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Half-Submerged Cultivation Method for the Microbial Desulfurization of Waste Latex Rubber

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ABSTRACT: The common method for microbial desulfurization is the submerged cultivation method. However, its cost is high because of the high consumption of the medium. To cut costs and improve the desulfurization effect, the new half-submerged cultivation method was used in the microbial desulfurization of waste latex rubber (WLR) by *Sphingomonas* species With this method, much more WLR was added per unit volume of the culture medium to be desulfurized, and the desulfurization process was done without stirring. The technical conditions, such as the addition of WLR, the addition of polysorbate 80 (Tween 80), and the desulfurization time, for the half-submerged cultivation method were studied, and its desulfurization effect was compared with that of the traditional submerged cultivation method. The results show that the optimum conditions for the half-submerged cultivation method were the addition of 40% w/v WLR in the medium without Tween 80 and desulfurization for 10 days. The X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy results demonstrate that the decreases in the content of sulfur, S—C bonds, and S—S bonds on the surface of WLR after desulfurization by the half-submerged cultivation method were greater than those after desulfurization by the submerged cultivation method. The composite of waste latex rubber desulfurized by the submerged cultivation method (SDWLR) and styrene–butadiene rubber (SBR) had better mechanical properties than the composite of waste latex rubber desulfurized by the half-submerged cultivation method (HDWLR) and SBR. Scanning electron microscopy photographs showed that the combinations of HDWLR and the matrix were better than those of SDWLR and the matrix. Compared with the submerged cultivation method, the half-submerged cultivation method not only reduced the cost of desulfurization but also improved the desulfurization effect. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41039.

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INTRODUCTION

The treatment of waste rubber is a serious and worldwide problem. The huge amounts of waste rubber produce both health and environmental hazards. Nowadays, there is growing interest in reusing waste rubber as a source of raw material for environmental and economic reasons.

To date, extensive studies have been done to find a satisfactory method to recycle waste rubber. A number of physical and chemical devulcanization methods have been proposed.[1–6] Thermal and mechanical energy or chemical desulfurization reagents can break the crosslinking bonds in waste rubber. However, these methods normally require the use of hazardous chemicals or a great deal of energy. In addition, some byproducts, such as CO_2 and SO_2, adversely affect the global environment.

In recent years, many scholars[7,8] have focused on microbial devulcanization, which produces no pollution and has a low energy consumption. The devulcanization processes of different microorganisms on rubber have been studied.[9–11] Sato et al.[12] found that *Ceriporiopsis subvermispora* devulcanized NR sheets, but no devulcanization of rubber was observed in cultures of *Dichomitus squalens*. Bredberg et al.[13] reported that *Pyrococcus furiosus* could be used to desulfurize ground tire rubber. Strains belonging to *Thiobacillus* species,[14–16] such as *T. ferrooxidans*, *T. thiooxidans*, and *T. thioparus*, were reported to destroy the crosslinking sulfur bonds in rubber.

A number of efforts have been made to improve the microbial desulfurization effect through the adjustment of the process conditions. We previously reported[17] that Tween 80 had a toxic effect on *Alicyclobacillus* species, but the growth of the microbe was vigorous, and a good desulfurization effect was obtained when the

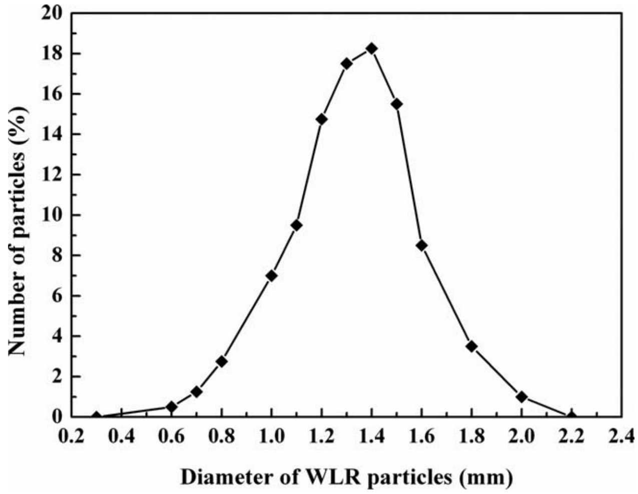

Figure 1. Particle size distribution of WLR.

proper technique was used: the mixing of waste latex rubber (WLR) with Tween 80 followed by the addition of the mixture into the culture media. Jiang et al.[18] improved a biomass of *T. ferrooxidans* by adjusting the initial Fe^{2+} concentration in the medium and found that the biomass increased and the effect on natural rubber was improved with increasing initial Fe^{2+} concentration. In these studies, major attention was paid to the growth of microorganisms and the improvement of biomass.

One problem with microbial desulfurization is that many microorganisms are sensitive to additives in rubber. Thus, Bredberg and coworkers[13,19] reported a detoxification process in which waste rubber was immersed in ethanol to extract the rubber additives. Furthermore, Bredberg et al.[20] used 15 species of wood-rotting fungi to detoxify waste rubber and found that *Resinicium bicolor* was the most effective. However, the detoxification effect was limited. If a high biomass is expected, the amount of waste rubber added to the medium should not be too high. Therefore, the submerged cultivation method is considered to be the optimum method for the microbial desulfurization of WLR. However, there is a concern over the high consumption of media, which leads to a high cost and a large amount of wastewater needing treatment.

