

The Effect of High Power Ultrasound on EPDM Gum in Extrusion Process

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ABSTRACT: High power ultrasound treatment of ethylene propylene diene monomer (EPDM) gum in extrusion process was found to affect its structure and properties. In comparison with the original EPDM gum, the ultrasonically treated samples were found to contain some amount of gel with sol having a higher molecular weight, possibly due to chain branching. Gel fraction and dynamic properties of the ultrasonically treated gums and their vulcanizates were measured as a function of processing condi-

tions. Measurements of the stress-strain characteristics, dynamic properties, and hardness of EPDM vulcanizates prepared after treatment indicated a possibility of controlling their properties by varying processing parameters. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3698–3707, 2007

Key words: ethylene propylene diene monomer (EPDM); ultrasound; structure

INTRODUCTION

The study of effects of ultrasound on materials is a rapidly growing research area.^{1–4} Some of the most important aspects of a prolonged exposure of polymer to ultrasound under static conditions have been its application to the polymerization in solution,^{5,6} degradation of polymer solutions,^{7,8} and modification of polymer film surfaces.⁹

Studies on ultrasonic irradiation show that it can be used for degradation of polymers in solutions.^{1,3,7,8} The rate of polymer degradation under the influence of ultrasonic irradiation has been associated with cavitation effect. Propagation of ultrasound waves in solutions produces cavitation bubbles. The formation and collapse of the bubble plays an important role in degradation of polymers in solution. The kinetics of cavity growth and collapse are dependent upon local environmental properties, such as solution vapor pressure, viscosity, diffusion coefficient, thermal conductivity, and the frequency of the ultrasonic waves.¹⁰ Also, the basic effects of irradiation of a polymer solution with power ultrasound were reported using polystyrene in toluene as a model solution.¹¹ The degradation proceeds more rapidly at higher molecular weights and approaches

a limiting value, M_{lim} , about 30,000 Da below which no further degradation takes place.

Generally, ultrasonic degradation in solution is a nonrandom process. The cleavage of polymer chains preferentially takes place near the middle of the chain when compared with the random scission upon thermal degradation.⁴ The study of this process is of great importance because it can provide a powerful technique for the controlled high molecular weight polymer cleavage and consequently, the acquisition of low molecular weight polymer.¹⁰

Recently, ultrasonic devulcanization experiments have been conducted on several types of rubber, including ground tire rubber,^{12–14} SBR,¹⁵ NR,¹⁶ and silicone rubber,^{17,18} using an extruder ultrasonic reactor. These experiments indicated the feasibility of a continuous process of devulcanization or decrosslinking of rubbers. In particular, they have shown that a three-dimensional network breaks down within a short period of time on the order of seconds or less. As a most desirable consequence, ultrasonically treated rubber can be reprocessed, shaped and revulcanized in a manner similar to that employed with unvulcanized elastomer.

In this article, the effect of ultrasound on the structure and properties of unfilled ethylene propylene diene monomer (EPDM) gum was described. This research provides a possible new method to control the properties of EPDM vulcanizates prepared from ultrasonically treated gum in continuous process. Rheological properties, cure behavior, and molecular characteristics of the ultrasonically treated gum were also determined.

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EXPERIMENTAL

Material

EPDM (Keltan 2506) used in our experiments was obtained from DSM Copolymer (Baton Rouge, LA). Comonomer (ENB) contents is ~ 4.5 wt % and ethylene contents is 56 wt %. The number average and weight average molecular weight is 3.97×10^4 and 13.7×10^4 g/mol, respectively. Also, Mooney viscosity is 28 [ML (1 + 4) 125°C].

Ultrasonic reactor

The ultrasonic reactor described in our previous paper¹² was used in this study. In this reactor, a cone-tipped horn of 76.2 mm diameter was mounted coaxially to the extruder. A 3-kW ultrasonic power supply, a converter, and a 1 : 1 booster (Branson, Danbury, Connecticut) provided the longitudinal vibrations of the water-cooled horn with a frequency of 20 kHz. The amplitude range was from 5 to 10 μm . The rubber from the extruder flowed into the gap between the horn and the water-cooled die plate where the rubber was subjected to longitudinal (compressive) waves perpendicular to the flow direction. A flush-mounted thermocouple and a pressure gauge were inserted into the barrel to measure the pressure and the temperature of the rubber at the entrance to the die.

Ultrasonic treatment

The extruder was preheated to 120°C. The temperature was kept uniform for all barrel zones. The gap between the die plate and horn and amplitude of ultrasound were adjusted to the chosen values. The EPDM gum cut into small cubes of about 12 mm size was loaded into the hopper by the belt feeder. The feeder, providing "starved feed" to the extruder, controlled the output. In the extruder, EPDM gum was compressed and conveyed by screw to the zone of ultrasonic treatment in the gaps between the horn and the die plate in the reactor. The rubber flow rate was 0.42 g/s. A die of uniform gap of 1.016 mm with a radial length of 19 mm was used in these experiments. After reaching the steady state conditions indicated by pressure transducer and ultrasonic power wattmeter, the ultrasonically treated sample was collected. The entrance pressure before the ultrasonic treatment zone, the temperature in the rubber after the ultrasonic treatment zone, and the ultrasonic power consumption were measured.

After collecting, the gel fraction of the ultrasonically treated rubber was measured. Prior to vulcanization, the samples were compounded with curatives using a two-roll mill (Dependable Rubber Machinery, Cleveland, Ohio). The cure recipe was 5 phr of zinc oxide, 1 phr of stearic acid, 1.5 phr of sulfur, 1 phr of

tetramethylthiuram disulfide, and 0.5 phr of MBT (2-mercapto-benzothiazole).

Molding

The vulcanization of sheets of dimensions of $127 \times 127 \times 2$ mm³ was carried out using a compression molding press at 160°C and by applying a pressure of 13.8 MPa for time corresponding T_{90} of maximum torque on the cure curve. The sheets were used for the measurement of mechanical properties.

Characterization

A Monsanto oscillating disc rheometer (Monsanto Instrument Company, Akron, OH) was used to obtain the torque-time curve at a temperature of 160°C according to ASTM D 2084.

