The Effect of Physical Treatments of Waste Rubber Powder on the Mechanical Properties of the Revulcanizate

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ABSTRACT: The diversiform physical treatment processes of waste rubber powder were carried out using grinding process, ozone treatment, and ultrasonic treatment. The effects of these processes on hardness, specific gravity, crosslink, tensile strength, elongation, and dynamic mechanical properties were studied. Also, the morphology and the chain structure changing of waste rubber powder were studied by SEM and XPS, respectively. The ozone/ultrasonic treatment was found to be the most effective treatment to improve the mechanical properties of waste rubber powder revulcanizate. The effect of mechanism may be due to the sulfur crosslinkage network changed to a cyclic form. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3048–3056, 2009

Key words: physical treatment; waste rubber powder; ozone/ultrasonic treatment; cross-linkage network

INTRODUCTION

The large number of waste tire has become a significant problem with the increase in the number of automobiles each year. Many attempts[1–3] to recycle waste tire have been undertaken for environmental reasons. The recycling of the waste tire can be divided into three categories: its use as source of heat through incineration, the original shape, and grinding of waste tire to increase mechanical properties. One of the main approaches to rubber recycling is reclaiming or devulcanization. It took a long time to develop several kinds of recycling waste tire including microwaves,[4] bioreactor,[5] milling,[6] and devulcanization techniques.[7,8] Landfill is one of the early ways to dispose discarded rubber products. In 1970, ~ 70% of the scrap rubber was discarded into landfill. With decreasing available sites and cost increase, disposing waste tire into landfill is rapidly being discarded.

Scrap rubber is commonly used as a fuel in the cement industry. The shredded tire chips were burned in the boilers. Tire contains more than 90% organic materials and have value of 32.6 mJ/kg when compared with coal (18.6–27.9 mJ/kg).

In the microwave technique,[9,10] a controlled microwave energy at a specified frequency and energy level is released with sufficient energy to cleave sulfur crosslink bonds. Thus, in this process, waste elastomer can be reclaimed without depolymerization to a material capable of being recompounded and revulcanized having physical properties essentially equivalent to the original vulcanizate. Ultrasonic energy is being used for surface modification. The process involved devulcanization of crosslinked rubber. Pelofsky[11] reported the first work of ultrasonic energy in 1973 and was patented. However, information on the ultrasonic properties of the devulcanized rubber was not mentioned. Ultrasonic reclaiming of vulcanized natural rubber (NR) was reported by Okuda and Hatano[12] in 1987. Later, Isayev et al. published a number of articles about the ultrasonic process.

The advantage of powder utilization is that it is easy to apply by using simple equipment. Although much work[13–16] has been done, problems still remain. The difficulty in recycling waste tire is that the scrap of the tire is a crosslinked polymer, which is hard to melt and process. Generally, methods of obtaining the powder from the waste tire are cryogenic grinding[17] and ambient grinding. In cryogenic grinding, shredded tire are frozen with liquid nitrogen. The cryogenic ground rubber has a smaller particle size and lower surface area when compared with an ambient ground rubber, but cryogenic

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TABLE I
Formulation of Waste Tire Powder

Weight of rubber kinds (%)		Thermal Composition (%)	
NR[a]	40	Hydrocarbon	59.8
SBR[b]	15	Carbon black	27.8
BR[c]+IIR[d]	45	Ash	8.3

[a] Natural rubber.
[b] Styrene butadiene rubber.
[c] Butadiene rubber.
[d] Butyl rubber.

grinding has more process expense than ambient grinding.

The most common surface treatment for materials is introducing oxygen-containing functional groups onto the surface of the materials. Oxidation can be achieved by air, oxygen, or ozone.[18] This can be achieved by using ozone or ultrasonic treatment. The ultrasonic waves at a certain level in the presence of pressure and heat rapidly break up the three-dimensional network in crosslinked rubbers. The mechanism that causes the degradation of crosslinked elastomers is still in debate. However, it is believed that most of the physical effects caused by ultrasonic waves are usually attributed to cavitations, the rapid growth, and contraction of microbubbles as high intensity sound waves propagate in the rubber.[19–21] The application of the ozone/ultrasonic technique is the most modern process of devulcanization, which is based on the ultrasonic devulcanization technique. This technique can be applied in continuous process for waste tire treatment and can possibly increase the mechanical properties.

The development of suitable technology in waste rubber recycling is an important issue faced by the rubber industry. Thus, the objective of the study is to produce high-valued product from a cheap waste tire with improved properties. An efficient grinding machine was first designed in our laboratory and used in the powdering of waste rubber tire. Subsequently, ozone/ultrasonic devulcanization were applied onto the surface of waste tire powder. The ultrasonic reactor was attached to the die of the extruder making it a continuous system. Furthermore, an attempt to produce good and economically rubber ballast-mat and rubber block using surface-modified rubber powder was also studied.