In this study, *Sphingomonas* species were selected to desulfurize WLR by a new method: the half-submerged cultivation method. This method does not rely on the improvement of biomass alone to obtain a good desulfurization effect but instead focuses on improving the efficiency of each microorganism. The cost of this method is low because the medium consumption decreases significantly. The technical conditions for desulfurization by this method were ascertained. The effect of microbial desulfurization was evaluated by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and energy-dispersive spectrometry.

EXPERIMENTAL

Materials

WLR homogenized from Qingdao Siwei Latex Rubber Factory (China) was mixed on a two-roll mill and cut into small particles. The size distribution of the WLR particles was analyzed with an optical microscope. The average diameter of the WLR particles was less than 1.4 mm, as shown in Figure 1.

SBR 1502 was provided by China Petrochemical Co., Ltd., Qilu Branch. Carbon Black N330 was supplied by Tianjin Dolphin Carbon Black Development Co. Glutaraldehyde was provided by Sinopharm Chemical Reagent Co., Ltd. Tween 80 was supplied by Tianjin Yili Chemical Co., Ltd. Other reagents were purchased locally.

Desulfurization Process

The *Sphingomonas* species strain was selected from the soil of a coal mine in Sichuan Province, China. According to the analysis of the 16S rDNA gene sequencing result, the *Sphingomonas* species genes were 99% similar to *Sphingomonas* species CanClear 1. The culture medium included $K_2HPO_4{\cdot}3H_2O$ (4.0 g/L), KH_2PO_4 (4.0 g/L), $MgSO_4{\cdot}7H_2O$ (0.8 g/L), NH_4Cl (0.4 g/L), $CaCl_2$ (0.01 g/L), $Na_2S_2O_3{\cdot}5H_2O$ (10.0 g/L), glucose (2.0 g/L), peptone (1.0 g/L), and yeast extract powder (0.1 g/L). The medium and Tween 80 were autoclaved at 115°C before incubation. WLR was detoxified by immersion in 75% (v/v) ethanol for 3 h.

The desulfurization process by the submerged cultivation method was as follows: after 24 h of vigorous growth of *Sphingomonas* species at a pH of 7.0 and 30°C in a 500-mL flask (each with 20 mL of medium), 10% w/v desulfurized waste latex rubber (DWLR) and 0.1% w/v Tween 80 were added to the medium, and then, the flask was stirred at 200 rpm in an oscillation incubator for 10 days at 30°C. The DWLR was washed with deionized water and then dried at room temperature.

The desulfurization process by the half-submerged cultivation method was as follows: after 24 h of vigorous growth of *Sphingomonas* species at pH 7.0 and 30°C in some 500-mL flasks (each with 20 mL of medium), variable amounts of DWLR (30, 40, 50, and 60% w/v) and variable amounts of Tween 80 (0, 0.2, 0.4, 0.6, and 0.8% w/v) were added to the medium, and then, the flasks were placed in a biochemistry incubator and let stand for different times (2, 4, 6, 8, 10, 12, and 14 days) at 30°C. The DWLR was washed with deionized water and then dried at room temperature. The half-submerged cultivation method mainly differed from the submerged cultivation method in that much more DWLR was added to the medium, and the desulfurization process was done without stirring.

Preparation of Vulcanizates

Styrene–butadiene rubber (SBR) was mixed on a two-roll mill (Shanghai Rubber Machinery Works, Shanghai, China), and then, other additives and WLR, waste latex rubber desulfurized by the submerged cultivation method (SDWLR), or waste latex rubber desulfurized by the half-submerged cultivation method (HDWLR) was added to the blends. The formulation of the SBR composites is listed in Table I. The optimum curing times for the mixtures were determined with an oscillating disk rheometer (Beijing Huangfeng Machinery Works, Beijing, China). The composites were vulcanized with a plate vulcanization machine (Shanghai Rubber Machinery Works, Shanghai, China) at 15 MPa and 150°C for the optimum curing time.

Table I. Compound Recipe

Material	Weight (phr)
SBR	100
Carbon black N330	30
WLR, SDWLR, or HDWLR	20
Zinc oxide	4
Stearic acid	2
1,3-Diphenyl guanidine	0.6
2,2′-Dibenzothiazoledisulfde	1.2
Sulfur	2

Characterization

Swelling Value and Crosslinking Density Measurements. Small pieces of samples were immersed in toluene for 72 h at 30°C. The swelling value was calculated as the ratio of the weight of the swollen sample to that of the dried sample. The crosslinking density was calculated with the Flory–Rehner equation[21] with an interaction parameter of 0.393 for the rubber and toluene.[22,23]

Surface Elemental Analysis. The elements and covalent bonds on the surfaces of WLR, SDWLR, and HDWLR were measured with an Escalab 250 X-ray photoelectron spectrometer (Thermo Electron Corp.) with an Al Kα X-ray source (1486.6 eV). The core-level signals were obtained at a photoelectron take-off angle of 45° with respect to the sample surface.

Chemical Group Analysis. The chemical groups on the surface of WLR, SDWLR, and HDWLR were analyzed with a Tensor 27 FTIR spectrometer (Bruker Optik GmbH, Germany) at a resolution of 4 cm^{-1} with 64 scans being averaged.