The gel fractions of the original EPDM gum, ultrasonically treated gum, and vulcanized EPDM were measured by a Soxhlet extraction method using benzene as a solvent. The samples were preweighed and then placed in the Soxhlet and allowed to swell in benzene for 24 h. After Soxhlet extraction, swollen samples were dried in an air-oven at 50°C for 24 h. Gel content (g) was determined by the following equation:

$$g = \frac{W_d}{W_r}$$

where W_d is the weight of dry gel after extraction and W_r is the weight of rubber before extraction.

The crosslink density of the gel in vulcanized EPDM was measured by the swelling technique¹⁹ using benzene as a solvent. A finite amount of solvent can be absorbed by a crosslinked polymer, depending on the similarity of the chemical structure between polymer and solvent. The swelling of rubber in solvent is controlled by the entropy of the dilution of the polymer-solvent pair by the polymer chains assuming elongated configurations, but constrained by the crosslinks of the polymer networks. The samples were preweighed and then placed in the Soxhlet and allowed to swell in benzene for 24 h. After Soxhlet extraction, swollen samples were dried in an air-oven at 50°C for 24 h. The crosslink density can be characterized by average molecular mass of the network chain, i.e., the average chain length between two crosslink network junctions. This can be expressed either by the average molecular weight between crosslinks (M_c) or by the number of the network chains per unit volume (ν_e). The crosslink densities are determined by Flory-Rehner equation¹⁹:

$$\nu_e = - \frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_1 \left(V_r^{1/3} - \frac{1}{2} V_r \right)}$$

where V_1 is the molecular volume of the solvent, χ is the solubility parameter expressing the first neigh-

boring interaction free energy, v_e is the effective number of chains in a real network per unit volume, and V_r is the volume fraction of the polymer in the swollen network in equilibrium with pure solvent. The volume fraction of rubber network in the swollen phase was calculated from equilibrium swelling data:

$$V_r = \frac{\frac{W_r}{\rho_r}}{\frac{W_r}{\rho_r} + \frac{W_s}{\rho_s}}$$

where W_r is the weight of dry rubber, W_s is the weight of solvent, ρ_r and ρ_s are the density of rubber and solvent, respectively. For the EPDM-benzene system, χ is $0.488 + 0.271V_r$,²⁰ the molecular volume of benzene V_1 is $89.1 \text{ cm}^3/\text{mol}$ and the density of benzene is 0.864 g/cm^3 . The density of EPDM is 0.86 g/cm^3 . The gel fraction and crosslink density of virgin EPDM vulcanizates were 0.95 and 127 mole/m^3 , respectively.

The dynamic behavior of virgin and ultrasonically treated EPDM gum and vulcanized EPDM rubbers was investigated, using an Advanced Polymer Analyzer 2000 (APA 2000[®]) from Alpha Technology (Akron, OH) at a temperature of 100 and 80°C , respectively. Instron Tensile Tester (Model 5567, Instron Corporation, Norwood, MA) was used for the stress-strain measurement at the room temperature according to ASTM D 412 (type C). Crosshead speed was 500 mm/min .

The glass transition temperature and thermal stability of virgin and ultrasonically treated EPDM gum and vulcanizates were measured using Dupont DSC (2920 modulated DSC) and Dupont TGA (TA instrument, New Castle, DE), respectively. The scanning rate was 20°C/min .

Nuclear magnetic resonance (NMR) spectroscopy has proven to be a powerful method for the investigation of molecular structure and monomer sequence distribution.²¹ In this study, the changes of molecular structure and monomer sequence distribution in EPDM gum before and after ultrasonic treatment were investigated using ^1H NMR and ^{13}C NMR. Namely, ^1H NMR spectroscopy was performed to measure ENB contents of virgin and ultrasonically treated gums. ^1H NMR spectra were recorded at 300 MHz on a Varian Gemini-200 spectrometer (Varian Inc., Palo Alto, CA). ^1H NMR spectra were acquired using 10% solutions in *ortho*-dichlorobenzene- d_4 (Aldrich). Typically 128 scans were accumulated to provide adequate sensitivity. ^{13}C NMR spectroscopy was employed to measure ethylene contents of EPDM gums. ^{13}C NMR spectra were recorded at 100 MHz on a Varian Inova-400 spectrometer. Solvent was 1,4-dichlorobenzene. ^{13}C NMR study was carried out at 125°C . Acquisition

time was 1.2 s and recycle delay was 20 s. Experimental time was 20 h.

To measure the change of molecular weight and molecular weight distribution (MWD) of EPDM gum after ultrasound treatment, high temperature gel permeation chromatography (GPC) was used. Samples were dissolved in 1,2,4-trichlorobenzene (TCB) at 140°C for about 6 h. It was noticed that most part of each sample dissolved fairly easily except for gel part. Sample solutions were filtered off-line before they were injected into the columns. High temperature GPC (Water 150 C plus, Waters, Milford, MA) was employed. Differential refractive index and differential viscometer detectors were utilized. Mobile phase was TCB and columns were 4 linear mixed beds "B" PL (Polymer Lab) gel column. Flow rate was 1.0 mL/min and injection volume was $150 \mu\text{L}$. The GPC columns were calibrated using a commercial set of polystyrene standards. The number and weight average molecular weights of virgin and ultrasonically treated EPDM gums were calculated from universal calibration.

