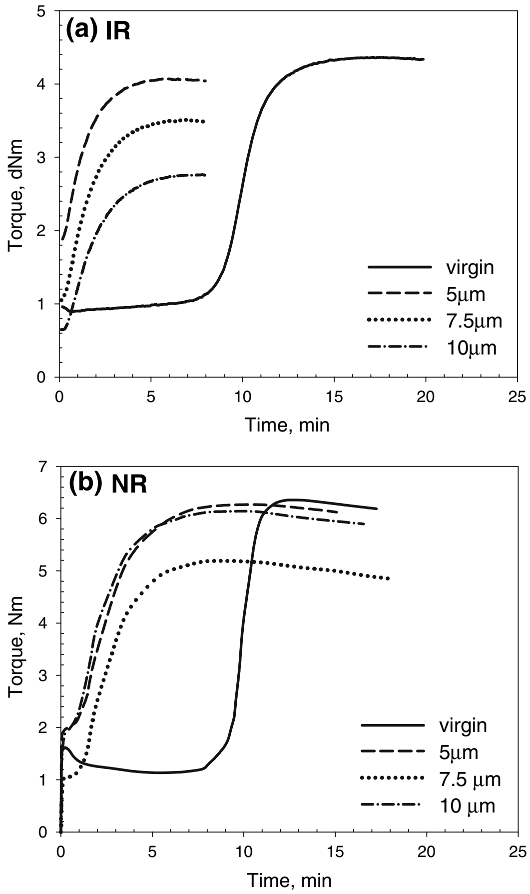

Fig. 1 Cure curves at 160 °C for IR (**a**) (obtained by APA) and NR (**b**) (obtained by ODR) of virgin rubber and devulcanized rubbers obtained at various ultrasonic amplitudes with a die gap of 2.54 mm, a flow rate of 0.63 g/s and a barrel temperature of 120 °C

suggests that the revulcanization reaction starts immediately once the compounds were heated to the desired temperature. However, there were also some observed differences in these two rubbers. For example, the torque of IR in revulcanization is lower than that in the vulcanization at all the amplitudes. It was also seen that with increase of the ultrasonic amplitude, the torque monotonously decreased, which suggests that the ability for the devulcanized rubber to undergo revulcanization is weakened with the increase of ultrasonic amplitude. In contrast, the torque of NR in revulcanization only slightly drops compared with that in the vulcanization. Furthermore, the revulcanization torque of NR at first drops with an increase of the ultrasonic amplitude from 5 to 7.5 µm, but then it increases with a further increase of amplitude from 7.5 to 10 µm. The torque value for 10 µm revulcanization is close to that in the vulcanization, which shows completely different trends with what is observed in IR. The difference in the ability to undergo vulcanization for 10 µm devulcanizates is probably due to the fact that NR contains a higher concentration of *cis*-1,4-isoprene units than IR does. Hence, it is possible that after devulcanization NR contains a higher amount of the carbon–carbon double bonds than IR. This higher content of regular conjugated units could provide a higher probability of crosslinking contributing to better revulcanization. In addition, if one only considers the NR and IR vulcanization (recipe 1 shown in Table 1), one can observe that after the induction period the steeper slope and more severe drop of torque in NR indicates that the cure rate of NR is much faster than IR. This may lead to the vulcanized IR sheets being more uniform than those of NR.

Die characteristics and power consumption

Generally, the amplitude of ultrasound, the pressure in the devulcanization zone and the residence time of rubbers in the reactor are the three major operating parameters which affect the degree and the rate of devulcanization. If the amplitude is too small or the pressure is too low, no devulcanization takes place. The devulcanization process is very fast and it usually takes place within several seconds. In fact, the mean residence time of rubber in the devulcanization zone is from 3.9 to 21.3 s based on the experimental flow rates of 2.55–0.47 g/s. Figures 2 and 3 show, respectively, the power consumption and die pressure as a function of ultrasonic amplitude at different flow rates for IR (a) and NR (b) vulcanizates in the devulcanization process. During the devulcanization of both rubbers, die pressure drops with the increase of amplitude and a decrease of flow rate (Fig. 3). It indicates that higher amplitude and longer residence time subject the materials to more intense treatment leading to a higher degree of devulcanization that in turn reduces the viscosity. In contrast, for two rubber vulcanizates the power consumption shows different behavior as the amplitude increases. The power consumption of NR showed a maximum value at the intermediate amplitude of 7.5 µm and drops at both lower and higher ultrasonic amplitudes, except when the flow rate is as high as 2.52 g/s. Evidently, during the ultrasound extrusion, the devulcanization and revulcanization occur simultaneously, competing with each other. It was argued [18] that unlike other rubbers such as SBR, BR and EPDM, in NR the revulcanization dominates over the devulcanization at the highest amplitude used and through a certain range of flow rate. At very high flow rate, and hence the short residence time, it is possible that the broken NR chains do not have sufficient time to meet each other and consequently to combine together (revulcanization). Consequently, it leads to further devulcanization and results in a continuous increase of power consumption for NR at the high flow rate of 2.52 g/s. However for IR, the maximum on the power consumption curve is not observed at all the flow rates applied. Instead continuous increase with the increase of ultrasonic amplitude is observed. The difference in the behavior of power consumption with amplitude reveals that for NR the revulcanization could dominate over the devulcanization process at higher amplitude and over a certain range of flow rate. The exact reason for such a behavior is unclear. However, this is possibly due to high content of regular structure of NR macromolecular chain. For IR, similar to the other synthetic rubbers, the devulcanization always prevails because of its lower content of regular structure than that in NR. The explanation of the behavior of power consumption is also supported by the data obtained on crosslink density and gel fraction reported below.