Total Elemental Analysis. The total elemental contents of WLR, SDWLR, and HDWLR were analyzed by the use of a Vario EL cube elemental analyzer (Elementar Analysensysteme GmbH, Germany).

Mechanical Property Measurements. The Shore A hardness of the composites was measured with a rubber hardness apparatus

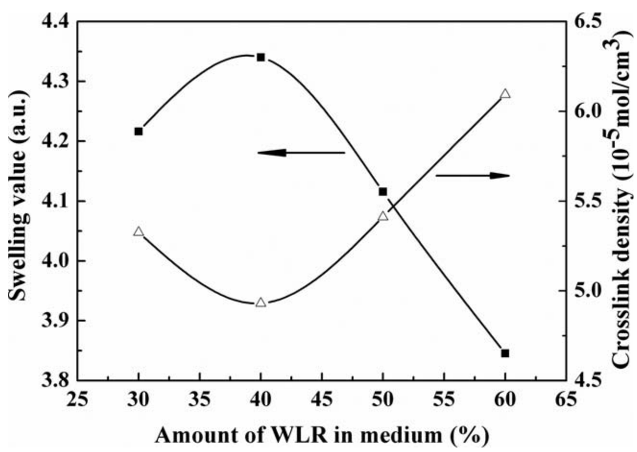

Figure 2. Effect of the amount of WLR on the swelling value and crosslinking density of the HDWLR.

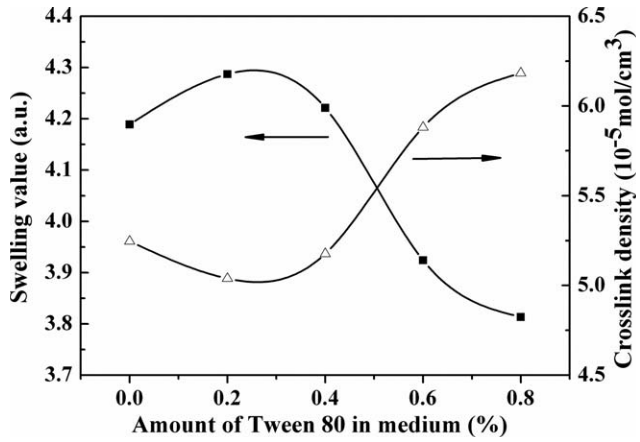

Figure 3. Effect of Tween 80 on the swelling value and crosslinking density of the HDWLR.

(Shanghai 4th Chemical Industry Machine Factory, China) according to ASTM D 2240-2005. The tensile strength of the composites was measured with a CMT4104 electrical tensile tester (Shenzhen SANS Test Machine, China) at room temperature according to ASTM D 412-2006.

Morphology. The morphology of the tensile fracture surface of the SBR composites filled with WLR, SDWLR, or HDWLR was observed with an S-4800 scanning electron microscope (Hitachi, Japan). The sulfur contents on the tensile fracture surfaces of the samples were investigated with an energy dispersive X-ray spectrometer in combination with SEM.

The WLR samples were taken out of the culture medium during the desulfurization process. After they were washed with phosphate buffered saline, the WLR samples were fixed with 3% glutaraldehyde at 4°C for 2 h and then dehydrated through a series of graded ethanol solutions and lyophilized. The morphology of the *Sphingomonas* species adhering on the surface of WLR in the desulfurization process was observed with an S-4800 scanning electron microscope (Hitachi, Japan).

RESULTS AND DISCUSSION

Technical Conditions for Desulfurization by the Half-Submerged Cultivation Method

Effect of the Amount of WLR. The effect of amount of WLR on the swelling value and crosslinking density of the HDWLR is shown in Figure 2. With increasing amounts of WLR, the swelling value of HDWLR increased, and the crosslinking density decreased, probably because a large amount of WLR leads to the metabolism of most *Sphingomonas* species close to the rubber surface and, then, most of the microorganisms play a role in the desulfurization process. HDWLR had a high swelling value and a low crosslinking density at 40% w/v WLR in the medium. However, at 50% w/v WLR or more, the swelling value of HDWLR decreased significantly, and the crosslinking density increased obviously; these were indications that the microorganisms did not grow normally because of the toxic additives in WLR and the lack of space to grow. Therefore, the 40% w/v WLR level was optimum in terms of the desulfurization effect and economy.

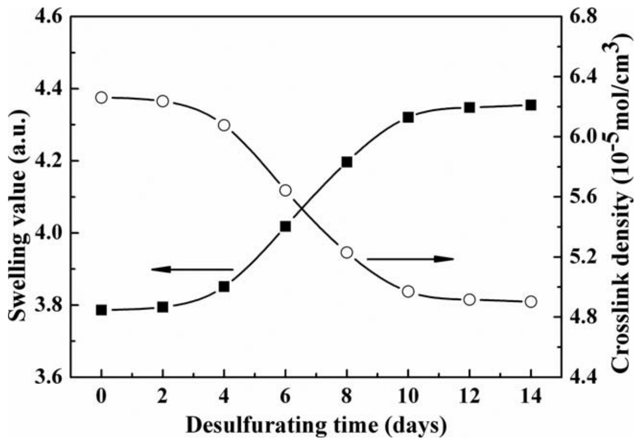

Figure 4. Effect of the desulfurization time on the swelling value and crosslinking density of the HDWLR.