RESULTS AND DISCUSSION

Die pressure and power consumption

Figure 1 shows the die pressure at the entrance to treatment zone and ultrasonic power consumption versus ultrasonic amplitude. The die pressure of the ultrasonic treatment zone is substantially reduced as the amplitude of ultrasound is increased. It is believed that ultrasound facilitates the flow of rubber through the gap not only because of reduction of the friction in the presence of ultrasonic waves, but also

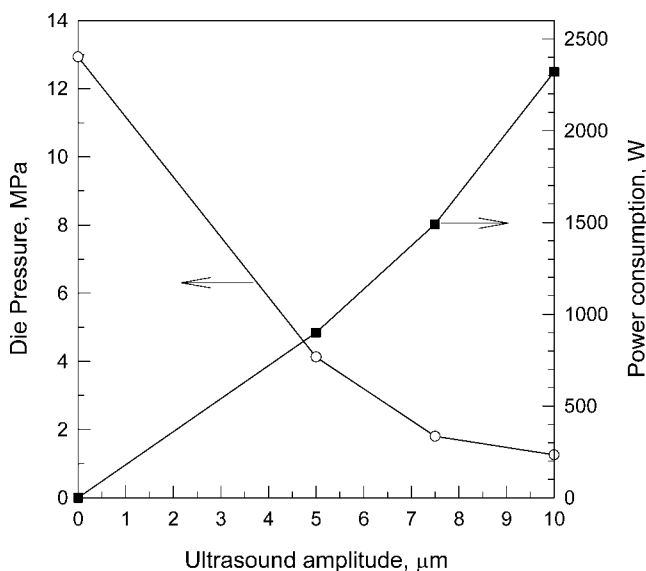


Figure 1 Die pressure and ultrasonic power consumption versus amplitude.

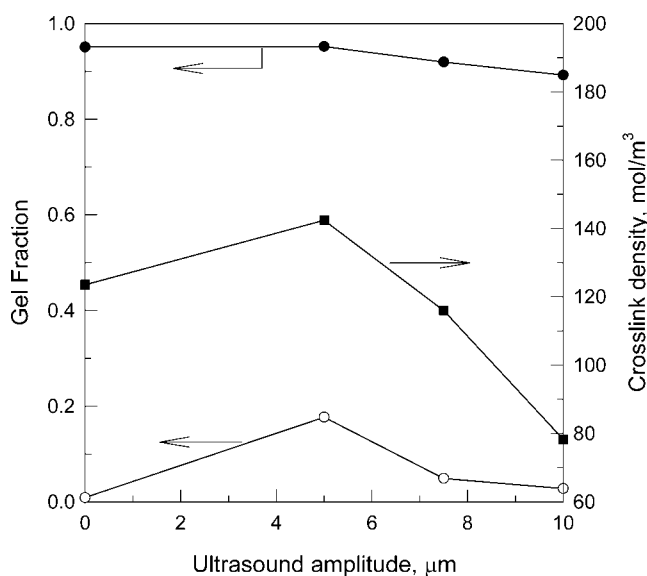


Figure 2 Gel fraction and crosslink density versus ultrasonic amplitude for ultrasonically treated EPDM gum (open symbols) and their vulcanizates (solid symbols).

because of structural changes (degradation and gel formation, as shown later) taking place as rubber gum enters the ultrasonic treatment zone. Evidently, reduction of the friction is a dominant factor in decrease of the die pressure rather than increase of the die pressure because of gel formation.

The measured ultrasonic power consumption is expended to dissipation losses and breakage of the bonds leading to degradation or material change. One cannot estimate experimentally what part of power is consumed by degradation alone. In addition, the power expended on heat dissipation in the material and the power transmitted by the traveling wave through the rubber gum cannot be separated.

A quantitative analysis of the amount of ultrasound energy consumed in reduction of the friction and in structural changes of the material is beyond scope of this article. The only measurable losses are the initial power consumption of the acoustic system when the horn works without loading, i.e., in absence of pressure and without material under the horn. In obtaining Figure 1 these losses are subtracted from the total power consumption. Ultrasonic power consumption increases with amplitude of ultrasound. This indicates that as ultrasonic amplitude increases, the more energy was transmitted into rubber gum.

Extrusion of EPDM vulcanizates without imposition of ultrasound leads to the EPDM particle without devulcanization.²² Similarly, it was also reported.²³ that EPDM vulcanizate sample exiting the extruder with imposition of ultrasonic waves changed from a solid to a soft and sticky material, which can be easily milled to form a smooth, continuous sheet. However, a

sample exiting the extruder without imposition of ultrasonic waves was still in a powder form. Therefore, ultrasonic treatment is an essential requirement to achieve devulcanization or degradation of rubber.

Gel fraction and crosslink density

Figure 2 presents the gel fraction of ultrasonically treated EPDM gum and gel fraction and crosslink density of vulcanized EPDM rubber versus the ultrasound amplitude. Clearly, during ultrasonic treatment of EPDM gum a certain amount of gel is created depending on amplitude. Both the gel fraction of ultrasonically treated samples and crosslink density of vulcanized EPDM have maximum at 5 μm and then decreased with amplitudes. But gel fraction of vulcanized samples is only slightly affected by ultrasound amplitude because vulcanized samples are already fully cured. Maximum amount of gel of 0.18 was produced at 5 μm . This sample also exhibits its maximum crosslink density upon curing.

Similarly, it was reported²⁴ that at ultrasound amplitude of 5 μm , the crosslink density and gel fraction had a maximum value and then decreased with amplitude for treated virgin unvulcanized SBR. However, the maximum amount of gel that was generated is much less in case of EPDM (18%) than that in case of SBR gum (72%).

Cure behavior

Figure 3 represents the cure curves for vulcanization of untreated and ultrasonically treated EPDM rubber. The maximum torque of the sample ultrasonically treated at 5 μm is higher than those of the

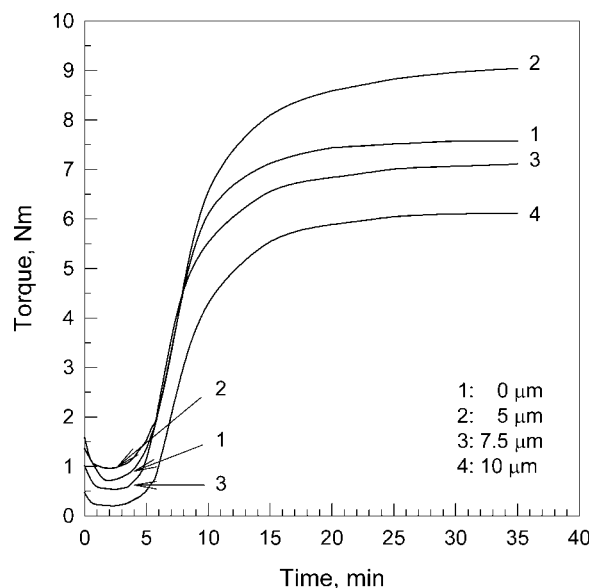


Figure 3 Cure curves of untreated and ultrasonic treated EPDM gum obtained various amplitudes.