EXPERIMENTAL

Materials

In this study, the large size of rubber powder (30–40 mesh) was used to make a fine powder, which was donated by Korea Resources Recovery and Reutilization Corporation (KORECO, Inchon, Korea). The rubber tire powder has the following composition: hydrocarbon, 59.8%; carbon black, 27.8%; ash, 8.3%; acetone extractable volatiles, 4.1%; as shown in Table I. The materials composition of the waste tire are also summarized in the same table.

Preparation of the grinding machine

A self-designed grinding machine (SDGM) used in this study is shown in Figure 1. The grinding machine has dimensions of 427 cm × 150 cm × 325 cm with rotating speed of 11,000 rpm. The machine is used for obtaining fine rubber particles for efficient recycling waste tire and to make high-valued products.

Preparation of the powdered rubber

The large size of waste rubber powder was ground using SDGM. The advantage of this technique is that we can obtain a fine elastic rubber powder economically. The rubber powder obtained from this machine have polydispersed particle sizes, and the these particles are in the average size of 50 mesh.

Ozone/ultrasonic treatment GRT powder

After grinding the GRT powder by SDGM, the sample was treated with ozone generated in dry oxygen in an ozone generator (Pacific Ozone). These powders were fed into the extruder with $L/D = 30$ equipped with ultrasonic die attachment. Schematic drawing of ozone/ultrasonic reactor is shown in Figure 2. A 10-kW ultrasonic power supply, a converter, and a booster were used to provide the

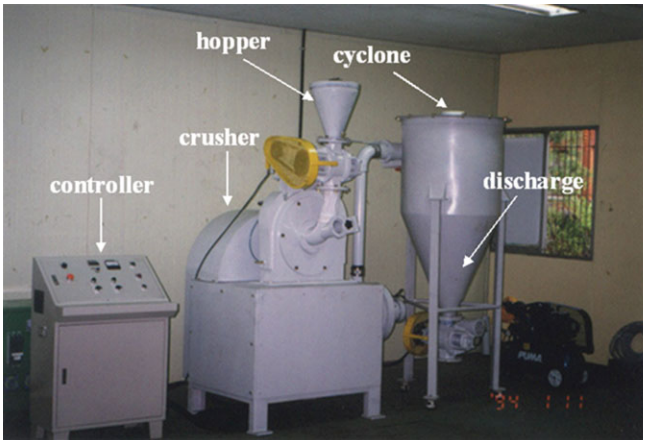

Figure 1 Self-designed grinding machine (SDGM). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

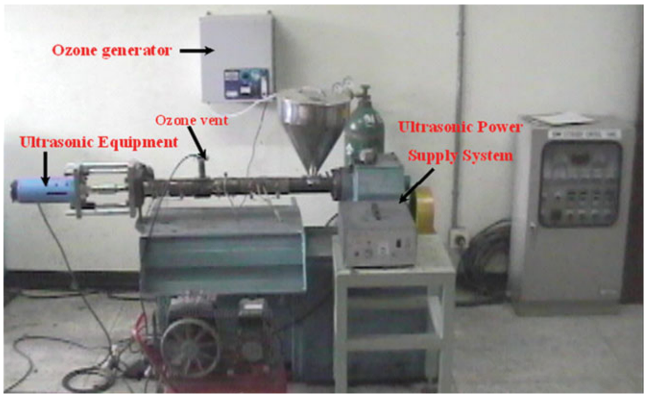

Figure 2 Photograph of ozone/ultrasonic reactor.[22] [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

longitudinal vibration of horn with a frequency of 20 kHz. The devulcanized samples were obtained at various processing conditions. The properties of GRT rubber powder are dependent on the extruder flow rate and temperature. The rubber flow rate in the process was controlled by screw speed. A die gap varied 1–3 mm with radius of 30 mm was used in this experiment. As shown in Figure 2, a die was attached to the extruder at the nozzle from the devulcanization section, which is an important factor for devulcanization.

Rubber sheet from GRT powder

The compression-molded of untreated and ozone-treated GRT powder sheets were carried out after mixing in a stirrer. The mixture was compressed by hot-press with 50 tons hydraulic capacity to produce a rubber sheet at a temperature of 150°C. The crumb rubber compound was cured in 150°C for 15 min. After storing the rubber sample for 1 day, the dumbbell type-3 shape specimen was prepared for mechanical testing.