Effect of Tween 80. To improve the desulfurization effect, the surfactant Tween 80 was used to increase the probability of contact between WLR and the *Sphingomonas* species because WLR was lipophilic but the *Sphingomonas* species were hydrophilic The effect of the content of Tween 80 on the swelling value and crosslinking density of HDWLR is shown in Figure 3. At 0.2% w/v Tween 80 in the medium, the swelling value of HDWLR increased slightly, and the crosslinking density of HDWLR decreased slightly. The probable reason was that the growth and metabolism of most of the microorganisms were close to the rubber surface because of the large amount of WLR in the medium. At 0.4% w/v Tween 80 or more, the desulfurization effect became poor, as indicated by the decrease in the swelling value and the increase in the crosslinking density. This was because Tween 80 had a toxic effect on the *Sphingomonas* species, and most of the microorganisms were killed when there was too much Tween 80 in the medium. Thus, Tween 80 should not be added because of the desulfurization effect and process simplification.

Effect of the Desulfurization Time. The effect of the desulfurization time on the swelling value and crosslinking density of HDWLR is shown in Figure 4. At desulfurization times of less than 4 days, the swelling value and the crosslinking density of HDWLR differed little from those of WLR. At a desulfurization time of about 4 days, the swelling value of DWLR began to increase, and the crosslinking density began to decrease with increasing desulfurization time. High degrees of desulfurization of WLR were obtained after about 10 days of desulfurization. The increase in the degree of desulfurization degree became inconspicuous after a desulfurization time of 10 days, as indicated by the leveling off of the swelling value and crosslinking density. Therefore, the optimum time for the desulfurization of WLR by the *Sphingomonas* species with the submerged cultivation method was 10 days.

Table II. Surface Elemental Contents of WLR, SDWLR, and HDWLR

Element	WLR (%)	SDWLR (%)	HDWLR (%)
C	83.45	80.28	74.25
O	15.83	19.33	25.49
S	0.72	0.39	0.27

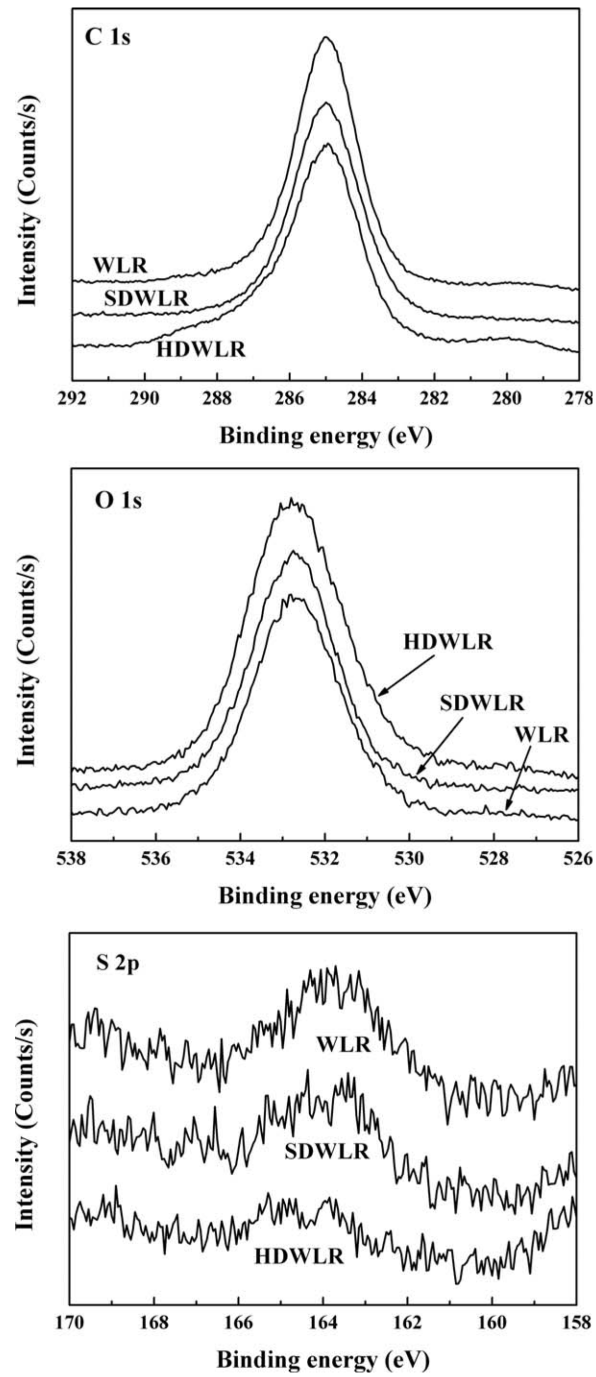

Figure 5. XPS spectra (C, O, and S) of WLR, SDWLR, and HDWLR.