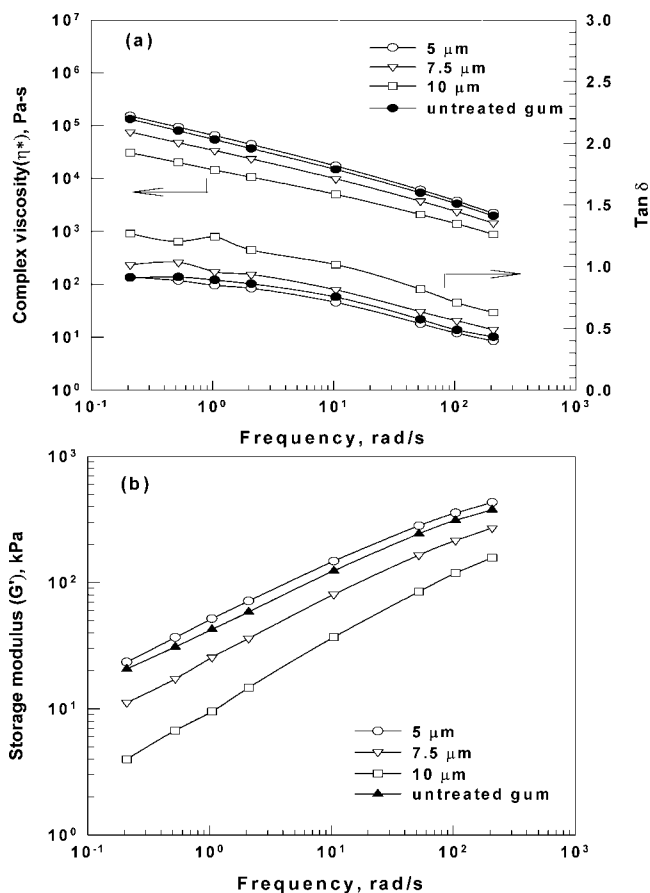


Figure 4 Complex viscosity and $\tan \delta$ versus frequency (a) and storage modulus G' versus frequency (b) for untreated and ultrasonically treated EPDM gum at strain amplitude of $\gamma_0 = 0.07$ and 100°C .

untreated sample and samples treated at 7.5 and 10 μm . This trend is well in agreement with gel fraction and crosslink density as shown in Figure 2. Also, at 7.5 and 10 μm , the maximum and minimum torque decreases with amplitude. The scorch time is increased at 10 μm . These facts clearly indicate that at a higher amplitude, ultrasound treatment of EPDM gum causes backbone chain breakage, as also shown later by structural analysis of the samples.

Dynamic viscoelastic properties

Dynamic viscoelastic properties of virgin and ultrasonically treated EPDM gums and vulcanizates are measured using APA 2000 (Advanced Polymer Analyzer). Figure 4(a) shows the complex viscosity and $\tan \delta$ versus frequency of untreated and ultrasonically treated gum at strain amplitude of $\gamma_0 = 0.07$ and 100°C . One can see that complex viscosity of ultrasonically treated sample at 5 μm is the highest. With the increase of ultrasonic amplitude to 7.5 and 10 μm , the complex viscosity of those samples decreases. This decrease of viscosity is well matched with reduction of the gel fraction and minimum tor-

que on cure curve, as depicted in Figures 2 and 3, respectively. Again, the ultrasonic irradiation of EPDM rubber at 5 μm causes an increase of viscosity. But, the viscosity decreases at higher ultrasonic amplitude. These results indirectly illustrate that there are the competing reactions of crosslinking and degradation during the ultrasonic treatment. Also, one can conclude that the degradation of main chain becomes dominant at higher ultrasonic amplitude.

The $\tan \delta$ behavior of ultrasonically treated samples, as shown in Figure 4(a), indicates the trend opposite to that of complex viscosity, also depicted in Figure 4(a). The $\tan \delta$ of ultrasonically treated samples goes through a minimum at 5 μm , and then increases with amplitude. The $\tan \delta$ value is an indication of elastic properties of ultrasonically treated EPDM gum. It means that the elasticity of the treated sample increases at an amplitude of 5 μm and then, decreases with further increase of the ultrasonic amplitude. This hypothesis is also supported by Figure 4(b) that shows an increase of storage modulus at 5 μm and a decrease at higher ultrasonic amplitudes. It is interesting to see plot of G' versus G'' for

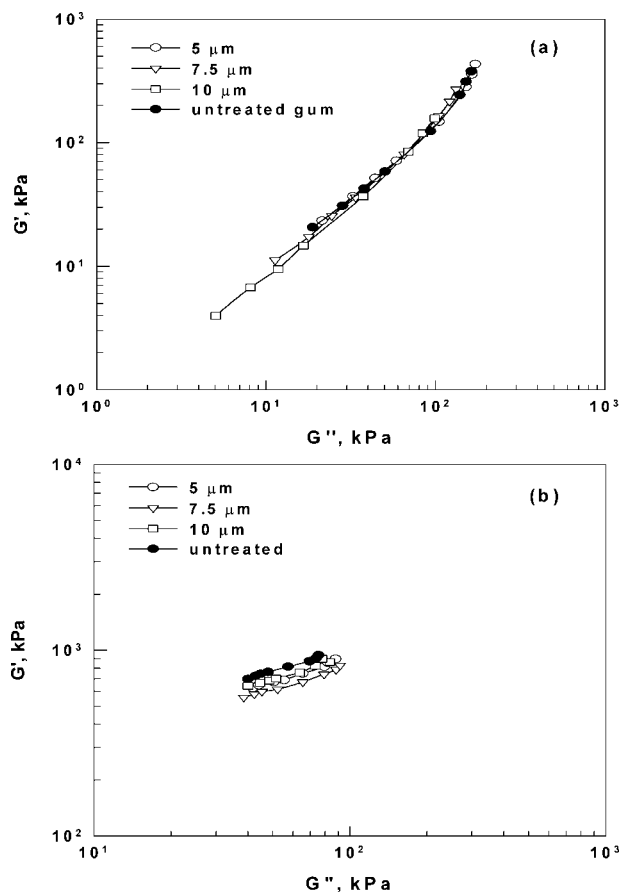


Figure 5 G' versus G'' for untreated and ultrasonically treated EPDM gum at strain amplitude of $\gamma_0 = 0.07$ and 100°C (a) and G' versus G'' for vulcanizates of untreated and ultrasonically treated EPDM gum at strain amplitude of $\gamma_0 = 0.042$ and 80°C (b).