Material characterizations

Methods of mechanical measurement

The tensile properties were determined using a UTM (Instron series IX Automated Materials Testing System 7.25) equipped for tensile strength and elongation, and tear strength in accordance with KSM (Korea Standard Method) 6518. The instrument was operated at 500 mm/min crosshead speed with a 10 kN load cell. The hardness measurement was carried out using a spring type (Shore A) durometer, and the value was determined by the average of four experimental results.

Scanning electron microscopy

The morphology of the gold-coated GRT particle surface was observed with a Hitachi S-415A SEM at an accelerating voltage of 5 kV.

X-ray photoelectron spectroscopy

To measure the surface analysis of waste tire powders, the X-ray photoelectron spectroscopy (XPS) spectra were obtained using an XPS with a testing parameter of VG MT Clam 2 system and using Mg Kα photon source. An electron take-off angle of 37° was used. The binding energies of hydrocarbon component peak at 285 eV were used as reference.

Advanced rheometric expansion system

A circular specimen with diameter of 25 mm and 5 mm thickness was used to measure the dynamic properties using a Rheometric Scientific, Suffix-CE. The machine was operated at 5% strain amplitude at frequencies ranging from 1 to 100 Hz.

RESULTS AND DISCUSSION

Effect of grinding

Figure 3 shows the SEM photographs of Sa and Sb rubber powder showing differences in their particle

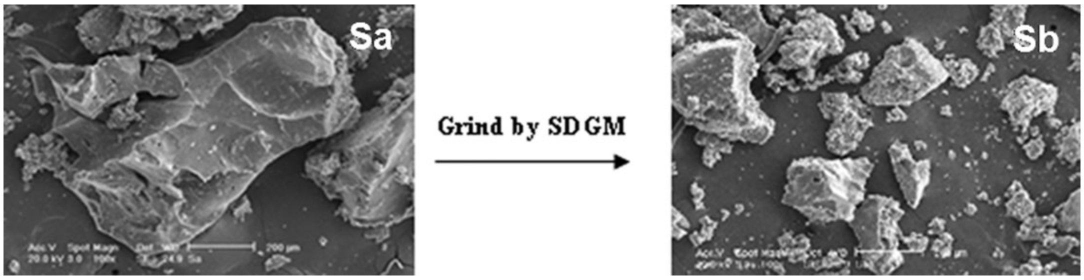

Figure 3 SEM photographs of different sizes of GRT powders: (Sa) before grinding and (Sb) after grinding by using SDGM.

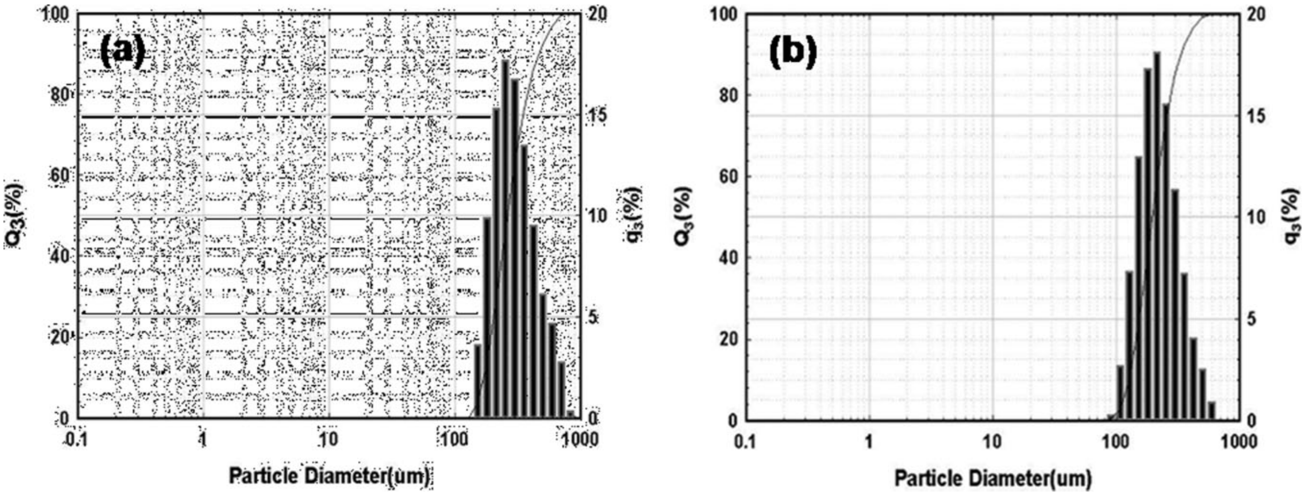

Figure 4 Comparison of the particle size distribution of waste tire powder: (a) before grinding and (b) after grinding.