Structural Analyses of WLR and DWLR

XPS Analysis. The contents of the elements C, O, and S on the surfaces of WLR, SDWLR, and HDWLR as measured by XPS are shown in Table II and Figure 5. The S peak areas of the SDWLR surface and HDWLR surface decreased by 45.8 and

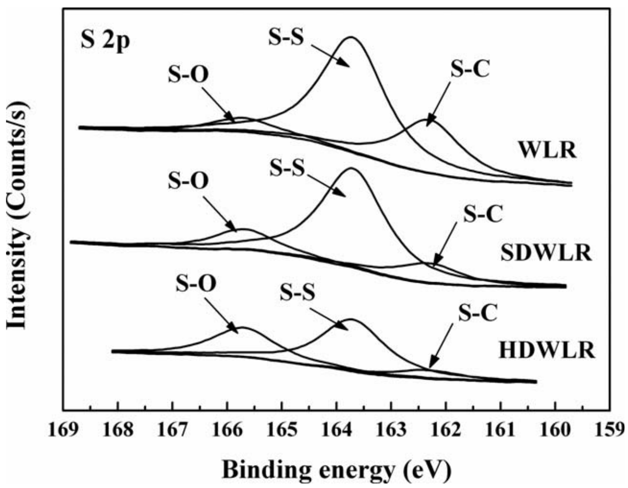

Figure 6. Structural changes in the sulfide bonds on the surfaces of the SDWLR and HDWLR.

62.5%, respectively, from that of the WLR surface, and the O peak areas of the SDWLR surface and HDWLR surface increased by 22.1 and 61.0%, respectively, from that of the WLR surface. These differences indicated that the *Sphingomonas* species oxidized the crosslinked sulfide bonds to sulfur–oxide groups on the WLR surface more effectively in the half-submerged cultivation method than in the submerged cultivation method.

Three-second splits of the S2p peaks at 162.3, 163.7, and 165.7 eV were assigned as the bonding energies for S—C, S—S, and S—O bonds, respectively.[7] The structural changes in the sulfide bonds on the surface of SDWLR and HDWLR are shown in Figure 6. After desulfurization with the submerged cultivation method, the frequencies of the S—C and the S—S bonds decreased by 62.7 and 14.1%, respectively, and the frequency of the S—O bonds increased by 47.8%. After desulfurization with the half-submerged cultivation method, the frequencies of the S—C and the S—S bonds decreased by 84.3 and 55.6%, respectively, and the frequency of the S—O bonds increased by 106.5%. These results demonstrate that the *Sphingomonas* species broke the crosslinked sulfide bonds on the WLR surface more effectively in the half-submerged cultivation method than in the submerged cultivation method. Additionally, the formation of sulfur–oxide groups on the HDWLR surface improved the surface activity of DWLR.

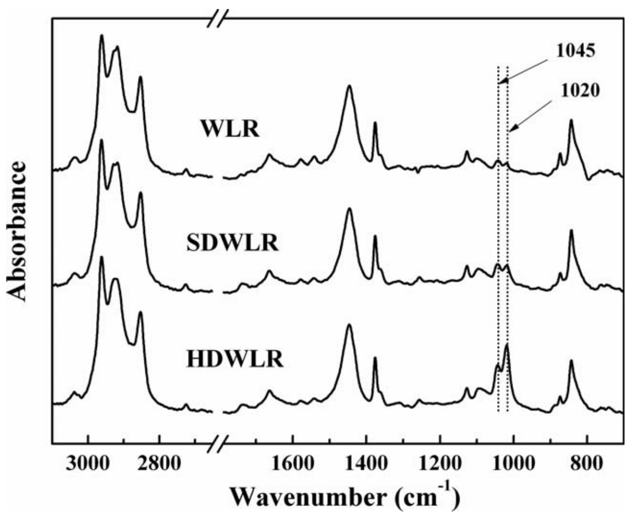

Figure 7. FTIR spectra of WLR, SDWLR, and HDWLR.

Table III. Total Elemental Contents of WLR, SDWLR, and HDWLR

Element	WLR (%)	SDWLR (%)	HDWLR (%)
C	83.74	83.65	83.61
H	11.172	11.179	11.186
S	0.842	0.820	0.794

FTIR Analysis. The FTIR absorbance spectra of WLR, SDWLR, and HDWLR are shown in Figure 7. The peaks at 3100–2800 cm^{-1} for C—H stretching vibrations, 1447 and 1376 cm^{-1} for C—H bending vibrations, and 843 cm^{-1} for =C—H bending vibrations did not show any obvious changes after desulfurization. The peak at 1663 cm^{-1} for C=C vibrations also did not exhibit any significant changes. These results demonstrate that the main chains of WLR were intact after desulfurization by the *Sphingomonas* species The bands at 1020–1070 cm^{-1} corresponded to S=O vibrations, and this showed a slight increase after the desulfurization of WLR with the submerged cultivation method. This result shows that the desulfurization of WLR by the *Sphingomonas* species followed the 4S desulfurization pathway.[24] However, the S=O vibrations showed a significant increase after the desulfurization of WLR with the half-submerged cultivation method; this indicated that the half-submerged cultivation method had a better desulfurization effect than the submerged cultivation method.

