The Biological and Chemical Desulfurization of Crumb Rubber for the Rubber Compounding

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ABSTRACT: The disposal of used car tires has become a major environmental problem, especially in densely populated countries that use motor vehicles as the principle means of transportation. Widespread recycling of waste tires has not taken place because it has not proven to be cost effective. Although there are obvious environmental reasons for recycling waste tires, to date it has not proven to be economically valuable. The aim of this study is to find a more economical way of recycling used car tires. This was done by the "unvulcanization" of vulcanized crumb rubber by two different treatments; chemical treatment with di-(cobenzanidophenyl)disulfide, and microbial treatment with *T. peromatabolis.* The experimental results indicate that the processing of crumb rubber, as well as the end-product properties, were enhanced by both these treatments, with the microbial treatment being the most effective. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1543–1549, 1999

Key words: desulfurization; crumb rubber; rubber compounding

INTRODUCTION

Vulcanizing technology has brought significant improvement to the rubber industry since Charles Goodyear successfully applied the process in 1841. Most rubber articles cannot be made without vulcanization, because unvulcanized rubber does not maintain its shape after a large deformation, and it can be very sticky.[1] However, vulcanization poses a problem to the recycling field when the recycling has become one of the most important issues through the world. For example, recycling waste tires falls into this category, because of the severe environmental problems that they cause.

The question, now, is why the vulcanized material is hard to recycle, and how do we recycle with this material? The main reason is that the vulcanized materials are difficult to melt or dissolve by simply heating. These materials, therefore, are compounded with a virgin material to improve mechanical performance or to reduce the cost.

Unfortunately, much research work has reported that the mechanical performance is impaired by the addition of vulcanized crumb rubber. This is thought to be caused by the low interfacial force between the crumb rubber and virgin polymer matrix. By removing the sulfur bond in the crumb rubber, thereby unvulcanizing it, there is less of an impairment in the mechanical performance in the rubber compound formed.

Unvulcanization is defined as being "the removal of the sulfide function in the polymer chain, completely or partially, which is formed during vulcanization."[2] A number of methods for the unvulcanization of rubber have been reported. For

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Table I Composition of Scrap Tire Used in This Study

Composition	Content (phr)
Polymer Base (NR)	100
Carbon Black	78.3
Additives	
Total	32.7
Oil	18.4
Sulfur	3.0
Accelerator	2.1
Antidegradant	1.8
Stearic acid	0.7
Wax	0.6
Ash	6.1

example, the chemical reagent triphenyl phospine, changes polysulfide into monosulfide or dissulfide.[3] Saville and Watson[4] removed polysulfide bonds with propanethiol and piperidine. Campbell[5] effectively removed disulfide and polysulfide bonds by using hexane-1-thiol. By treatment with dithilthreol, Goethals[6] changed disulfide bonds into thiol group bonds. Gregge and his coworkers[7] removed polysulfide and disulfide bonds from vulcanized polybutadiene by treatment with polylitium. Methyl iodide has also proved to be effective for unvulcanization.[8]

Unvulcanization has also been achieved with the use of a microbial agent; *Thiobacilus* has been shown to be particularly effective.[9,10] However, microbial treatment has not been popular for commercial methods compared to chemical treatment, because it is hard to control circumstances with microbial agents.

Normally, unvulcanized rubber has been recycled as a tool of compounding such as reinforcing material. However, it is often pointed out that weak mechanical properties pose a problem for a final product. Furthermore, recycling brought processing problems when it was compounded with virgin rubber.

This article involves the development of new rubber blends based on natural rubber, which have been produced by mixing recycled crumb rubber in a powder form as a filler. To do this, the first step is unvulcanization of crumb rubber, and the second step shown demonstrates its recyclability by blending with virgin natural rubber.

For the first step, this article shows the results that were achieved by using both chemical and microbial treatments for unvulcanization of crumb rubber.

The chemical reagent that was in chemical treatment was di-(cobenzanidopheny)-disulfide, and it enabled the polysulfide bond from polymer chain to be destroyed. In the microbial treatment, *T. perometabolis* was used to removed the sulfur function in the polymer.[11–13] The results indicated that the mechanical performance of the rubber compounds thus produced was enhanced by using either the chemical or the microbial-treated crumb.