Structures of devulcanized rubber

Gel fraction and crosslink density

The network structure characterization of the vulcanizates, devulcanizates and revulcanizates is mainly performed by the measurement of the gel fraction and crosslink density. Figures 4 and 5 show, respectively, the gel fraction and crosslink density of IR and NR devulcanizates and revulcanizates as a function of the ultrasonic amplitude. It was found that for IR devulcanizates the gel fraction and crosslink density continuously drops with the increase of amplitude. This is quite consistent with the power consumption variation with the amplitude for IR devulcanizates discussed earlier. The experimental results of NR devulcanizates show that the gel fraction and crosslink density initially decreases when the ultrasonic amplitude increases from 0 to 7.5 µm, and then increases with the further increase of amplitude from 7.5 to 10 µm. This

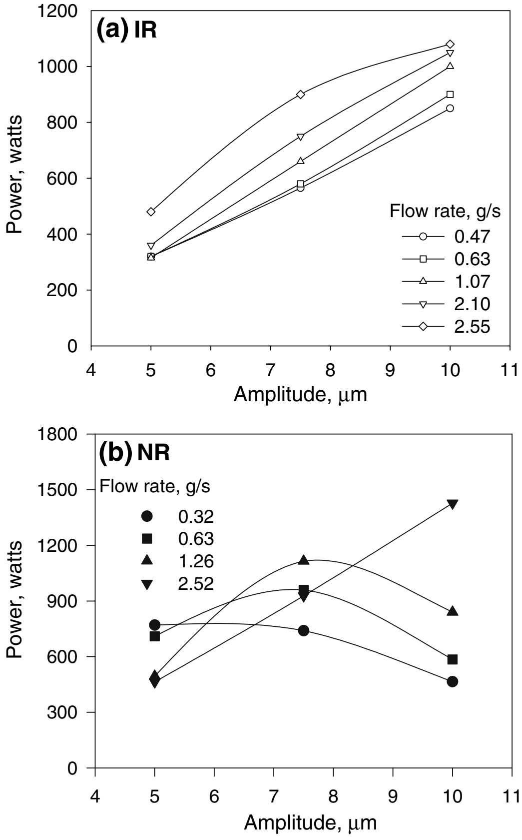

Fig. 2 Power consumption for IR (**a**) and NR (**b**) rubbers devulcanized at various flow rates at a barrel temperature of 120 °C and a die gap of 2.54 mm

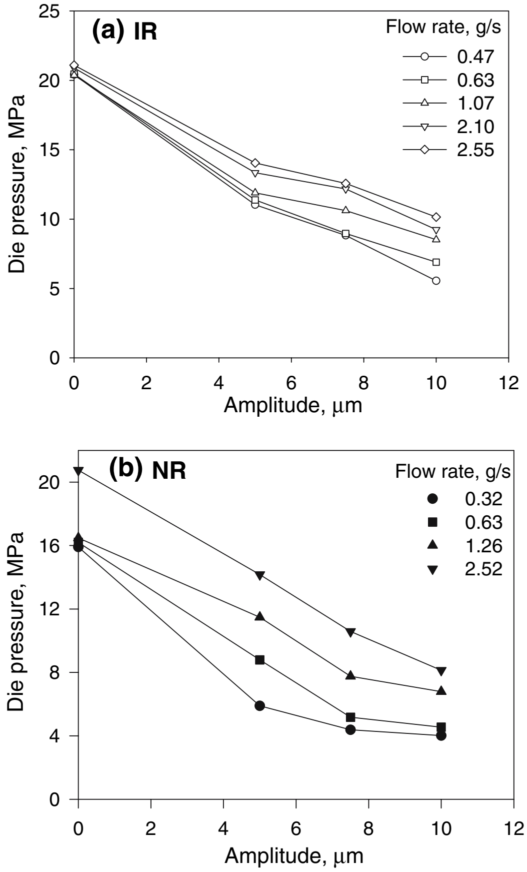

Fig. 3 Die pressure for IR (**a**) and NR (**b**) rubbers devulcanized at various flow rates at a barrel temperature of 120 °C and a die gap of 2.54 mm

