

Solid-phase preparation method of silica-supported 2,2'-methylenebis(6-tert-butyl-4-methyl-phenol) and its antioxidative behavior in styrene-butadiene rubber

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ABSTRACT: A solid-phase preparation method is applied to the synthesis of a novel supported rubber antioxidant, silica-supported 2,2'-methylenebis(6-tert-butyl-4-methyl-phenol) (SiO₂-2246), by directly reacting 2,2'-methylenebis(6-tert-butyl-4-methyl-phenol)(antioxidant 2246) with silica. FTIR, Raman spectroscopy and TGA confirm that the antioxidant 2246 is chemically bonded on the surface of the silica particles. The SEM observation shows that the SiO₂-2246 is homogeneously dispersed in the styrene-butadiene rubber (SBR) matrix. The results of the apparent activation energy and the attenuated total reflectance infrared spectrometry indicate that the antioxidative efficiency of the SiO₂-2246 in SBR is superior to the corresponding low-molecular-weight 2246. The thermal oxidative stability of the SBR/SiO₂-2246 composites is much higher than that of the SBR/SiO₂/2246 composites by comparing their mechanical properties retentions and crosslinking densities. Additionally, the advantages of SiO₂-2246 also include low migration, low volatility, and low pollution. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43014.

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INTRODUCTION

Antioxidants are widely used in rubber industry in the form of low molecular weight organic compounds. The antioxidants with low relative molecular mass have many disadvantages, such as low antioxidative efficiency, easy migration,¹ easy volatility at higher temperatures,² and pollution to environment and so on. To overcome those disadvantages of the conventional rubber antioxidants, a novel type of supported rubber antioxidants, silica-supported 2-mercaptobenzimidazole (SiO₂-s-MB)³ was successfully prepared recently in our laboratory. It was found that the styrene-butadiene rubber (SBR) composites with the supported antioxidant exhibited better mechanical properties than those with corresponding low molecular antioxidant MB due to the improved dispersion and enhanced interfacial interaction between silica and rubber. At the same time, the antioxidative efficiency of SiO₂-s-MB in SBR composites was superior to that of the corresponding low molecular antioxidant MB, and the color contamination, migration and volatility of SiO₂-s-MB were lower than those of MB, indicating that the supported antioxidant is environmentally friendly. Besides, Guo *et al.*⁴

have synthesized RT-silica and it also found that the novel antioxidant has similar advantages, such as high antioxidative efficiency, low migration, and low volatility, etc.

On the other hand, silica plays a more and more important role in the reinforcement of rubbers.⁵ Especially silica can dramatically reduce rolling resistance in green tires.⁶ The compatibility between silica and nonpolar rubber is poor because there are a large number of polar hydroxyl groups on the surface of silica particles. However, it is due to the abundant high-activity hydroxyl groups on the surface of the particles, silica can easily react with many reactants, resulting in high dispersed silica (HDS) or easy dispersed silica (EDS). The modified silica can counterpoise the rolling resistance, wet skid resistance and abrasive resistance, and hence shows a huge potential in the application of green tire and other rubber products.

Silica-supported antioxidants belong to the scope of modified silica which adopts small molecular weight rubber antioxidants and coupling agents as the modifiers. They have not only the advantages of modified fillers but also the functions of excellent antioxidants, and are a kind of multifunctional rubber additives.