size and sharpness surfaces. The code Sa and Sb denote before grinding and after grinding using SDGM, respectively. These photographs clearly indicate that Sb rubber powder has more regular shapes with smoother surfaces when compared with Sa rubber powder. This is due to the high-speed rotation of the grinding machine. The particles were crushed into small pieces and most of them lost their sharpness and properties. In this aspect, grinding technique may be the important factor in the physical properties of rubber powder. In addition, the crosslink densities of revulcanized with Sa and Sb powders will have different results because of the size reduction during grinding process. Because of the high shear stress, the chemical bonds were broken. This may be explained by the fact that the chain reactivities were increased in the end group of the broken chains of particles. It is also important to note the size distribution of the crumb rubber as shown in Figure 4. It can be seen that Sa rubber powder has slightly larger particle size and broader size distribution than Sb. Figure 5 shows that the tensile properties of untreated rubber powder were improved with decreasing particles size. This is because Sb has larger surface area than Sa rubber powder.

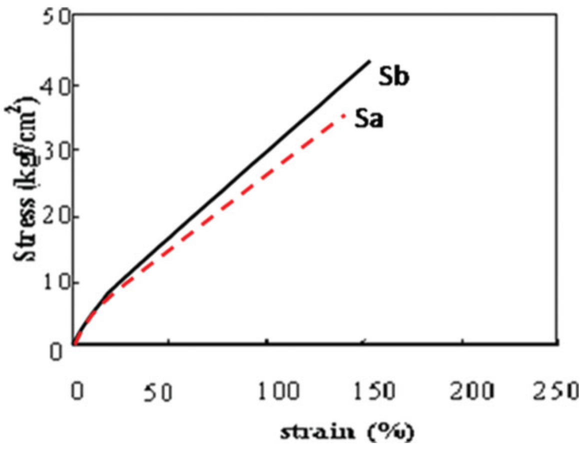

Figure 5 Stress–strain curves of revulcanizate of untreated rubber powders. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of ultrasonic treatment

The change in structure also affected the revulcanization of waste rubber powder, which leads to the changes of molecular structure as shown in Figure 6. The crosslink density of revulcanized samples was also determined by swelling test, and the results are summarized in Table II.

The fine rubber powder (Sb) was used to determine the effect of ultrasonic treatment because it has better mechanical properties than Sa rubber powder. Figure 7 shows the conditions of ultrasonic

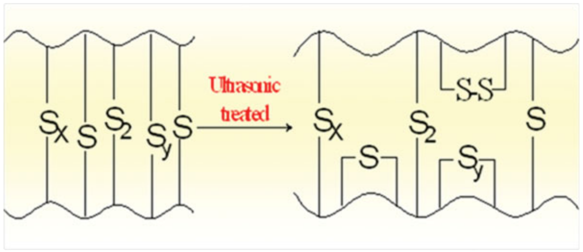

Figure 6 Structural feature of a sulfur-vulcanized rubber by devulcanization.[23] [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Physical Properties of Revulcanized Rubber After Curing

	Samples			
Physical properties	Before grinded (Sa)	After grinded (Sb)	Ultrasonically treated (Sb-U)	Ozone/ultrasonically treated (Sb-O/U)
Hardness, Shore A	71.5	74.5	68.2	69.3
Specific gravity	1.13	1.15	1.11	1.12
Crosslink density (mol/cm^3)	1.613×10^{18}	1.777×10^{18}	1.858×10^{18}	1.907×10^{18}
Tensile strength (MPa)	3.2	4.2	4.7	5.1
Elongation (%)	135	148	155	160