behavior is quite different from what is observed in IR devulcanizates. However, it is still consistent with the power consumption variation with the amplitude in NR devulcanizates. The observed power consumption and network structure change with amplitude during NR devulcanization suggests that when the amplitude goes from 7.5 to 10 µm, the revulcanization process dominates over the devulcanization, which is the dominating process at lower amplitudes. This unique phenomenon in NR could again be due to its highly regular main chain structure. The gel fraction and the crosslink density of both rubber devulcanizates obtained at the flow rate of 0.63 g/s and revulcanized by recipe 2 were evaluated (shown in Figs. 4 and 5 and labeled as open symbols). For NR, the revulcanizates have substantially higher gel fraction and crosslink density than their respective devulcanizates. Similar to NR, the crosslink density of the IR revulcanizates is higher than that of the respective devulcanizates. However, for IR, the revulcanizates at 5 and 7.5 µm have the gel fraction close to the corresponding devulcanizates. Only at the amplitude of 10 µm, IR revulcanizate shows a higher gel fraction than its devulcanizate. These findings show that NR exhibits a better ability to undergo revulcanization than IR does. The results also indicate that in the presence of additional sulfur, the devulcanized rubbers are all capable of undergoing revulcanization. It also means that the entire amount of C=C bonds were not consumed in the vulcanization of virgin rubbers. There was still a fair amount of C=C bonds left in the devulcanized samples. Further calculations of the relative amount of C=C bonds and sulfur points towards this indication. For example, by taking the molecular weight of repeating units in the rubber and sulfur 68.11 and 32, respectively, in the recipe 1, one obtains the content of the C=C bonds equal to 100(g)/68.11(g/mol) = 1.468 mol and that of the sulfur equal to 2(g)/32(g/mol) = 0.0625 mol. This result shows a large amount of unsaturated units was left in the vulcanizates. They preserve the ability of the devulcanized rubber to undergo revulcanization.

The treatment of the ground rubbers with ultrasound not only leads to the network rupture but also unavoidably causes the main chain scission. In order to investigate the relative degree of these two effects, a simple model based on the random ruptures of chains and crosslinks [19–21] is applied to interpret all the experimental data by fitting the

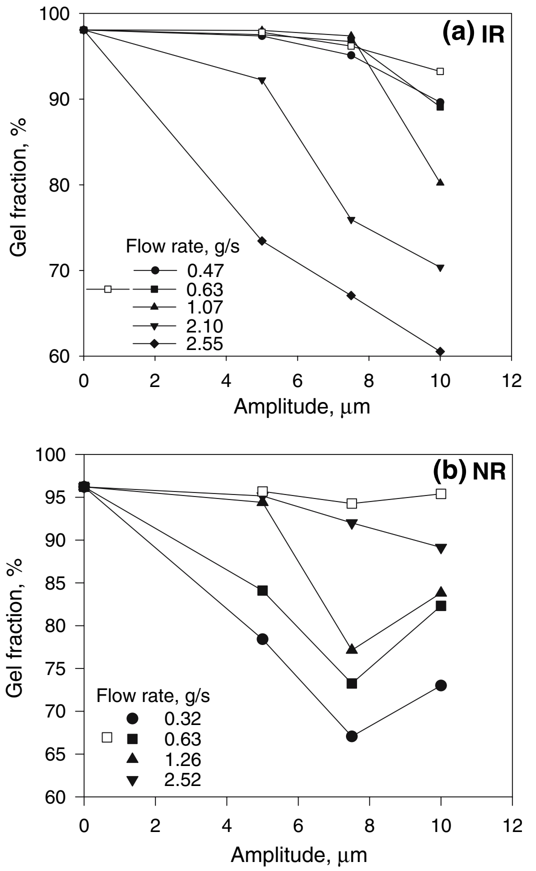

Fig. 4 Gel fraction of the devulcanized (*solid symbols*) and revulcanized (*open rectangle*, for flow rate of 0.63 g/s only) IR and NR rubbers as a function of ultrasonic amplitude obtained at various flow rates at a die gap of 2.54 mm and a barrel temperature of 120 °C