For the second step, the vulcanized crumb was blended with a natural rubber, and compared its properties to the unvulcanized crumb-filled blend. Blending with the unvulcanized crumb improved the mechanical performance of the rubber blends. One more thing of advantage with using unvulcanized crumb is to make the rubber recycling process easier.

Our future work will involve producing new rubber products to apply with unvulcanized recycled rubber.

EXPERIMENTAL

Materials

We used an ambient crumb rubber form obtained from waste tires, the particle size range being smaller than 0.1 mm. Our chemical analysis of the crumb rubber is summarized in Table I. We studied both a chemical treatment and the microbial treatment of the crumb rubber: di-(cobenzanidophenyl)-disulfide for chemical treatment, and *T. perometabolis* for the microbial treatment.

The natural rubber compounds were made for measuring the mechanical performance (the recipe is shown in Table II).

Treatment of Crumb Rubber

In the chemical treatment, 5 g of “Neospagnol T-20” were mixed with 100 g of crumb rubber powder using an agitator at room temperature for

Table II Recipe of Natural Rubber Compounds

Composition	phr
Natural rubber	100
Stearic acid	3
Zinc oxide	5
Benzothiazyl disulfide	0.6
Sulphur	2.5

Table III Nutrients of *T. perometabolis*

Component	Concentration (g/L)
Yeast extract	5.0
$Na_2S_2O_3 \cdot 5H_2O$	5.0
KH_2PO_4	1.5
Na_2HPO_4	4.5
$MgSO_4 \cdot 7H_2O$	0.1
NH_4Cl	0.3

24 h. After agitation, the powder was washed by tap water and dried in an oven.

For the microbial treatment, first we made a nutrient summary in Table III. We injected *T. peromatabacilus* after insertion for 15 min at 100°C and 1.2 atm. The fermentation was carried out in a shake flask maintained at 30°C and 150 rpm. Then 10 g of the crumb rubber was put into 500 mL of nutrient in 1000-mL shake flask, and insected for 15 min at 100°C and 1.2 atm. Then it was put it into 20 mL of 700 mg/L nutrient at 30°C, maintaining 150 rpm. The treated rubber powder was washed for 12 h by tap water and dried for 24 h in the oven. The procedure of the microbial treatment is shown in Figure 1.

Prepare the Specimen

The procedure for mixing of the natural compounds was carried out in an internal mixer according to ASTM D 3192-89. Then the rubber compound was compression molded at 150°C for 10 min. The compressed sheet was cut into a dumbbell shape.

Test Methods

We measured hardness by using a shore-durometer. Tensile tests were carried out at room temperature, with a head speed of 300 mm/min. The optimum cure times of each compound were measured by using a Curometer.

Measurement of Crosslink Density

We used a swelling method for measuring crosslink density. The procedure is as follows: first, we put 0.1–0.3 g of the rubber into *n*-heptane for 72 h. The samples were washed, then weighed. Second, we dried the samples at 60°C in an oven for 24 h (deswelling) and weighed them again. To reduce error, we repeated this three times for each sample and averaged the results. Based on the experimental results, the crosslink density was calculated by the Flory-Rehner equation.[10]

Measurement of Sulfur Content

Sulfur content in the crumb rubber samples was measured to evaluate the degree of unvulcanization by chemical and microbiological treatment. We carried out this experiments by using a sulfur determinator.

Draw Growth Curve of Microbiology

T. peromatabolis (1 g) into 700 g/mL nutrient was put, and the optical density was measured every 3 h at 660 nm by using a UV spectrophotometer to draw its growth curve.

RESULTS AND DISCUSSION

Growth Curve of *T. perometabolis*

We measured the growth curves to find the optimum conditions of the *T. perometabolis,* which was used in the microbial treatment of the crumb rubber. The bacteria *Thiobacillus perometabolis* was cultivated in the shaker (the growth curve is shown in Fig. 2). The curve showed that there was