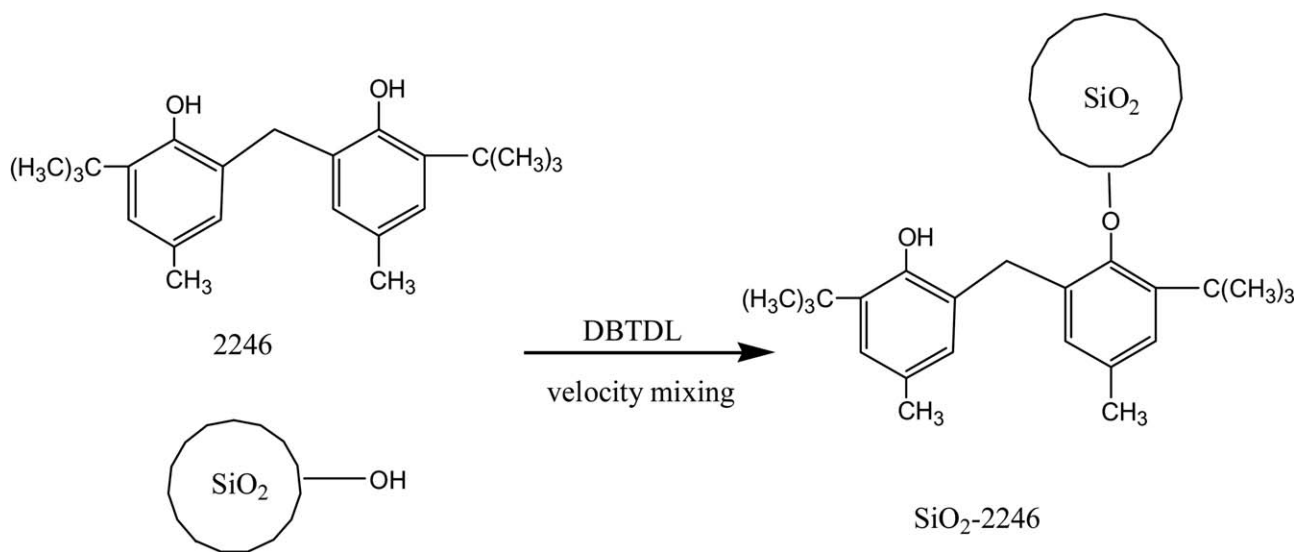


Figure 1. Synthesis route of SiO₂-2246.

However, there are obvious disadvantages in the solution method for preparing the silica-supported rubber antioxidants: complicated operation, low yield and environmental pollution. This method cannot be widely applied in industrial manufacturing.

Solid-phase preparation method^{7,8} has already been introduced to simplify the synthesis of peptides and to increase the reaction speed, and this method has been applied in other biological researches. However, solid-phase method is a novel preparation method for supported rubber antioxidants, which can reduce the deficiencies of liquid-phase preparation method. There are no waste and no pollution. The operation is easy with a high yield. Moreover, the solid-phase method products have the same advantages as the liquid-phase method, such as reducing migration and volatilization.

Solid-phase method was firstly applied in the synthesis of silica-supported antioxidants. Different from the liquid-phase preparation method, we did not use any solvent and all the reactions were totally taken place in solid condition. Besides, in the liquid method, silane-coupling agent is necessary. However in our research, silane-coupling agent is unnecessary. So we can conclude that this method possesses the advantages like easy operation and high yield, besides, with the no solvent and no waste, cost saving is the other advantage. Overall, this method is truly environmentally friendly.

Phenolic antioxidants,⁹ such as 2,2'-methylenebis(6-tert-butyl-4-methyl-phenol) (antioxidant 2246) containing phenolic hydroxyl groups, exhibit high activity in many chemical reactions. They can easily induce an alcohol esterification reaction with silica in the presence of a catalyst^{10,11} and forming silica-supported antioxidant 2246(SiO₂-2246). The resistance of the antioxidants to migration, volatilization and extraction can be improved by this method. Additionally, the anti-aging efficiency and mechanical properties of the vulcanizates can be enhanced by improving the dispersion of the antioxidant in a rubber matrix and the combination between silica filler and the rubber matrix.

In this study, a novel supported antioxidant, silica-supported 2246, was prepared by the reaction of antioxidant 2246 with silica under solid-phase conditions. In this novel antioxidant, the antioxidant 2246 molecule was chemically bonded onto the surface of the silica particles used as the supporter. The preparation and structure of the SiO₂-2246 and its dispersion in the SBR composites were investigated using Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The determination of apparent activation energy (*E*) and attenuated total reflectance infrared spectrometry (ATR-FTIR) allowed us to follow the oxidation process of SBR composites.^{12,13} Finally, the thermal oxidative stability of the SBR composites during long-term thermal aging was evaluated by observing the changes in the tensile strength, elongation at break and crosslink densities before and after aging.