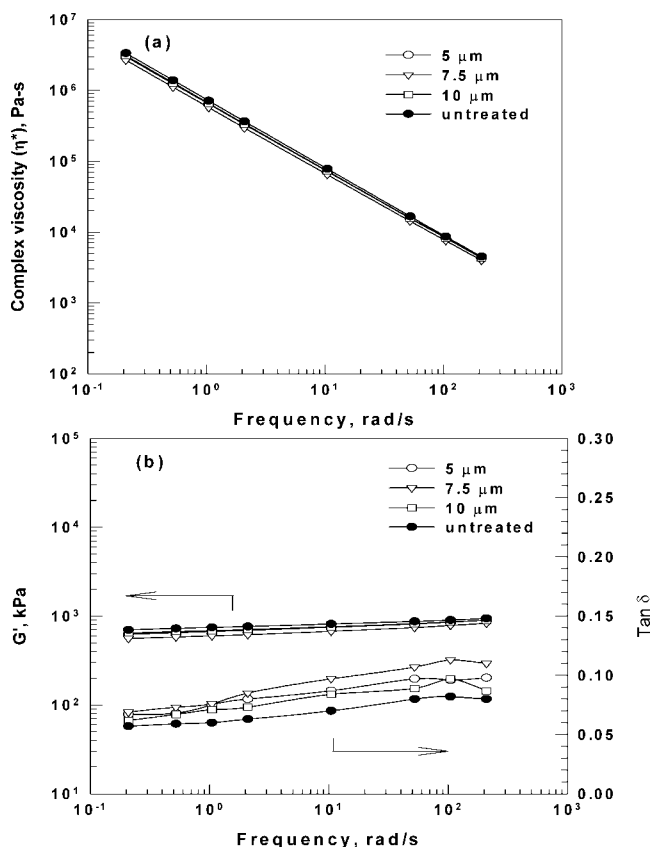


Figure 6 Complex viscosity versus frequency (a) and G' and $\tan \delta$ versus frequency (b) for vulcanizates of untreated and ultrasonically treated EPDM gum at strain amplitude of $\gamma_0 = 0.042$ and 80°C .

untreated and ultrasonically treated EPDM gum [Fig. 5(a)]. At low frequency region, the sample ultrasonically treated at an amplitude of 5 μm shows a higher storage modulus at the same loss modulus than the other treated samples. This observation also points toward a higher elasticity of the sample treated at an amplitude of 5 μm .

Figures 5(b)–6 depict the dynamic viscoelastic properties of vulcanized samples for untreated and ultrasonically treated samples at strain amplitude of $\gamma_0 = 0.042$ and 80°C . Complex viscosity of vulcanized samples [Fig. 6(a)] is almost same for untreated and 5 μm treated samples, while complex viscosity decreases slightly for samples treated at 7.5 and 10 μm . This trend is same for the storage modulus shown in Figure 6(b). The $\tan \delta$ values of vulcanizates prepared from ultrasonically treated samples are higher than those of untreated sample. This indicates that vulcanized samples prepared from ultrasonically treated EPDM gum are less elastic than that of untreated sample. This observation is also corroborated by Figure 5(b) where plot of G' and G'' for vulcanized samples are shown. At the same loss modulus, vulcanizates made of the ultrasonically treated samples have a lower storage modulus than

that of untreated sample. It indicates that the vulcanizate prepared from the untreated sample is more elastic than even the vulcanizate obtained from the sample treated at 5 μm , which in uncured state showed a higher elasticity than that of the virgin untreated sample.

Mechanical properties of vulcanizates

Figures 7 and 8 represent, respectively, the stress–strain behaviors and amplitude dependence of modulus, hardness and ultimate properties of vulcanizate of ultrasonically treated EPDM gum. Modulus of 100% and hardness of the vulcanizate prepared from sample ultrasonically treated at 5 μm increase, the tensile strength at break is practically intact, while the elongation at break passes through a minimum at 5 μm and increases with an ultrasonic amplitude. It is worthy to note from these data that the ultrasonic treatment for EPDM gum can be applied for modification of physical properties of EPDM gum and vulcanizates.

Structural analysis

Figure 9 represents amplitude dependence of the glass transition temperature of ultrasonically treated EPDM gum and their vulcanizates. The glass transition temperature of ultrasonically treated EPDM gum has a maximum at 5 μm and decreases at higher ultrasonic amplitudes. This maximum is possibly related to the decrease of the molecular mobility because of the maximum of gel formation occurs

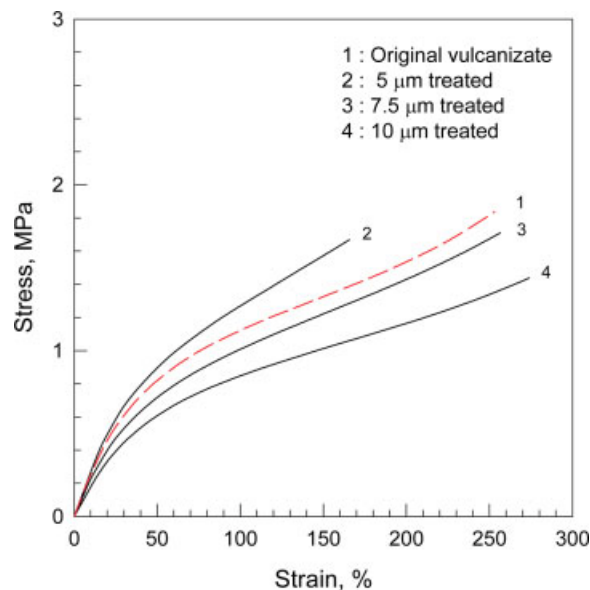


Figure 7 Stress–strain curves for vulcanizates of untreated and ultrasonically treated EPDM gum obtained at various amplitudes.