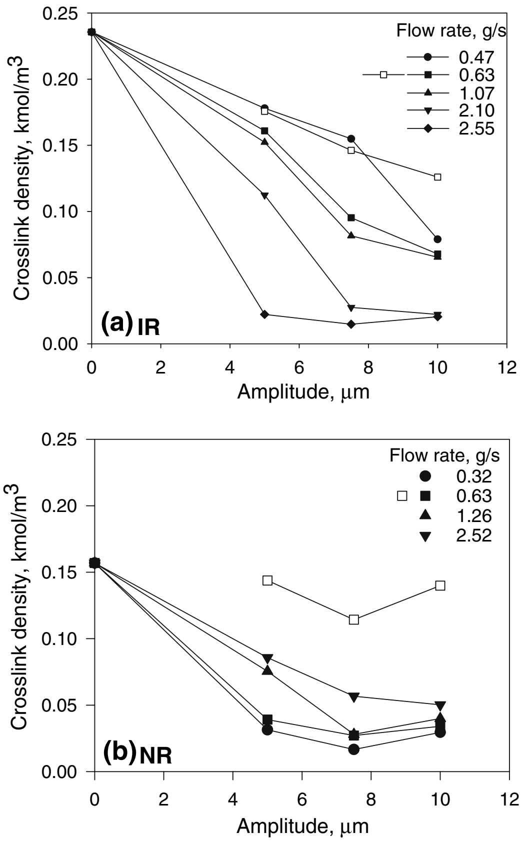

Fig. 5 Crosslink density of the devulcanized (*solid symbols*) and revulcanized (*open rectangle*, for flow rate of 0.63 g/s only) IR (**a**) and NR (**b**) rubbers as a function of ultrasonic amplitude obtained at various flow rates at a die gap of 2.54 mm and a barrel temperature of 120 °C

parameter k_p/k_α for each rubber, with k_p and k_α being the rate constants of the solely rupture of main chains and crosslinks, respectively. First, the dependence of the experimental normalized gel fraction on the normalized crosslink density of IR and NR devulcanizates was analyzed by taking the normalized quantities of original vulcanized rubber to be unity. There are two limiting cases in the model, with $k_p = 0$ indicating only crosslink rupture and $k_\alpha = 0$ indicating only main chain rupture. The experimental data characterizing the actual partial crosslink rupture and partial main chain scission in the rubbers should lie between these two limiting cases. The experimental and fitted results are shown in Fig. 6 for both rubbers. It was found that the limiting case of $k_\alpha = 0$ is independent of the rubber type and the molecular weight. The other limit of $k_p = 0$ and fitted curves to experimental data are both dependent on the molecular weight as well as the rubber type even though NR and IR share the same main chain structure. It should be noted that the number average molecular weight M_n of NR used is 180,400 [22], which is about 22% of the M_n of IR. With the higher molecular weight of IR, the curves shifted in the direction of lower crosslink density. This is reasonable, since the chain with the higher number of monomer units is able to accommodate a higher content of gel at the same crosslink density level. Nevertheless, the simulation results show that these two rubbers share close k_p/k_α values. For IR and NR, the k_p/k_α value of 4.1×10^{-3} and 4.2×10^{-3} are obtained, respectively. This means that the probability of main chain scission over the crosslink rupture is equivalent regardless the molecular weight as long as the rubbers have the same main chain structure and stereo-regularity. On the other hand, the very low k_p/k_α values found in the simulation of both rubbers indicates that the main chain scission is much more difficult to achieve than the crosslink rupture under the exposure of ultrasound. This is quite reasonable since the main chain (C–C) bond energy is about 346 kJ/mol being much higher than that of the crosslink network containing C–S (mono-sulfidic), S–S (di-sulfidic) and S_x (multi-sulfidic) with bond energies of 285, 268 and 251 kJ/mol [23], respectively. Therefore, low values of k_p/k_α resulting from the curve fitting are in an excellent

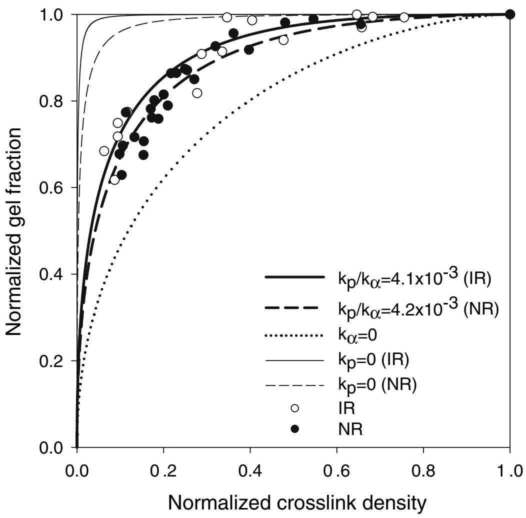

Fig. 6 Normalized gel fraction as a function of normalized crosslink density for devulcanized IR and NR rubbers

agreement with the bond energy values of main chains and crosslinks.