EXPERIMENTAL

Materials

Precipitated silica (SiO₂) was produced from Huiming Chemical, Jiangxi, China, and dried 2 hours at 80°C in a vacuum oven before used. Catalyst Dibutyltindilaurate (DBTDL) was obtained from FuChen Chemical Reagents Factory, Tianjin, China. SBR (1502) was offered by Guangzhou Institute of Rubber Products, China. Antioxidant 2246, zinc oxide (ZnO), stearic acid (St), accelerator N-cyclo-hexylbenzothiazole-2-sulphenamide (accelerator CBS), 2,2'-dibenzothiazyl disulfide (accelerator DM) and insoluble sulfur (S) were industrial grade products and used as received. Absolute ethanol was an analytical reagent.

Preparation of Silica-Supported Antioxidant

The synthesis route of silica-supported antioxidant SiO₂-2246 is shown in Figure 1. Totally 1.0 g of antioxidant 2246 was mixed with 15.0 g of SiO₂ in three-necked flask, along with a few drops of the catalyst (DBTDL). The mixture was stirred for 4 h at 50°C. After that, all the mixture was dried for 2 h at 80°C in a vacuum oven.

Table I. Composition of SBR Composites

Sample	Component						
	SBR	SiO ₂	ZnO+St	CZ+DM	SiO ₂ -2246	2246	S
SBR/SiO ₂	100	30	5 + 2	1.5 + 0.5	0	0	1.6
SBR/SiO ₂ /2246	100	30	5 + 2	1.5 + 0.5	0	2	1.6
SBR/SiO ₂ -2246	100	0	5 + 2	1.5 + 0.5	32	0	1.6

Preparation of SBR Composites

All rubber compounds were prepared in a φ 160 × 330 laboratory rubber mill. The rolls run at a speed ratio of 1 (front roll): 1.22 (back roll). After mixing, the compounds were left overnight before vulcanization. The vulcanization of the SBR compounds was operated in press at 160°C for optimum curing times T_{90} determined by a curemeter. The compositions of SBR composites are shown in Table I.

Characterization of SiO₂ and SiO₂-2246

The silica-supported antioxidant SiO₂-2246 was centrifuged five times with hot absolute ethanol at a speed of 4000 r min⁻¹. Then, it was extracted for 48 h in a Soxhlet extractor with absolute ethanol. After that, it was dried at 80°C under vacuum to constant weight.

The thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere with a NETZSCH TG209F1 at a heating rate of 10°C min⁻¹ from 30°C to 700°C. Raman spectra were determined by a HJY LabRAM Aramis microprobe Raman spectrometer. Fourier transform infrared (FTIR) spectra were obtained by a Perkin-Elmer-System 2000 infrared spectrometer with KBr pellets in the range of from 400 to 3700 cm⁻¹.

Characterization of the Oxidation Process

Thermal oxidation aging kinetic analysis^{14,15} is a method for determining the thermal oxidation stability, and it can provide significant mechanistic information about the thermal oxidation degradation. The TG curves of SBR vulcanizates with different antioxidants were obtained at different heating rate (5°C min⁻¹,

10°C min⁻¹, 20°C min⁻¹, 30°C min⁻¹) and from 30°C to 700°C.

For nonisothermal degradation, the apparent activation energy (E) of thermo-oxidative degradation was calculated using the Flynn-Wall-Ozawa method.¹⁶ The equation is as follow:

$$\lg \beta = \lg \left(\frac{AE}{RG(\alpha)} \right) - 2.315 - 0.4567 \frac{E}{RT} \quad (1)$$

Where β is the heating rate, α is the mass conversion rate, A is the thermal oxidation reaction conversion rate, E is the apparent activation energy, and R is the thermodynamic parameter.