experiment applied in this work. The amplitude of the power supply, pressure, temperature, feeding speed, and gap distance were the main operating parameters affecting the degree of devulcanization. It was observed that the very fast processing occurred in the devulcanization zone (10–20 g/min). Because the temperature effect on the rubber viscosity is complicated, the pressure in the treatment zone was used as the parameter in this study. Processing parameters during devulcanization strongly affected the mechanical properties of rubber powder. Figures 8 and 9 show the tensile properties of untreated rubber powder samples and ultrasonic treatment rubber powder with variable depths of the gap. The results show that the tensile properties of revulcanized samples after ultrasonic treatment were increased. This could be explained by the change in the molecular structure as shown in Figure 6, which leads to increased reactivity of the powder. It is known that during sulfur vulcanization, the sulfur forms structurally different intermolecular bonds and accordingly modifies the main chain. Campbell[24] reported that poly-, di-, and monosulfidic sulfur-vulcanized rubber of crosslinks strongly depend on the sulfur that act as accelerator in the compound. It is also known that in the process of devulcanization by different methods such as heating or thermomechanical treatment and the cleavage of polysulfidic crosslinks is accompanied by a significant increase in the mono and disulfidic crosslinks. Usually, the devulcanization of rubber occurred in the gap between the flat face of the horn and die plate in a reactor and between the horn and screw in the barrel reactor. The results of tensile properties for revulcanized rubber powder treated with ultrasonic at different gap depths were compared as shown in Figures 8 and 9. The most effective system in the tensile strength was observed when 1-mm gap depths were used because of the increasing ultrosonic power with decrease of die gap.[25] However, this was not the case in elongation at break. There was no difference in their elongation at break. Figure 10 shows the comparison of storage modulus (G') of the untreated and ultrasonically treated rubber-vulcanized sheet. This data suggests that the transformation of polysulfide links to mono-, di-, and cyclic sulfide links is the reason for the increase of storage modulus.[26,27] This may be due to the increase of mobility after ultrasonic treatment and again revulcanization. The principal route to this main-chain modification is thermal decomposition of polysulfidic crosslinks by ultrasonic reactor.

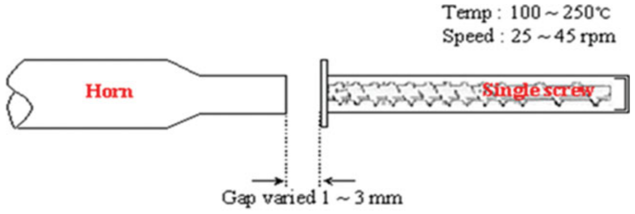

Figure 7 Experimental conditions of ultrasonic treatment. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

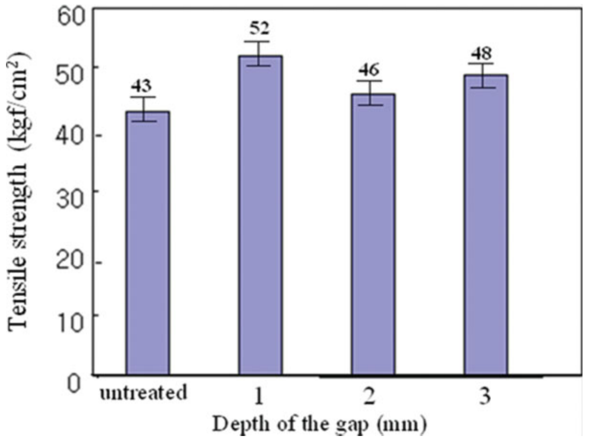

Figure 8 Tensile strength of the revulcanizates of untreated waste rubber powder and ultrasonic treatment with variable depths of the gap. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

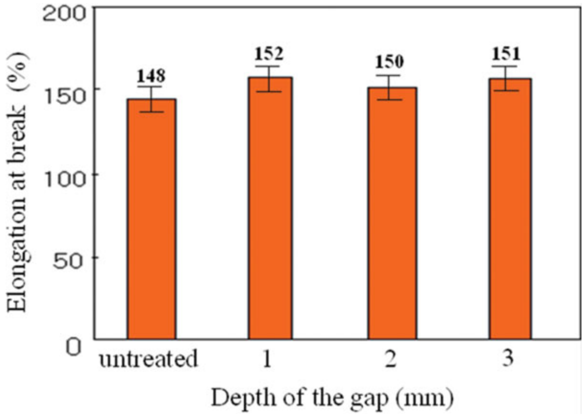

Figure 9 Elongation at break of the revulcanizates of untreated waste rubber powder and ultrasonic treatment with variable depths of the gap. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

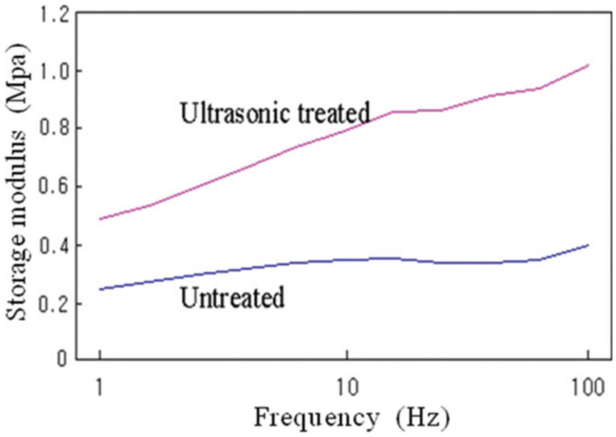

Figure 10 Storage modulus of untreated and ultrasonically treated revulcanized rubber sheet. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