Molecular characteristics of the devulcanized sol

The molecular characteristics of the sol parts of the devulcanized IR rubbers was determined by GPC. The results are shown in Fig. 7. The number (M_n) and weight (M_w) average molecular weight of virgin IR is 982,000 and 1,998,000, respectively. These values are somewhat lower than the values supplied by the manufacturer using the ThFFF method. In Fig. 7a, curves of the molecular weight distribution of the sol part extracted from the devulcanized rubber are shifted to the lower molecular weight compared to that of the virgin IR. This indicates the molecular weight of sol generated is decreasing significantly upon ultrasound treatment. Furthermore, the molecular weight changes with varying amplitudes. For example, at the amplitude of 7.5 and 10 μm, the sol of the devulcanized IR shows both low and high molecular weight tails, compared with that of 5 μm (Fig. 7a). Accordingly, the polydispersity (M_w/M_n) also varies with ultrasonic amplitude (Fig. 7b). The M_w/M_n for the 5 and 7.5 μm samples is narrower than that of virgin IR. At the same time, the M_w/M_n of the 10 μm is wider than that of virgin IR. This shows that the ultrasonic amplitude affects the molecular weight of sol and its distribution in a very complex way. It is speculated that at a low amplitude (5 μm), breakage of the macromolecular chains is less severe and, therefore, less amount of macroradicals was created at this low amplitude compared with that at higher amplitude. This would result just in the molecular weight reduction. At higher amplitudes (7.5 and 10 μm), more radicals are produced due to the exposure of rubber to more intense ultrasound (the ultrasonic power is proportional to the square of amplitude). Possibly, these radicals terminate either by disproportionation leading to generation of the low molecular weight tails or by coupling of several macroradicals leading to formation of the high molecular weight tails, as seen in Fig. 7a.

Rheological properties of devulcanizates

The rheological properties of the devulcanized rubbers are very important as far as the processing is concerned. The dynamic properties of virgin IR, its vulcanizate and devulcanizates were obtained by APA 2000. The results are shown in Figs. 8 and 9. Upon cure, the complex viscosity, defined as $\eta^* = \sqrt{\eta'^2 + \eta''^2}$ (η' and η'' are the real and imaginary part of the complex viscosity), increases by at least one order of magnitude compared with the virgin uncured rubber (Fig. 8a). After devulcanization, the complex viscosity is obviously lower than that of the cured rubber. With the increase of amplitude the complex viscosity drops even more. Particularly, the viscosity of the 5 μm sample is only slightly lower than that of the cured sample. However, it is still much higher than the viscosity of the uncured rubber over the entire frequency range. For the 7.5 and 10 μm samples, their viscosities are much lower than that of the cured sample. At a low frequency range, the viscosity of these samples is higher than that of the uncured rubber but at a relatively high frequency range, their viscosity is higher. This indicates that different degrees of shear thinning take place in virgin uncured IR, cured rubber and the devulcanized samples obtained at different amplitudes. Cured and devulcanized rubbers exhibit a greater dependence of the complex viscosity on frequency due to the presence of a substantial amount of the crosslinked structure compared with virgin uncured IR consisting of 100% of sol. This effect can be more clearly observed in Fig. 8b, where the complex viscosity is plotted as a function of the product of the viscosity and frequency. From this figure, the slope of the curve changes with the level of crosslinking of the materials; with the virgin vulcanizates and the 5 μm devulcanized sample exhibiting the greatest slope and the virgin uncured rubber showing the smallest slope. Furthermore, the loss angle of the virgin uncured IR decreases with frequency (Fig. 8a). Among all the rubbers, its value is the highest over almost the entire frequency range. For the devulcanized rubber the loss angle progressively increases with the increase of amplitude. The variation of the storage modulus versus the frequency for these materials is shown in Fig. 9. The plateau modulus is observed in the virgin cured sample and the 5 μm devulcanized sample indicating the occurrence of the complete cure for the virgin cured sample and only a slight de-crosslinking during the devulcanization at an ultrasonic