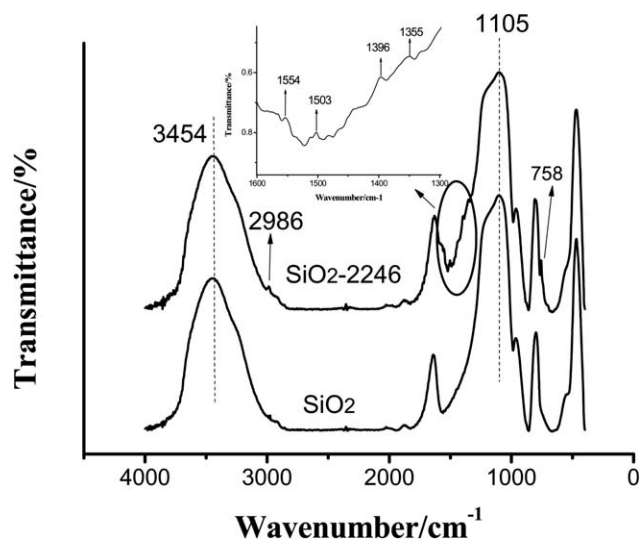
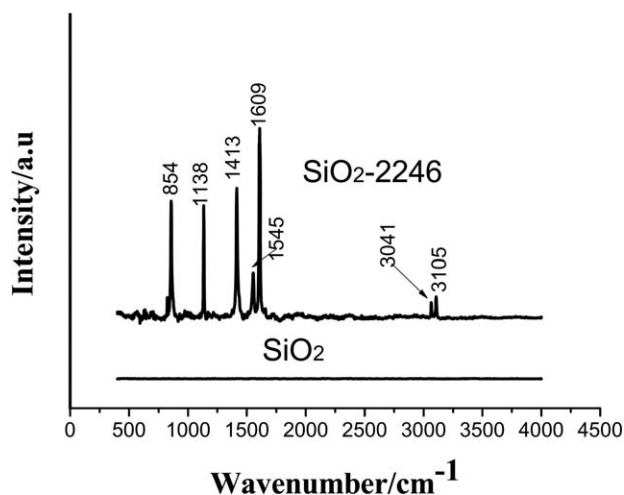
When α is constant, $\lg \beta$ vs. T^{-1} yields a straight line whose slope is the activation energy E . In this article, α was chosen as 0.005, 0.0075, 0.01, 0.015, 0.02, 0.025, 0.03, 0.04, and 0.05.

Morphology Analysis

Samples were fractured after cooling by immersing in liquid nitrogen, and then coated with a thin layer of gold. The dispersion of silica in SBR matrix was observed on NOVA NANO scanning electron microscope.

Long-Term Accelerated Aging

For thermal aging test, the rubber dumbbell samples of the SBR vulcanizates were placed in an air-circulating oven from GAO-Tech Corporation at 100°C for 3 days, 5 days, 7 days, and 9 days according to the ASTM D 573 standards. The mechanical properties were measured by U-CAN electron tensile testing machine according to the ASTM D 412 standards.

**Figure 2.** FTIR spectra of SiO₂ and SiO₂-2246.**Figure 3.** Raman spectra of SiO₂ and SiO₂-2246.

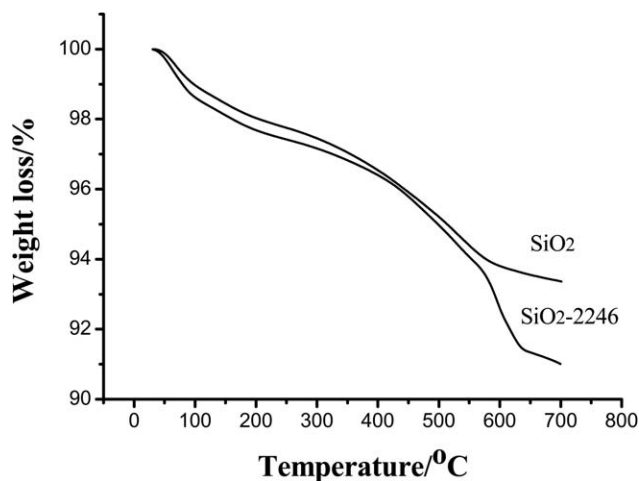


Figure 4. TGA curves of SiO₂ and SiO₂-2246.