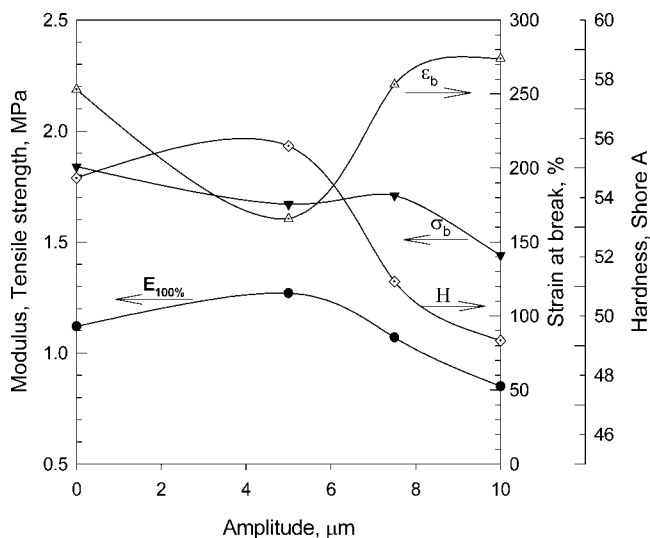


Figure 8 Modulus, tensile strength, elongation at break, and hardness of vulcanizates of ultrasonically treated EPDM gum versus ultrasonic amplitudes.

at 5 μm as previously discussed. With an increase of ultrasonic amplitude, the glass transition temperature decreases. It can be thought that the degradation of backbone chain can create short chains in the EPDM gum so that the mobility of molecular chain increases. After vulcanization of ultrasonically treated samples, their glass transition temperature is practically the same. It can be thought that vulcanization for ultrasonically treated sample leads to the same levels of molecular mobility.

Figure 10 depicts amplitude dependence of the thermal stability of ultrasonically treated samples and vul-

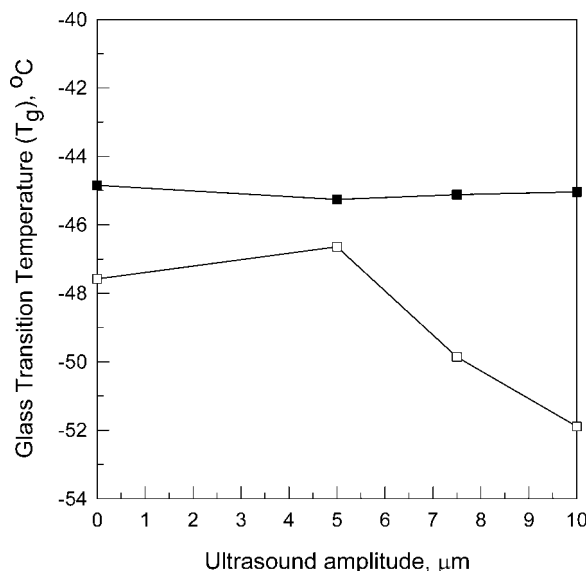


Figure 9 Glass transition temperature versus ultrasonic amplitude for ultrasonically treated EPDM gum (open symbols) and vulcanizates (solid symbols).

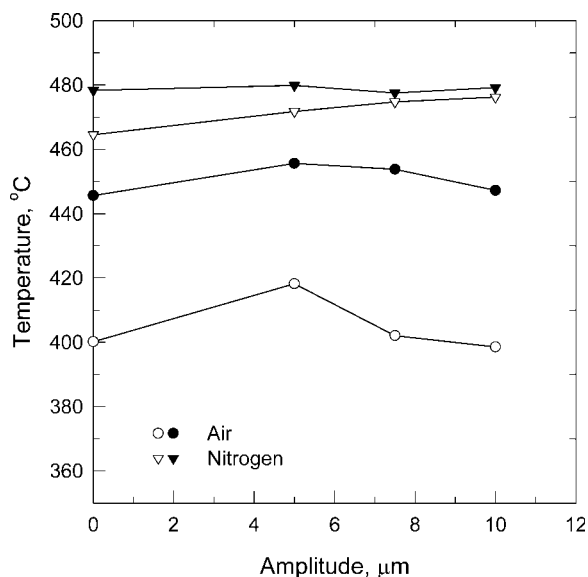


Figure 10 Temperature corresponding to a maximum of DTGA curves of ultrasonically treated EPDM gums (open symbols) and their vulcanizates (solid symbols) versus ultrasonic amplitude.

canizates. The thermal stability is determined as a temperature corresponding to the maximum of derivative of weight loss with respect to temperature versus temperature (DTGA) obtained by TGA. In case of nitrogen atmosphere, the thermal stability of ultrasonically treated gum increases with amplitude. However, their vulcanizates do not show significant changes with ultrasonic amplitude. In air environment, the thermal stability of ultrasonically treated gums and their vulcanizates is the highest at an amplitude of 5 μm .

¹H NMR spectra of untreated and ultrasonically treated EPDM gums are shown in Figure 11. These measurements are carried out to determine ENB contents. Note that EPDM-ENB has two resonance peaks from 5 to 6 ppm in a 3 : 1 ratio, reflecting E : Z conformational ratio.²¹ Also, one can observe that the peak of 4.80–5.01 ppm is increased in the sample ultrasonically treated at 10 μm , which possibly indicates the double bond formation.²⁵ Therefore, at high ultrasonic amplitude, degradation can induce double bond formation. The ENB content can be calculated by integrating the olefinic region and the aliphatic region 0–3.3 ppm and taking the appropriate ratios after subtracting the contribution of the third monomer (ENB) to the aliphatic intensity.²¹ The ENB concentration (in weight percent) may be calculated from the following equation.²¹

$$\text{ENB}(wt\%) = \frac{d \times 120}{d \times 120 + (a - 11d)/2 \times 140} \times 100 \quad (1)$$

where a and d are the integral of the aliphatic region and the olefinic region, respectively. The average