Element Content Measurements. The total contents of the elements C, H, and S in WLR, SDWLR, and HDWLR are shown in Table III. After the desulfurization of WLR with the half-submerged cultivation method, the total S content decreased by 2.6%. After the desulfurization of WLR with the half-submerged cultivation method, the total S content decreased by 5.7%. These results indicate that the half-submerged cultivation method had a better desulfurization effect than the submerged cultivation method. Combined with the XPS measurement results, the content measurement results confirm that the *Sphingomonas* species could break only the crosslinked sulfide bonds on the surface of WLR and that microbial desulfurization existed merely on the surface of the rubber.[10]

Swelling Value and Crosslinking Density Measurements. The swelling values and crosslinking densities of WLR, SDWLR, and HDWLR are shown in Figure 8. After the desulfurization of WLR with the submerged cultivation method and the half-submerged cultivation method, the swelling values increased by 8.9 and 13.9%, respectively, and the crosslinking densities decreased by 13.8 and 20.2%, respectively. The increase in the swelling value and the decrease in the crosslinking density were attributed to the destruction of

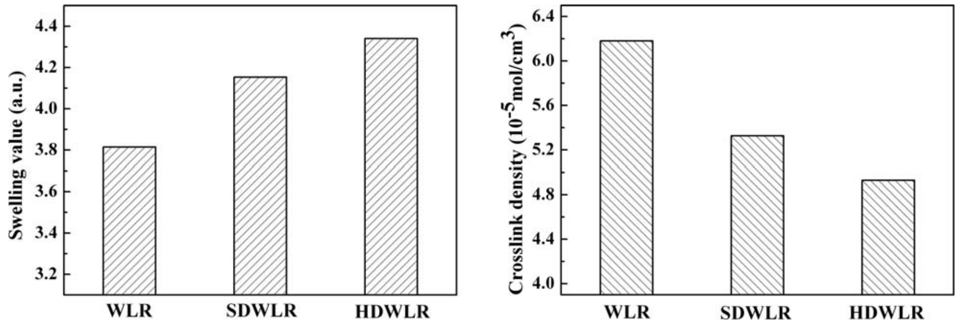

Figure 8. Swelling values and crosslinking densities of WLR, SDWLR, and HDWLR.

crosslinked bonds in the desulfurization process. Thus, the higher swelling value and lower crosslinking density of HDWLR compared to those of SDWLR were indications that the half-submerged cultivation method was more effective than the submerged cultivation method in the desulfurization of WLR.

Properties of the SBR Composites Filled with WLR, SDWLR, or HDWLR

Mechanical Properties. The mechanical properties of the SBR composites filled with WLR, SDWLR, or HDWLR are summarized in Table IV. The tensile strength and elongation at break of the DWLR/SBR composite were significantly higher than those of the WLR/SBR composite because the crosslinked sulfide bonds of DWLR were broken by the *Sphingomonas* species, and the surface of DWLR became much softer. Consequently, the compatibility between DWLR and the matrix increased and so did the interfacial bonding strength. Moreover, the higher tensile strength and elongation at break of HDWLR/SBR compared to those of SBR/SDWLR indicated that the half-submerged cultivation method was more effective than the submerged cultivation method in desulfurizing WLR.

Morphologies of the Fracture Surfaces. Figure 9 presents the SEM micrographs of the tensile fracture surfaces of the SBR composites filled with WLR, SDWLR, and HDWLR. The tensile fracture surface of the SBR composite filled with WLR in Figure 9(a) shows that many WLR particles were peeled off from the matrix and many holes were left on the fracture surface. One of the WLR particles that fell off of the SBR matrix is shown in Figure 9(a′). These indicate that the adhesion of WLR to the matrix was poor. As shown in Figure 9(b,b′), there were a few holes on the fracture surface of SDWLR/SBR, and some noticeable gaps were observed between the SDWLR and the matrix. These phenomena demonstrated that some crosslinking sulfide bonds on the surface of SDWLR were broken, but the degree of destruction was not very high. Figure 9(c,c′) shows that almost no holes were observed on the fracture surface of HDWLR/SBR, and the combinations of the HDWLR particles and the SBR matrix were very close. These phenomena demonstrate that there was greater interfacial adhesion between HDWLR and the matrix because of the good desulfurization effect of the half-submerged cultivation method.

The S element contents at the two-phase interface on the tensile fracture surfaces of the WLR/SBR, SDWLR/SBR, and HDWLR/SBR composites are shown in Figure 10. The results indicate that sulfur spread from the matrix to the inside of the DLWR particles across the broken crosslinked network structure on the surface of DWLR. The results also demonstrate that the degree of destruction of the crosslinked network structure was higher for HDWLR than for SDWLR.

Table IV. Mechanical Properties of WLR/SBR, SDWLR/SBR, and HDWLR/SBR

Sample	WLR/ SBR	SDWLR/ SBR	HDWLR/ SBR
Shore A hardness	61	61	61
Tensile strength (MPa)	19.3	20.7	22.5
Elongation at break (%)	446	471	492
Modulus at 100% elongation (MPa)	1.9	1.7	1.8
Modulus at 300% elongation (MPa)	9.2	8.4	8.5

Mechanism of Microbial Desulfurization

The morphology of the *Sphingomonas* species adhering to the surface of WLR in the desulfurization process is shown in Figure 11. As shown in Figure 11(a,a′), very few microorganisms could adhere to the surface of WLR in the desulfurization process by the submerged cultivation method. However, a large number of microorganisms adhered to the surface of WLR in the desulfurization process by the half-submerged cultivation method, as shown in Figure 11(b,b′).