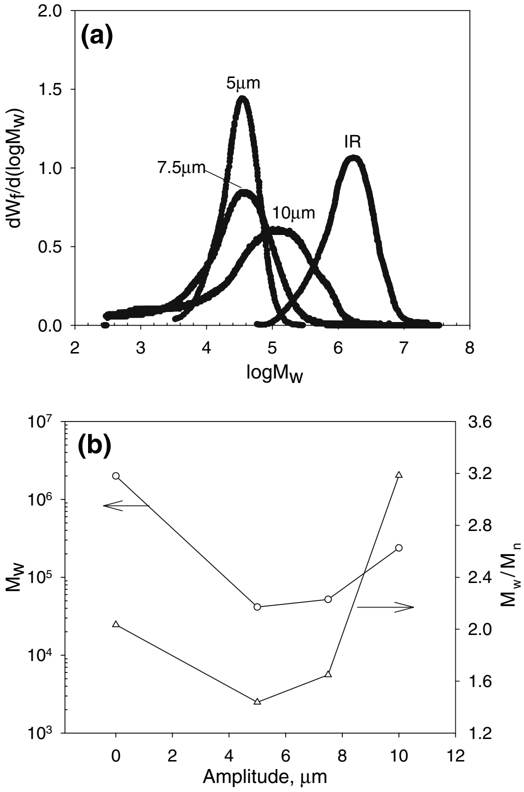

Fig. 7 Molecular weight distribution at various amplitudes (**a**), amplitude dependence of weight average molecular weight M_w and polydispersity M_w/M_n (**b**) of the virgin IR and the sol parts in devulcanized IR rubber obtained at a gap of 2.54 mm, flow rate of 0.63 g/s and a barrel temperature of 120 °C

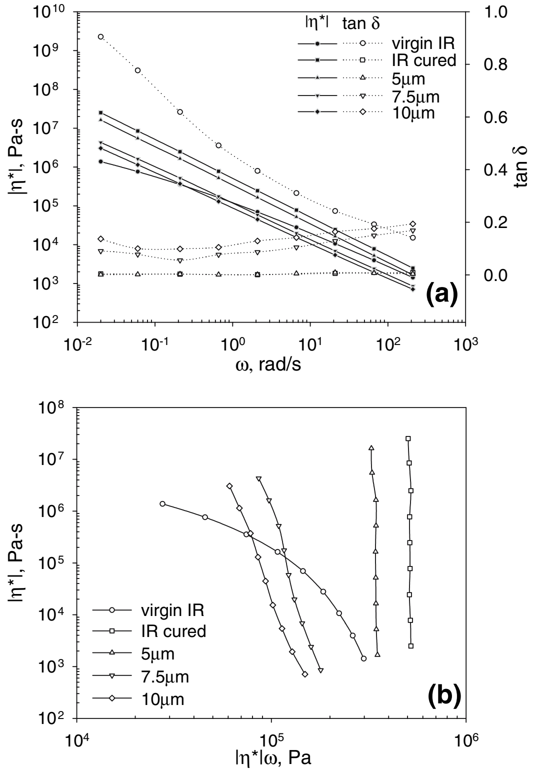

Fig. 8 The complex viscosity $|\eta^*|$ and tan δ of virgin IR, its vulcanizates and devulcanizates obtained at a gap of 2.54 mm, flow rate of 0.63 g/s and a barrel temperature of 120 °C as a function of frequency ω (**a**) and $|\eta^*|\omega$ (**b**), respectively, at a strain amplitude of 4.2%

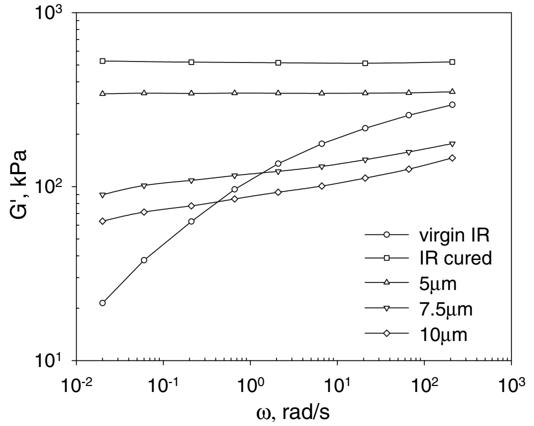

Fig. 9 The storage modulus G' of virgin IR, its vulcanizates and devulcanizates obtained at a gap of 2.54 mm, flow rate of 0.63 g/s and a barrel temperature of 120 °C as a function of frequency ω at 120 °C at a strain amplitude of 4.2%

amplitude of 5 µm. With a further increase of amplitude from 7.5 to 10 µm, more intense devulcanization takes place such that the storage modulus decreases and the plateau modulus gradually disappears. From all these figures (Figs. 8a, b, 9) it is observed that the more significant changes of all the properties take place when the amplitude increases from 5 to 7.5 µm, compared with the changes occurring when the amplitude increases from 0 to 5 or 7.5 to 10 µm. Therefore, from the rheological properties of these materials one concludes that the higher degree of devulcanization is achieved at higher ultrasonic amplitudes.