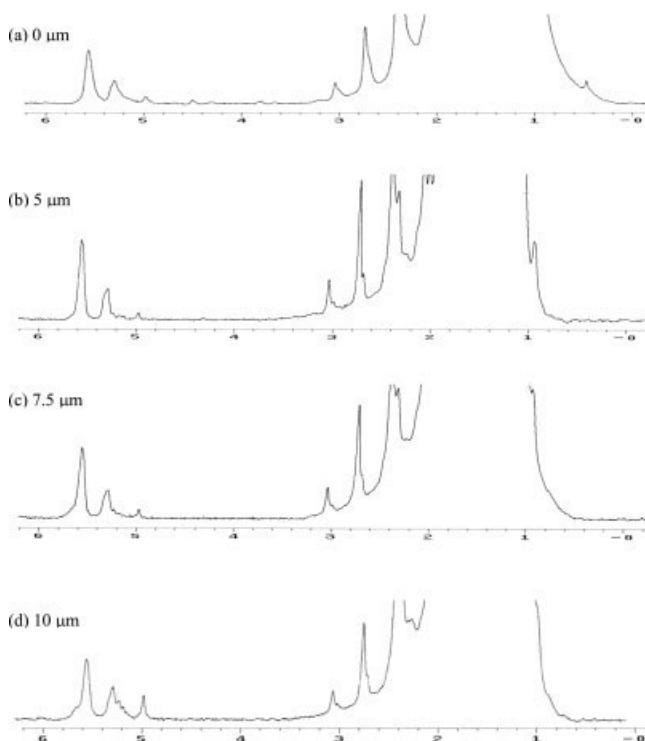


Figure 11 ^1H NMR spectra of untreated and ultrasonically treated EPDM gums.

monomer unit weight is taken to be 14, the mass of ethylene, for this calculation.

In Figure 12, ^{13}C NMR spectra of untreated and ultrasonically treated EPDM gum at amplitude of 5 μm . The resonance assignments and integral regions²¹ for EPDM-ENB are summarized in Table I.

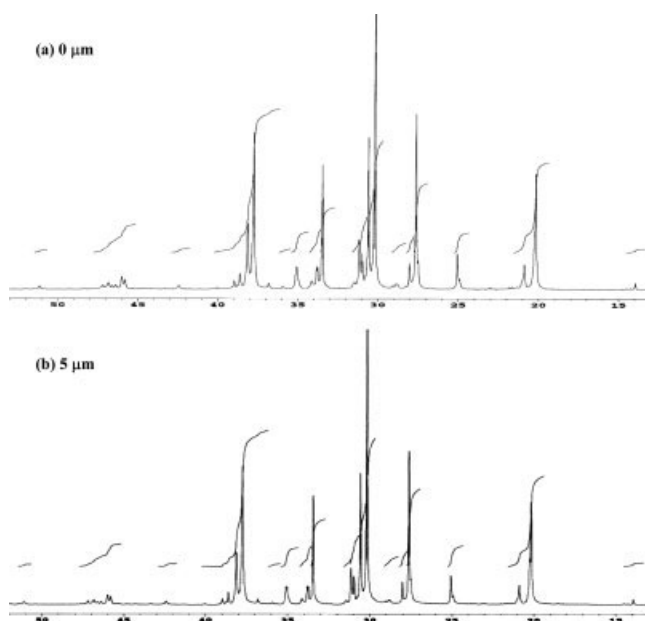


Figure 12 ^{13}C NMR spectra of untreated and ultrasonically treated EPDM gums.

TABLE I
 ^{13}C Spectral Assignments and Integral Regions for EPDM-ENB²⁰

Assignment	Integration limits (ppm)
ENB(C _{1E})	52.00–50.00
S _{αα} + ENB (C ₅ + C ₆) + C _{1Z}	48.50–44.50
ENB (C ₄)	43.00–41.00
S _{αγ} + S _{αδ}	39.40–36.85
ENB(C _{3E})	36.85–36.20
S _{αβ}	36.20–34.30
T _{γγ} + T _{γδ} + ENB(C ₇)	34.29–33.47
T _{δδ}	33.47–32.80
T _{βγ}	31.90–31.05
T _{βδ} + S _{γγ}	31.05–30.61
S _{γδ}	30.61–30.23
S _{δδ}	30.23–29.32
T _{ββ}	29.15–28.22
S _{βγ}	28.22–27.63
S _{βδ}	27.63–26.63
S _{ββ}	25.60–23.95
P _{ββ} + P _{βγ} + P _{βδ}	22.50–19.00

It was reported²¹ that there are four different calculation methods for ethylene content in EPDM. They are based on possible ways of combining resonance integral to obtain the monomer sequence distribution of EPDM. Our calculations are made based on their four different methods. Then the average value is obtained. In Figure 13, even though that ENB content is seen to attain a minimum in the sample ultrasonically treated at amplitude of 5 μm , change of the ENB content with ultrasonic amplitude is less than 1 wt %. As indicated earlier, the ultrasonically

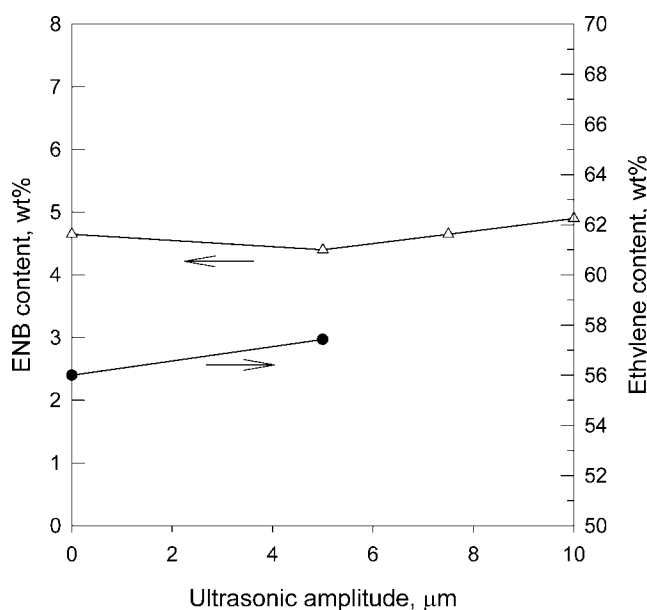


Figure 13 ENB content and ethylene content of ultrasonically treated EPDM gum versus ultrasonic amplitude.