A requirement for a good desulfurization effect is good contact between the microorganisms and the rubber. Mechanical oscillation and agitation have adverse effects on the microorganisms sticking to waste rubber. Tsuchii and Tokiwa[25,26] studied the effect of the stirring rate on the microbial disintegration of tire rubber particles by *Nocardia* species They found that some large colonies of microorganisms appeared at high stirring rates. However, it was difficult for the colonies to stick to the rubber particles, and thus, the effect of disintegration was low. In contrast, the microorganisms stuck to the rubber particles evenly when the medium was either not agitated or stirred at very low rates. There have been other reports on the detrimental effects

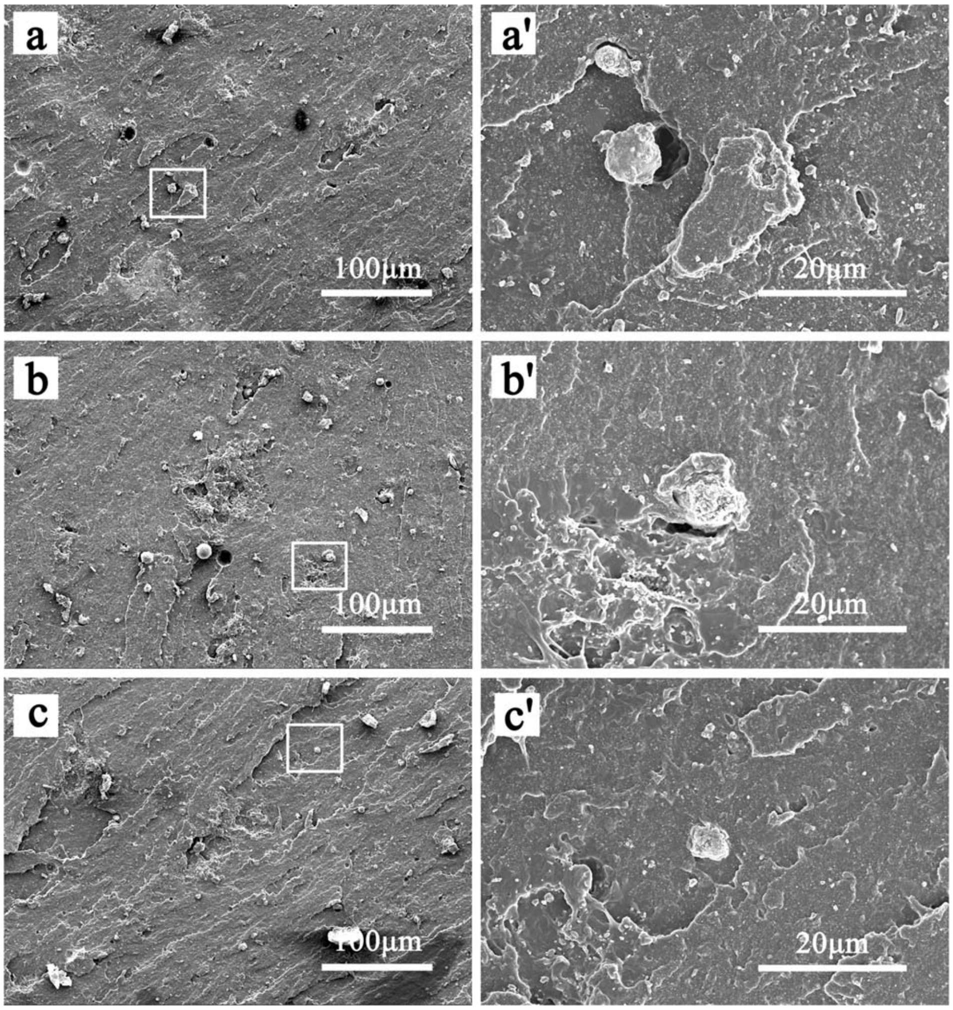

Figure 9. SEM photographs of the tensile-fractured surfaces of (a,a′) WLR/SBR, (b,b′) SDWLR/SBR, and (c,c′) HDWLR/SBR.

of mechanical agitation on microorganisms or cells on other materials.[27,28]

In this study, the states of the *Sphingomonas* species in desulfurization by the submerged cultivation method and the half-submerged cultivation method were very different, as shown in Figure 12. With the submerged cultivation method, many colonies of microorganisms were formed, but it was very difficult for them to maintain contact with WLR. Consequently, the microbial desulfurization reactions were adversely affected. Moreover, the high consumption of the medium led to a high cost, low equipment efficiency, and the formation of a large amount of wastewater.

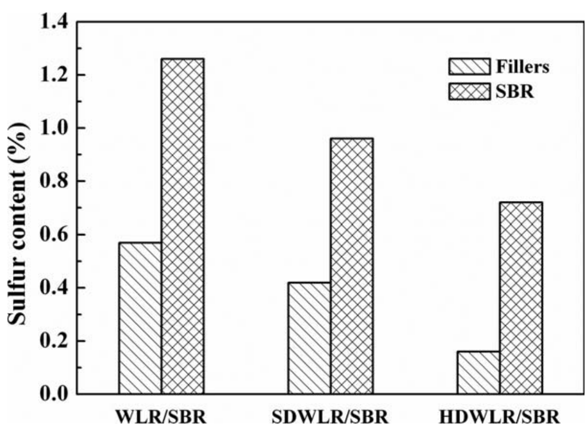

Figure 10. Comparison of the S element contents on the tensile fracture surfaces of WLR/SBR, SDWLR/SBR, and HDWLR/SBR.

On the other hand, most of the microorganisms grew on the surface of WLR with the half-submerged cultivation method because of the limited space and absence of mechanical agitation. The good contact between the microorganisms and rubber resulted in an excellent desulfurization effect. Another advantage of the half-submerged cultivation method was the very low medium consumption, which greatly lowered the cost and the amount of wastewater.