It should be noted that no comparison between dynamic properties of IR and NR was made, since the APA 2000 instrument was not available at the time when NR studies were performed [6].

Mechanical properties of revulcanized rubber

The stress–strain curves for IR and NR vulcanizates and revulcanizates observed at different ultrasonic amplitudes are shown in Fig. 10. The virgin IR vulcanizates show the tensile strength (σ_B) slightly lower than that of the virgin NR vulcanizates. This is probably attributed to the higher molecular weight and narrower molecular weight distribution of IR than those of NR (M_n: 180,400; M_w:

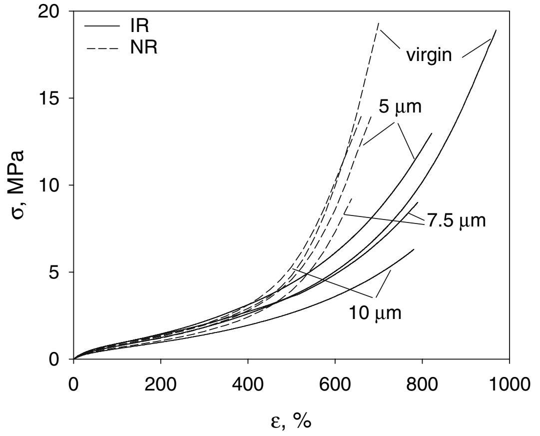

Fig. 10 The stress–strain curve for IR and NR vulcanizates and devulcanizates obtained at different ultrasonic amplitudes, a die gap of 2.54 mm, a flow rate of 0.63 g/s and a barrel temperature of 120 °C

1,116,000; M_w/M_n: 6.19) [22]. Also, NR has a higher amount of *cis*-1,4-isoprene structure (> 99%) than IR (98%). Higher degree of stereo-regularity would introduce stronger ability for stress-induced crystallization of NR which is evident by the rise of the tensile stress at lower strain. Evidently, stereo-regularity plays a more important role in affecting the mechanical properties than the molecular weight and its distribution. From Fig. 10, it was seen that both rubbers show a different extent of the stress-induced crystallization leading to a high tensile strength, which is a typical phenomenon for natural rubber. It was also noticed that IR vulcanizates and revulcanizates showed higher elongation compared with the respective NR vulcanizate and revulcanizates. Figure 11 shows the mechanical properties of IR and NR vulcanizates and revulcanizates as a function of the ultrasonic amplitude. In Fig. 11a, when the amplitude increases from 0 to 7.5 μm, the tensile strength (σ_B) decreases for both IR and NR revulcanizates. However, when the amplitude increases from 7.5 to 10 μm, the change of the tensile strength for these two rubbers is different. In particular, the tensile strength for IR revulcanizates continuously drops at the amplitude of 10 μm. In contrast, the strength for NR revulcanizates increases. This is probably because the revulcanization dominates over the devulcanization for NR at the ultrasonic amplitude of 10 μm as discussed earlier. This phenomenon is consistent with the gel fraction, crosslink density and power consumption results reported above. From Fig. 11b, generally the elongation at break (ε_B) for the NR revulcanizates shows the value close to its virgin vulcanizate. However, for the IR revulcanizates, the ε_B values are lower than that of virgin vulcanizate. Particularly, the ε_B value decreases linearly with the increase of the amplitude. Overall the ε_B values of IR vulcanizate and revulcanizates are higher than those of respective NR samples. In Fig. 11c, the change of modulus at 100% and 300% strain, E_{100} and E_{300} for the NR revulcanizates, with the amplitude has the same trend as the change of tensile strength. Namely, the modulus initially drops when the amplitude goes from 0 to 7.5 μm, but it increases when the amplitude increases from 7.5 to 10 μm. For IR revulcanizates, the modulus generally drops with the increase of amplitude except at the amplitude of 5 μm. The modulus at this amplitude is slightly higher than that of the virgin IR vulcanizate.