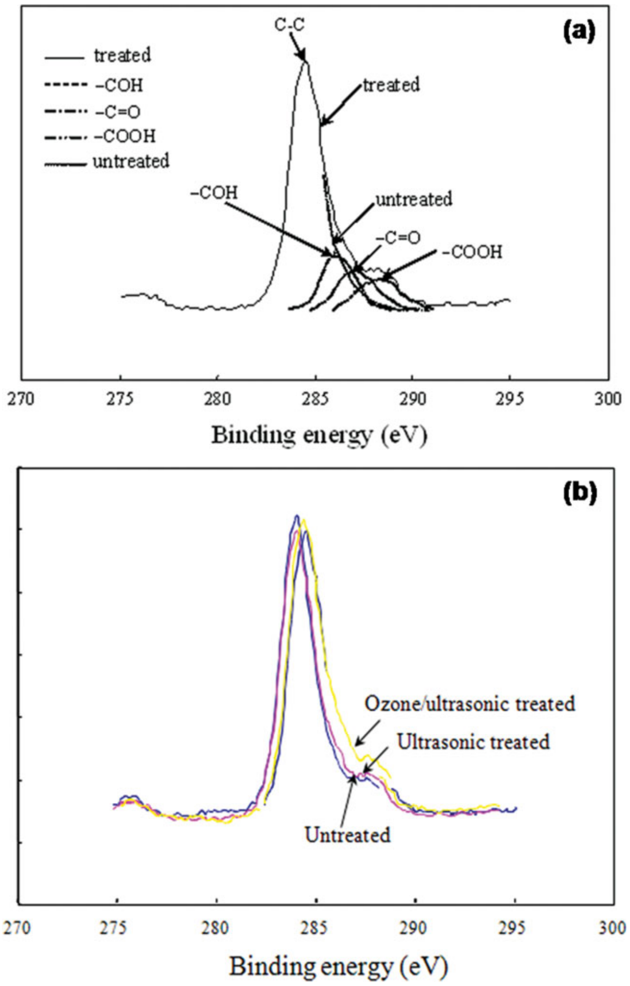

Figure 11 Carbon 1s XPS spectra of untreated ultrasonically treated and ozone/ultrasonically treated: (a) appearance of surface functional group by treatment and (b) compared with various treatments. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Ozone/ultrasonic treatment

The previous treatment was studied by Isayev's group.[28,29] Further investigations tried to find out the best modification method on the rubber powder. Normally, ozone attacks the double bond of the vulcanized chain. The ozone treatment tool was attached to the ultrasonic extruder (Fig. 3). The results of C1s XPS spectra were used to compare the effect of the treatments on the rubber powder. The tail on the high binding energy side of the main C1s peak shows that incorporation of oxygen onto the rubber surface gives rise to a variety of functional groups such as —COH, —C=O, and —COOH which correspond to binding energies of 286.1, 287.6, and 289.1 eV, respectively, as shown in Figure 11(a). Even though it is not easy to choose exact oxygen-functional groups from the XPS spectra, earlier studies reported that polar characteristics of a rubber surface increased with increasing amounts of oxygen-functional groups. Figure 11(b) shows the different functional group intensities. There was an increase in the extent of surface oxygenation with rubber treatment time under the same ozone flow rate (10 g/h). It is noticed that these experiments were dependent on the feeding speed of the extruder because of the continuous processing of ozone/ultrasonic system. Generally, a tire was used for 5 years. Therefore, these waste tires were already attacked by ozone in the environment for a long period of time. It further shows that the untreated waste tire-functional groups increases. However, ozone/ultrasonic treatment of rubber powder was found to increase the surface oxygen concentration,

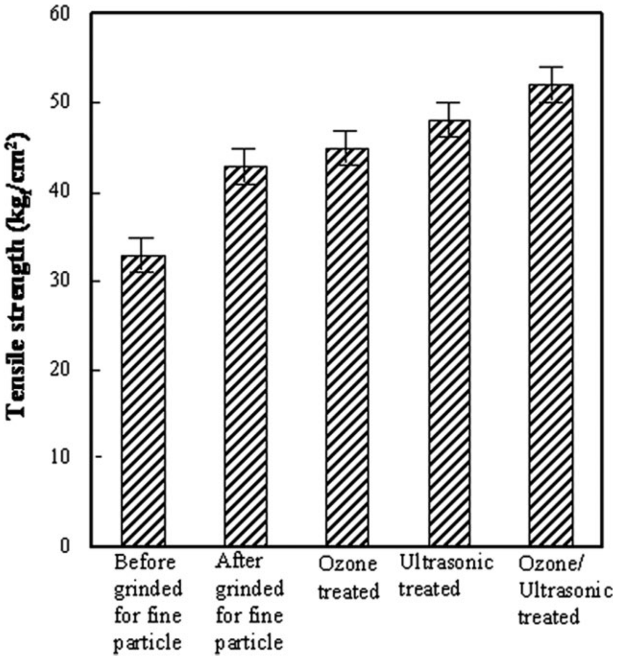

Figure 12 Comparison of tensile strength of revulcanized rubber sheet after curing.