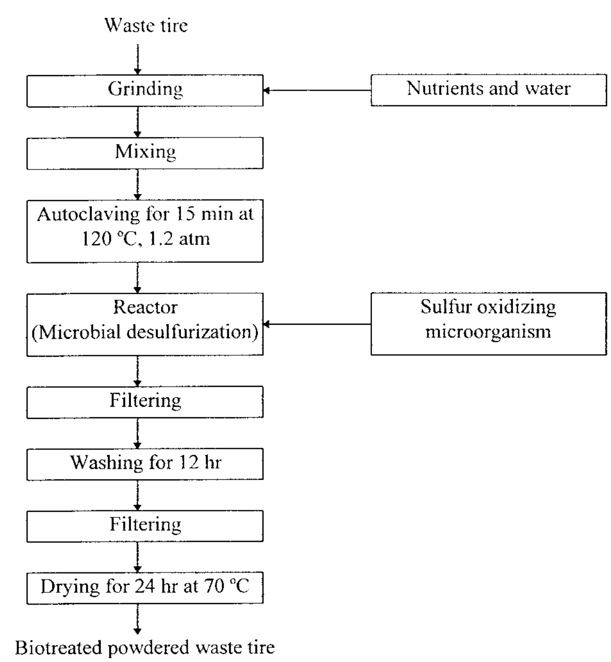

Figure 1 The microbial treatment of powdered waste tire.

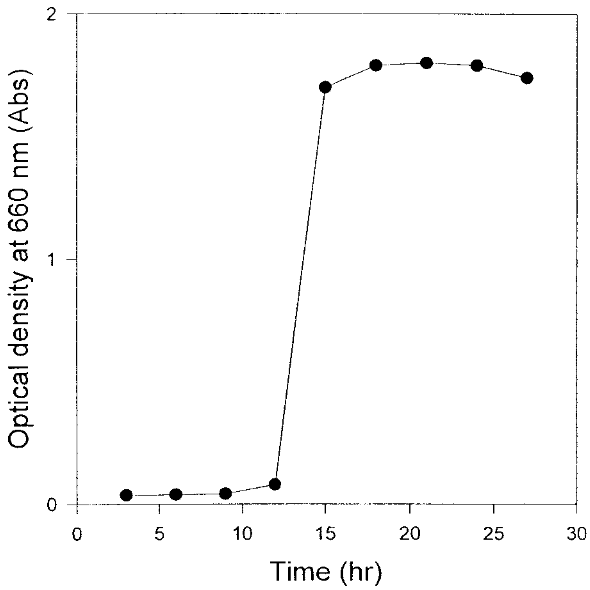

Figure 2 Growth curves of *T. perometabolis.*

an increase at the beginning, and than it flattened as a typical microbiologial growth curve. The activity time of the growth started from 12 h until 15 h to arrive at the top level of the curve after setting.

Change in Sulfur Content of the Crumb Rubber by Treatment

The sulfur content in the crumb rubber was measured to find the effect of the treatment of the crumb, which is summarized in Table IV. In the microbial treatment, the sulfur content was reduced with increasing treatment days. In the case of the 30-day microbial treatment, the sulfur content was reduced by up to 30% compared to that of the untreated crumb rubber. In the chemical treatment, the sulfur content of the crumb rubber was reduced 10% compared to that of the untreated crumb rubber.

Natural Rubber Compounds

The treated or the untreated crumb rubber was blended with natural rubber to investigate the effect of the treatment on the properties of the compound and on the processing. We evaluated the effect of the treatment by measuring the tensile properties, the optimum cure time, and the crosslink density of the samples.

Mechanical Properties

We compared the tensile strength and elongation of the untreated crumb rubber mixture with the treated crumb rubber mixture. The treatments were carried out by two methods—chemical and microbial. Figure 3 shows the effect of the chemical treatment compared to untreated crumb rubber with different loading content of the crumb. The result tells us to prevent reducing the tensile strength by the chemical treatment. The reason may explain that the interfacial force between the crumb rubber and the rubber matrix was strengthened by using the unvulcanized crumb rubber. Unvulcanization induced attachment to the double bond of the natural rubber compound. The vulcanized crumb rubber in the rubber blend is made as a stress concentration point when the external force is applied. Similarly to this, the longer treated time in the microbial example shows the better tensile strength, which is shown in Figure 4.

In comparing the chemical and the microbial treatments, less than 2.5 phr of the crumb rubber blend shows a similar value of the strength. However, when the crumb rubber blended more than 5 phr in the rubber compound, the microbial treatment is more effective than chemical treatment in maintaining tensile and elongation properties.

Processing

The optimum cure time is a very important variable in the recycle process. The vulcanized materials made difficulties in the process, especially vulcanizing. The effect of the crumb rubber on cure time was studied, which is shown in Figure 5. The cure time was shortened by adding a crumb rubber, as already reported by others.