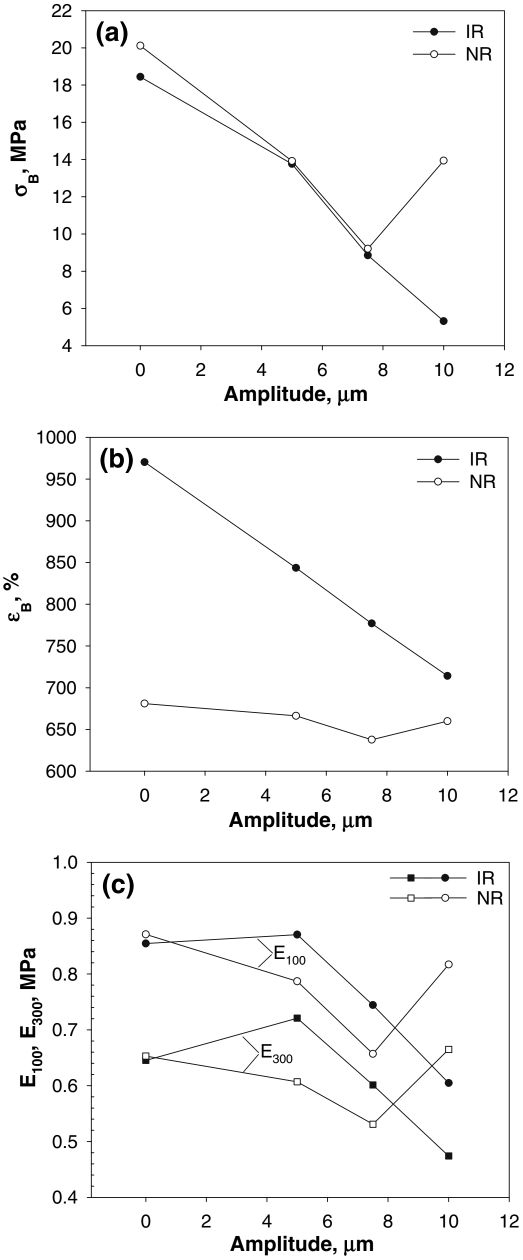

Fig. 11 Amplitude dependence of the tensile strength (**a**) and elongation at break (**b**) and modulus at 100% and 300% (**c**) of IR and NR vulcanizates and revulcanizates at a die gap of 2.54 mm, a flow rate of 0.63 g/s and a barrel temperature of 120 °C

Conclusions

Sulfur-cured vulcanizate of unfilled synthetic isoprene rubber (IR) was devulcanized using a coaxial ultrasonic reactor in the same way natural rubber done earlier. The two rubbers show some similarities in the vulcanization, devulcanization, revulcanization, and network structure. They have an induction period close to each other and show a reversion in the original vulcanization. The induction period is absent in revulcanization. The die pressure monotonously drops with the increase of ultrasonic amplitude. At all the ultrasonic amplitudes, the gel fraction and crosslink density are lower than the original cured rubber. This seems to be understandable since they share the same main chain structural unit—*cis*-1,4-isoprene. At the same time, they show some clear differences in the rate of vulcanization, the level of revulcanization and dependence of the degree of devulcanization on the amplitude. In particular, the cure rate of IR is lower than that of NR. This could make the vulcanized sheets of IR more uniform than those of NR. Unlike IR, the NR sample devulcanized at the highest amplitude 10 μm could reach a higher level of revulcanization than those of the 5 and 7.5 μm samples. This was revealed by the torque value attained upon revulcanization, the value of gel fraction and crosslink density, the value of power consumption and also the mechanical properties. The dynamic properties of the IR devulcanizates indicate that at the higher amplitude, the complex viscosity becomes lower and the loss angle becomes larger. These results are consistent with the gel fraction and crosslink density as well as the power consumption. Lower degree of shear thinning of samples devulcanized at higher ultrasonic amplitude was observed. Also, more significant changes of all the properties take place when the amplitude goes from 5 to 7.5 μm compared with those variations when the amplitude increases from 0 to 5 μm and 7.5 to 10 μm. The k_p/k_α values obtained from the simulation of the experimentally measured normalized gel fraction and crosslink density suggest that the crosslink rupture dominates over the main chain scission which is consistent with bond energy values of main chain and crosslinks. The almost equivalent ratio of k_p/k_α values for IR and NR rubbers indicate that they have the same probability of main chain scission and crosslink rupture ratio, which is evidently determined by the same main chain structures of both rubbers.

Acknowledgements The authors are grateful to the Goodyear Tire and Rubber Company for providing the IR rubber and also to the Akrochem Corp. for providing the cure ingredients.

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