wherein the rubber was treated simultaneously with both ozone and ultrasonic at a temperature of 150°C. In this process, the rubber powders have greatly improved the effectiveness of rubber powder in reinforcing with each other.

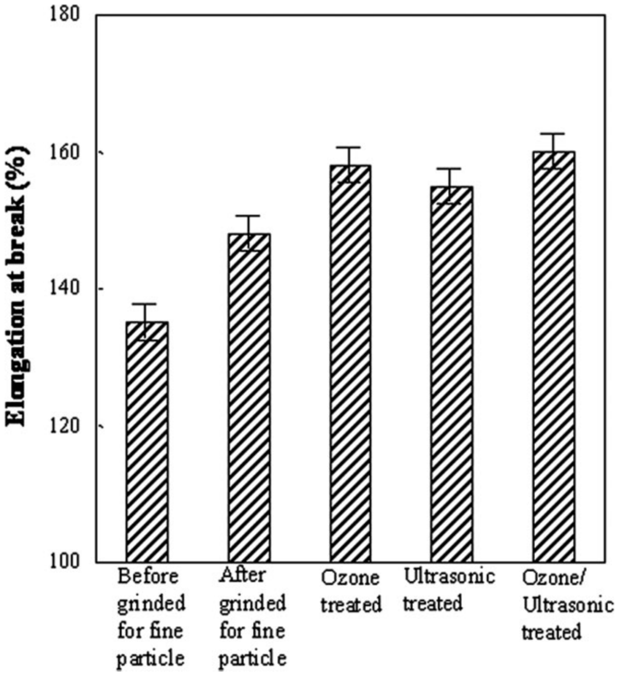

Figure 13 Comparison of elongation at break of revulcanized rubber sheet after curing.

Effect of the different physical treatments on the properties of revulcanized rubber

The rubber powder with different modifications method was sheet-molded and cured at 150°C. The

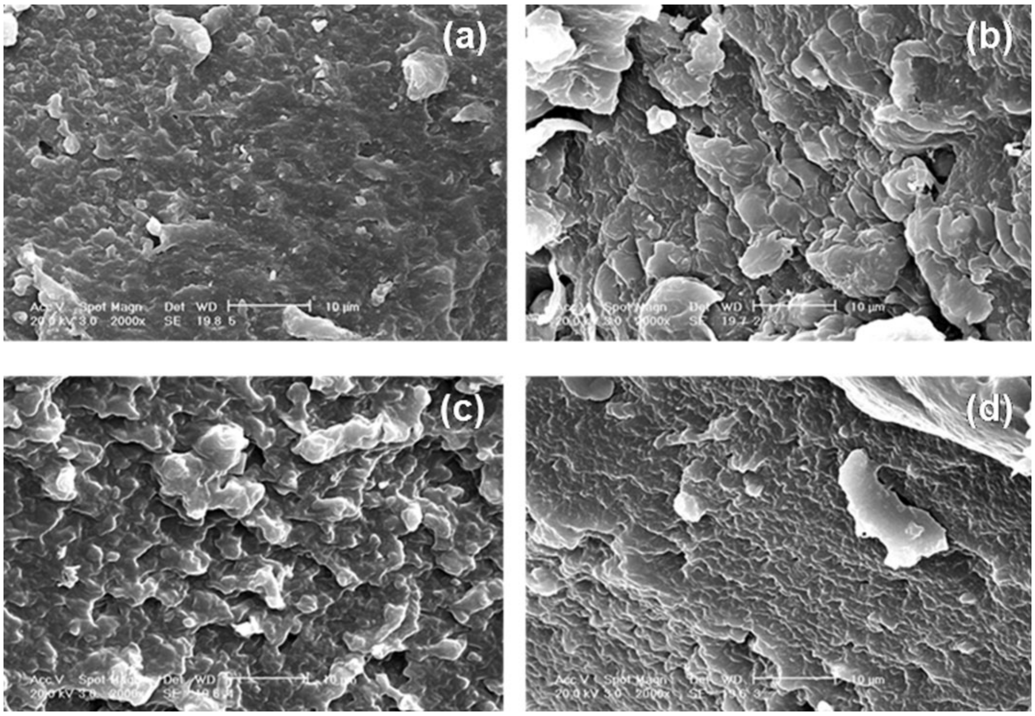

Figure 14 SEM photographs of waste tire powder particle: (a) untreated, (b) ultrasonically treated, (c) ozone treated, and (d) ozone/ultrasonically treated.