This result indicated that the cure time was delayed by treatment of the crumb rubber. This means that the residual sulfur in the crumb rubber participated in the vulcanization of the natural rubber compounds. Therefore, the shorter mi-

Table IV Sulfur Content of the Crumb Rubber

Samples	Sulfur Content (%)
Untreatment	1.33
Chemical treatment	1.22
Microbial treatment	
Treated days	
5	1.22
10	1.17
20	1.12
30	0.88

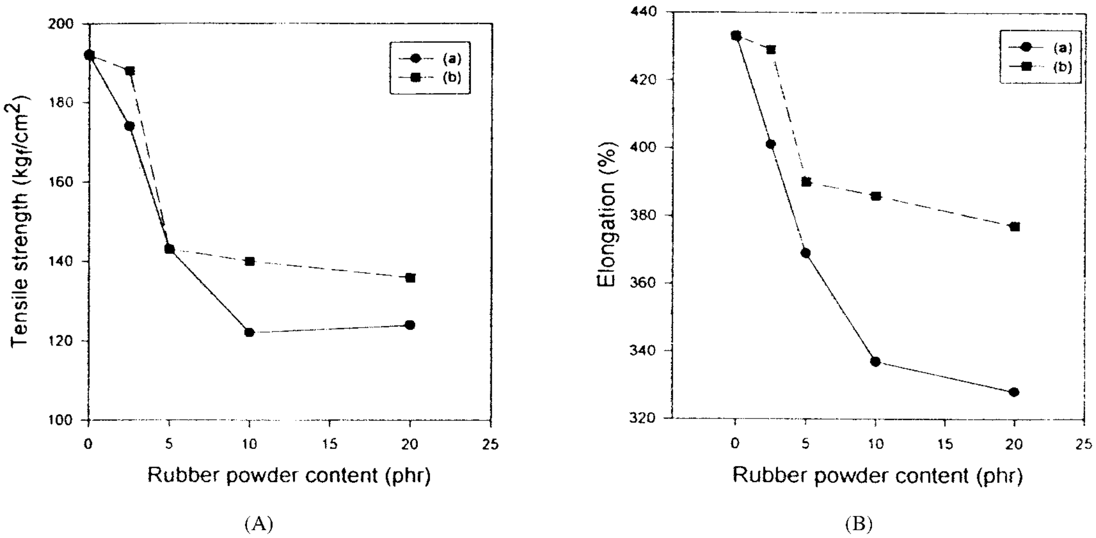

Figure 3 (A) Tensile strength vs. content of tire. (B) Elongation vs. content of tire: (a) untreatment; (b) chemical treatment.

crobial-treated crumb rubber made the shorter cure time (Fig. 6).

Actually, the vulcanization process is deeply related with crosslink density. The crosslink density of the rubber compounds increases linearly with an increase of the additional amount of the crumb rubber, as shown in Figure 7. The reason is that the crumb rubber contained sulfur, which leads to a higher value of crosslink density. The crosslink density of the treated crumb blend shows a lower value compared to that of the untreated crumb rubber blend. This phenomena tells us that sulfur chain is destroyed by treatment of the crumb. In the microbial treatment, the longer treated samples show the low crosslink density as same reason (Fig. 8).

These results tell us that remaining sulfur functions in the crumb participated in the vulcanizing reaction in rubber blending, which leads to processing problems because the vulcanization