CONCLUSIONS

Because of the high cost of the traditional submerged cultivation method, we put forward a half-submerged cultivation method. The optimum amount of WLR used for

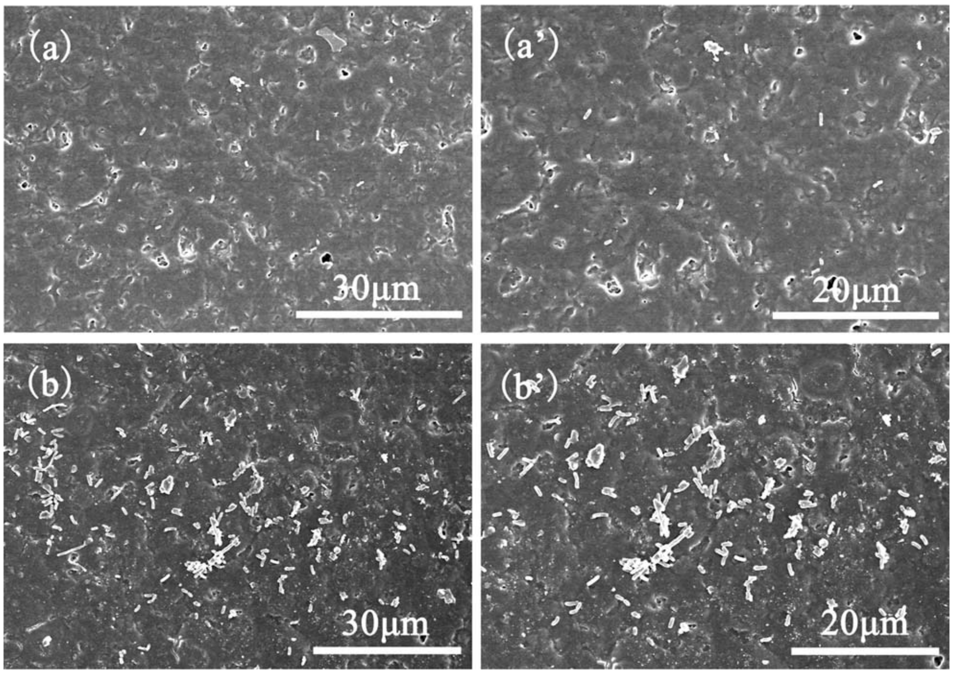

Figure 11. Morphology of *Sphingomonas* species adhering to the surface of WLR in the desulfurization process by (a,a′) the submerged cultivation method and (b,b′) the half-submerged cultivation method.

desulfurization by the new method was 40% w/v, and Tween 80 was not needed for this method. For best desulfurization effect and economy, the desulfurization time for WLR by this method was 10 days.

The contents of sulfur, S—C, and S—S bonds on the surface of HDWLR were lower than those on the surface of SDWLR, the content of S—O bonds on the surface of HDWLR was higher than that on the surface of SDWLR, and the content of sulfone groups on the surface of HDWLR was higher than that on the surface of SDWLR. The improvement of the hydrophilic properties after desulfurization by the half-submerged cultivation method was more obvious than that after desulfurization by the submerged cultivation method. The mechanical properties of the HDWLR/SBR composite were higher than those of the SDWLR/SBR composite. There were more chemical bonds and greater interfacial forces between HDWLR and the matrix than between SDWLR and the matrix. To summarize, the half-submerged cultivation method not only had a lower cost of desulfurization but also had a better desulfurization effect than the submerged cultivation method. Predictably, the half-submerged cultivation method could have significant implications for the reclamation of rubber.

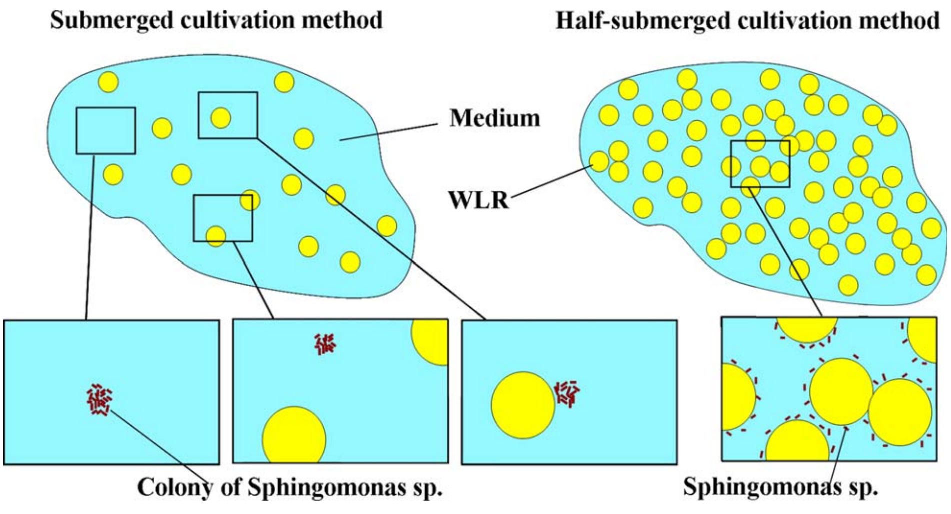

Figure 12. Comparison of states of *Sphingomonas* species in desulfurization by the submerged cultivation method and the half-submerged cultivation method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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