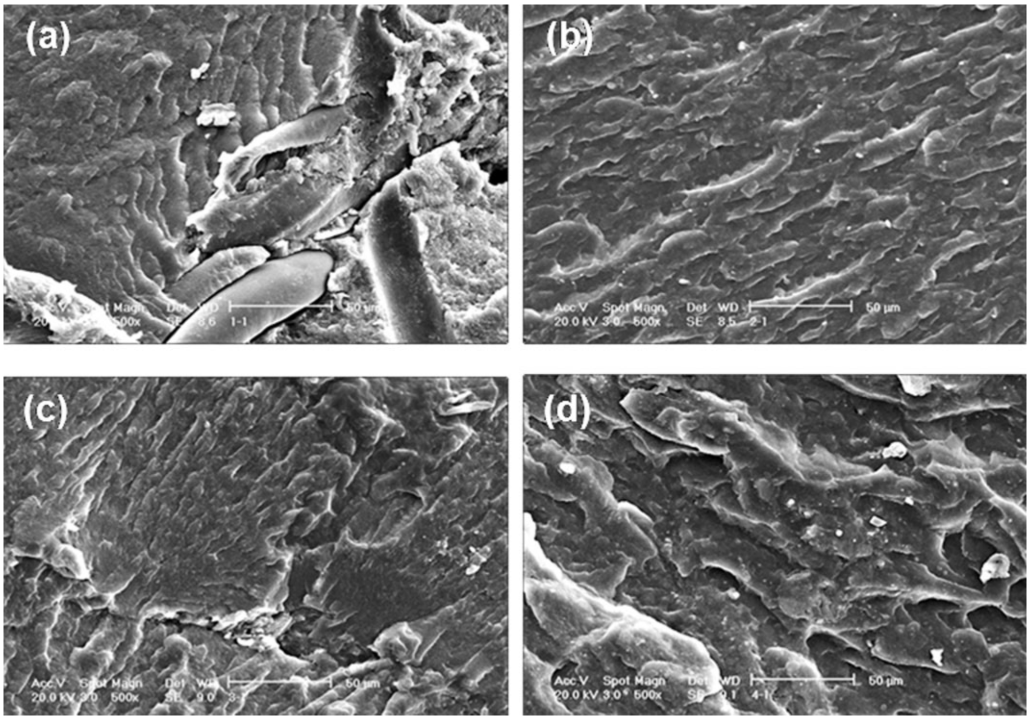

Figure 15 SEM photographs of waste tire sheet after revulcanization: (a) untreated, (b) ultrasonically treated, (c) ozone treated, and (d) ozone/ultrasonically treated.

comparison of tensile strength of revulcanized rubber sheets is shown in Figure 12 and Table II. As mentioned earlier that after grinding the rubber powder into fine particles, the tensile strength increased observably. The tensile strength further improved when the powder was ozone-treated and ultrasonically treated. Combination of ozone and ultrasonic treatment on the surface of rubber power gave a better tensile strength than single treatment. The results of elongation at break have similar trends; although the combination of two treatments is almost the same with ozone treatment (Fig. 13 and Table II). The ultrasonically treated powder show lower elongation at break when compared with ozone treated and ozone/ultrasonically treated. Figure 14 shows the SEM micrographs of untreated waste rubber powder particle and different surface modification methods. The figure shows that the surface of tire powder treated by devulcanization is rougher than untreated tire powder. The comparative observation of waste tire sheets after revulcanization [see Fig. 15(a)] untreated and different treatments [Fig. 15(b–d)] demonstrated quite clearly the effect of surface modification methods on waste tire sheets. The rougher surface indicated the enhanced mechanical properties after revulcanization because of the increase of surface energy (Fig. 15).

CONCLUSIONS

The effects of physical treatments of waste rubber powder on the mechanical properties of the revulcanizate were studied. The small size of waste rubber powder showed better mechanical properties than the big one. The 1-mm gap length showed the most effective tensile strength when using ultrasonic treatment. The mechanical properties of this study using ultrasonic and ozone combination treatment system was considered the best process method to fabricate revulcanizates.

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