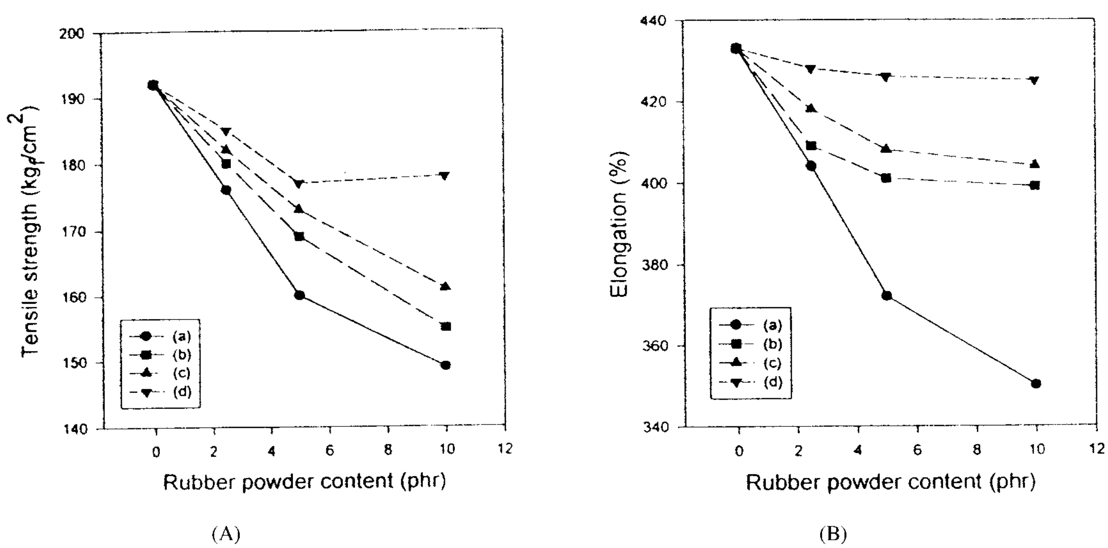

Figure 4 (A) Tensile strength vs. content of tire with different microbial treated days. (B) Elongation vs. content of tire with different microbial treated days: (a) treated for 5 days; (b) treated for 10 days; (c) treated for 20 days; (d) treated for 30 days.

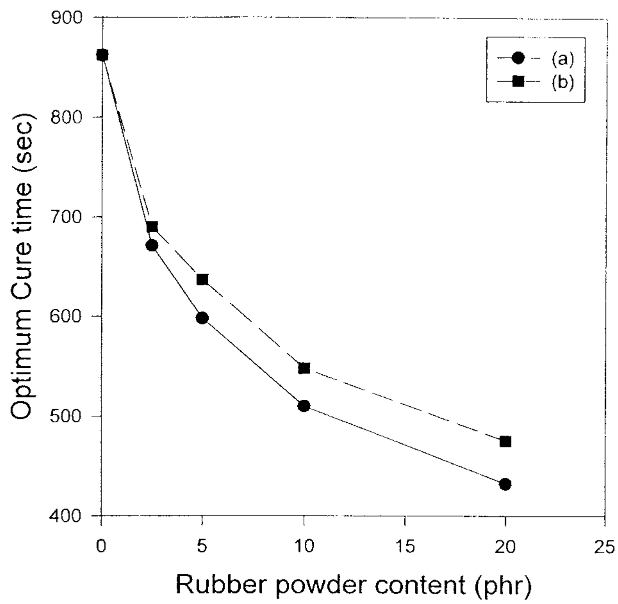

Figure 5 Optimum cure time vs. content of tire: (a) untreatment; (b) chemical treatment.

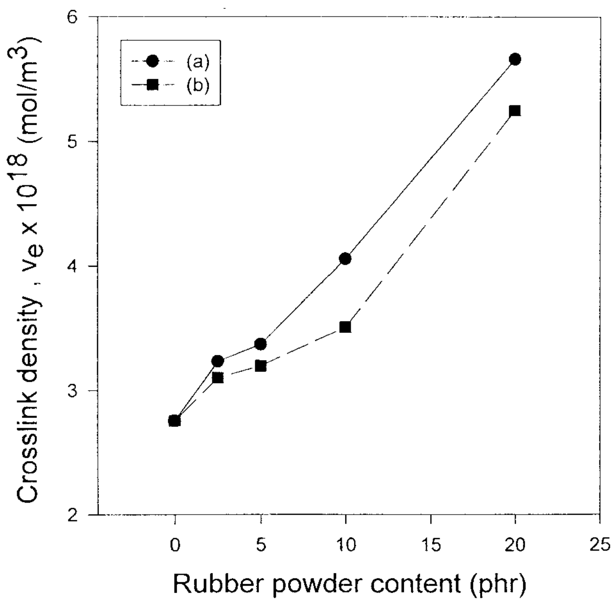

Figure 7 Crosslink density vs. content of tire: (a) untreatment; (b) chemical treatment.

process required exact conditions such as time, temperature, amount of sulfur, etc. In the case of recycling with crumb rubber, however, many variables with the crumb make operation conditions predictable to the operator, which leads to difficulty in determining the optimum processing conditions.

Therefore, the unvulcanized crumb rubber reduces the processing problem.