treated EPDM gum contains a certain amount of gel with the highest amount being 0.18 in the sample treated at amplitude of 5 μm . Based on this observation, one can draw a conclusion that the gel is not only created by radicals derived due to rubber unsaturation, i.e., double bond in ENB comonomer, but also generated via H-abstraction from the rubber chain by the radical formed upon ultrasound irradiation, i.e., the recombination of two EPDM macroradicals.²⁶

In addition, it is seen from Figure 13 that a maximum of the ethylene content increases by about 1.5 wt % in the sample ultrasonically treated at 5 μm . Clearly, the ethylene content change of EPDM gum during the ultrasonic treatment is not significant. From free-radical chemistry²⁷ it is known that there is a certain selectivity with respect to H-abstraction, specifically, from allyl and alkyl groups. Also, it was reported²⁸ that during peroxide crosslinking of ethylene-propylene rubber chain scission occurs due to abstraction of a tertiary hydrogen atom from propylene unit, while crosslinking arises from attack at a secondary hydrogen atom from ethylene unit. The calculated relative reactivity of tertiary to secondary hydrogen atom is 6 to 1. Based on this fact, one can conclude that hydrogen abstraction from tertiary carbon atoms of propylene unit in EPDM backbone and the subsequent chain cleavage (β scission) of the formed radical during the ultrasound irradiation is predominant over crosslinking of ethylene sequence. Therefore, the ethylene content of EPDM backbone chain shall increase because of reduction of polypropylene units due to β scission. However, it is believed that radical formation by ultrasonic irradiation is relatively random process since insignificant changes of ethylene content were observed.

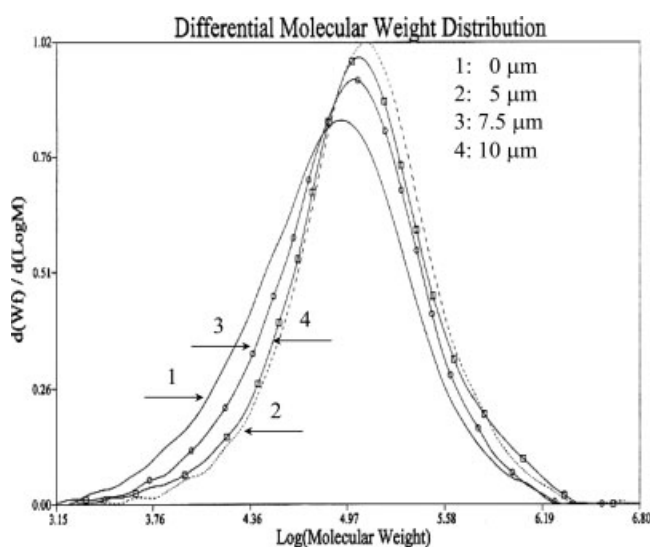


Figure 14 Differential molecular weight distribution of untreated and ultrasonically treated EPDM gums.

TABLE II

Molecular Weights and Molecular Weight Distribution of Untreated and Ultrasonically Treated EPDM Gum

Sample	M_n	M_w	M_w/M_n
0 μm	39,700	137,000	3.45
5 μm	73,300	198,400	2.71
7.5 μm	53,000	157,600	2.97
10 μm	62,300	201,000	3.23

The MWD curves of the EPDM gum after ultrasound treatment are shown in Figure 14. The weight and number average molecular weights and MWD are shown in Table II. It is seen that the ultrasonic treatment of the samples shifts the MWD curves and the average molecular weight of the EPDM samples to the higher molecular weight leading to increase the molecular weight averages. However, the change of MW and MWD as a function of the ultrasonic amplitude is not simple linear function. It should be pointed out that the GPC results do not completely reflect the molecular weight properties of the whole sample because a crosslinked portion (gel) is filtered out prior to injecting sample solution into the GPC columns. Even though the sol part of EPDM is utilized in the GPC measurements, one can see the changes of M_w , M_n , and MWD. The highest M_w and MWD are shown by the EPDM gum treated at 10 μm . At the same time this sample shows the lowest torque on cure curve (Fig. 3) and the lowest complex viscosity (Fig. 4). This seems to be contradictory in view of high molecular weight for this sample. However, one should recall that this sample had the lowest amount of gel among the treated samples. This can explain the contradiction.

However, similar effects were reported by Watanbe and coworkers²⁹ at high speed stirring of EPDM solutions. They reported an increase of M_w and M_n and a decrease of MWD from 5.0 to 3.1. Evidently, both high-speed stirring and ultrasound treatment reported here cause a mechanochemical breakage of polymer main chain (random chain scission) leading to radical formation. Because of the radical formation during chain scission, broken chains can reconnect different chains or react within chains to form crosslink (gel) and branch structure.³⁰ As a result, one is likely to obtain a higher molecular weight sample after ultrasound treatment due to a possibility of formation of the branched structure of polymer chain.

CONCLUSION

Structure and physical properties of EPDM gum and their vulcanizates can be controlled using the ultrasonic treatment. It is shown that during ultrasonic treatment of EPDM gum a certain amount of gel can

be formed. The amount of gel depends on parameters of the process. Maximum of the gel formation occurs in the gum ultrasonically treated at amplitude of 5 μm . Therefore, the tensile modulus and hardness of EPDM vulcanizates obtained from ultrasonically treated gum is higher at amplitude of 5 μm with tensile strength being practically intact. With an increase of ultrasonic amplitude, random scission of backbone chain is predominant over the gel formation reaction. One can conclude that there are competing reactions of the gel formation and degradation during the ultrasonic treatment. Also, due to imposition of the ultrasonic waves, mechanochemical reaction occurs in EPDM gum that changes structure of EPDM molecular chains. Gel formation reaction, the random chain scission and branching of EPDM chains possibly occur.

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