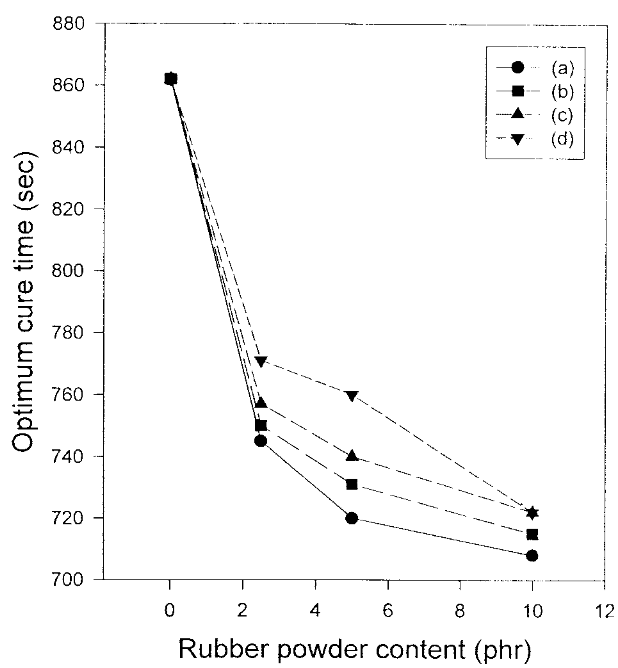

Figure 6 Optimum cure time vs. content of tire with different microbial treated days: (a) treated for 5 days; (b) treated for 10 days; (c) treated for 20 days; (d) treated for 30 days.

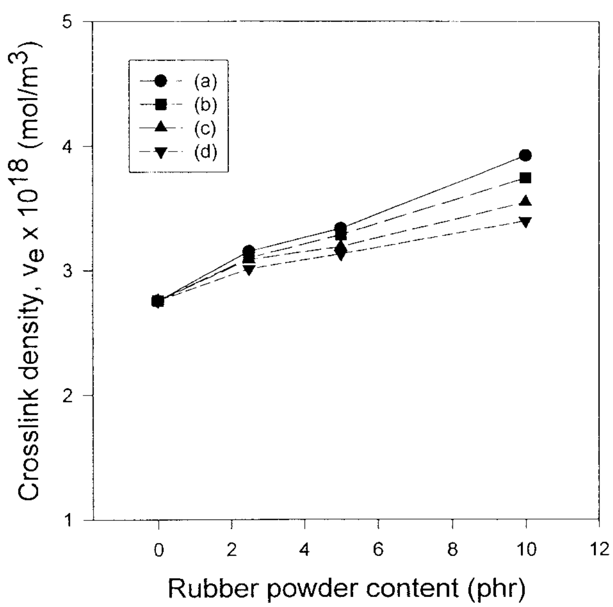

Figure 8 Crosslink density vs. content of tire with different microbial treated days: (a) treated for 5 days; (b) treated for 10 days; (c) treated for 20 days; (d) treated for 30 days.

CONCLUSION

The use of a vulcanized crumb rubber caused problems in recycling of the waste tires. Therefore, we tired to solve this with the unvulcanization technique for effective recycling.

This article described the unvulcanizing process by both chemical and microbial treatment. First, we characterized the crumb rubber and the unvulcanized. The sulfur content in the crumb rubber was decreased up to 8% by chemical treatment and 30% by a 30-day microbial treatment.

Next, we investigate the effect of the treatment on the recycled products. We used natural rubber compounds with the crumb rubber, which was obtained from the waste tires. The mechanical performance of the natural rubber compounds blended with the treated crumb rubber showed better than that of the blended with the untreated crumb. The best results showed up in the 30-day microbial-treated rubber blend, which has almost the same value of tensile strength of unfilled natural rubber compound in this system.

Optimum cure time of the rubber blends was shortened by adding the crumb rubber. By treatment of the crumb rubber the cure time of the rubber blends is longer compared to the untreated crumb in it, because the sulfur bonding of the crumb rubber is partially distorted in the rubber matrix. This was recognized by measuring the crosslink density of the rubber blends. The remaining sulfur in the vulcanized crumb rubber caused the processing problems. Therefore, the experimental results indicated that the removal of sulfur functions in the crumb by treatment leads to a reduction in the process problems in the compounding process with recycled material.

Therefore, we believe that unvulcanization of the vulcanized crumb has both technological and economical advantages for recycling.

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