Crosslinking Density Analysis

During the aging process, rubbers were believed to occur in two changes: chain scissions and chain crosslinking,^{17–19} resulting in a change in crosslinking density. The crosslinking density was determined using the equilibrium swelling method in toluene and calculated according to the classical Flory-Rehner equation.²⁰ The equation is as follow:

$$\ln(1 - \varphi_2) + \varphi_2 + \chi_1 \varphi_2^2 = -\frac{v_2}{V} V_s \left\{ \varphi_2^{\frac{1}{f}} - \frac{2\varphi_2}{f} \right\} \quad (2)$$

Where φ_2 is polymer volume fraction in a swollen sample, $\frac{v_2}{V}$ is volume fraction of elasticity active chains, f is functionality, and χ_1 is interaction parameter. The value of equilibrium swelling can be a practical criterion of solubility.

RESULTS AND DISCUSSION

Characterization of Silica-Supported 2246

Figure 2 shows the FTIR spectra of SiO₂ and SiO₂-2246. The broad strong bands between 3700 cm⁻¹ and 3200 cm⁻¹ are assigned to the stretching vibration of silanol hydroxyls and

adsorbed water. The absorption of the stretching vibration at 1105 cm⁻¹ is also observed.

For the FTIR spectrum of the SiO₂-2246, the characteristic absorption peaks for bending vibration in at 1355 cm⁻¹ and 1396 cm⁻¹ are observed. However, the absorption peaks at 1503 cm⁻¹ and 1554 cm⁻¹ are attributed to stretching vibration of aromatic carbon skeleton, and the absorption at 758 cm⁻¹ is characteristic of the aromatic bending vibration. Additionally, an absorption peak for the stretching vibration for the asymmetrical stretching vibration of methyl at ~2986 cm⁻¹ is observed.

Figure 3 displays the Raman spectra of the pristine SiO₂ and the SiO₂-2246. Compared to the spectrum of SiO₂, the spectrum of the modified SiO₂ is so strong that the Raman spectrum of the pristine SiO₂ appears as a straight line. In the spectrum of SiO₂-2246, the characteristic absorption peaks for benzene are observed at 1609 cm⁻¹, 1545 cm⁻¹, and 854 cm⁻¹, which are due to the absorption of aromatic ring, and ring stretching vibrations, respectively. The peaks at 3041 cm⁻¹ and 3105 cm⁻¹ are attributed to methylene asymmetric and symmetric stretches, respectively. The characteristic absorption of methylene swing vibration is observed at 1413 cm⁻¹, and the stretching vibration at ~1138 cm⁻¹ is also observed.

The TGA curves of SiO₂ and SiO₂-2246 are presented in Figure 4. SiO₂-2246 shows worse thermal stability than the pure SiO₂, which is due to the decomposition of 2246 on the surface of the SiO₂. Based on the weight loss between SiO₂ and SiO₂-2246, the supported rate of 2246 on silica is determined to be 34.01%.

Kinetics of Thermo-Oxidative Degradation

The kinetics of the thermo-oxidative degradation was used to investigate and compare the anti-aging properties of SBR vulcanizates. Figure 5 illustrates TGA curves of the SBR vulcanizates with supported antioxidant SiO₂-2246 at different heating rates and the corresponding plot of lgβ vs. T⁻¹ according to Flynn-Wall-Ozawa equation.

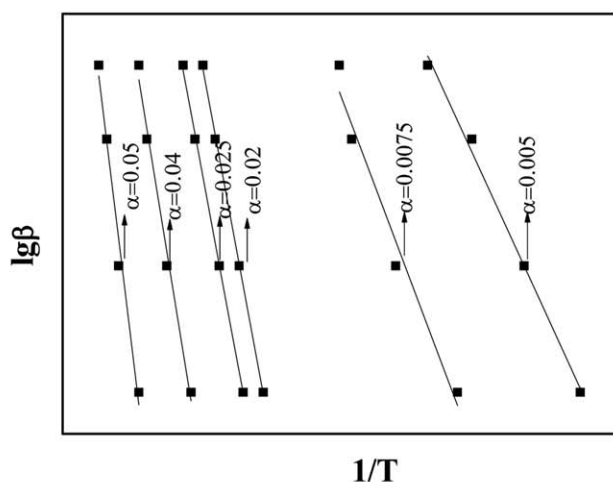
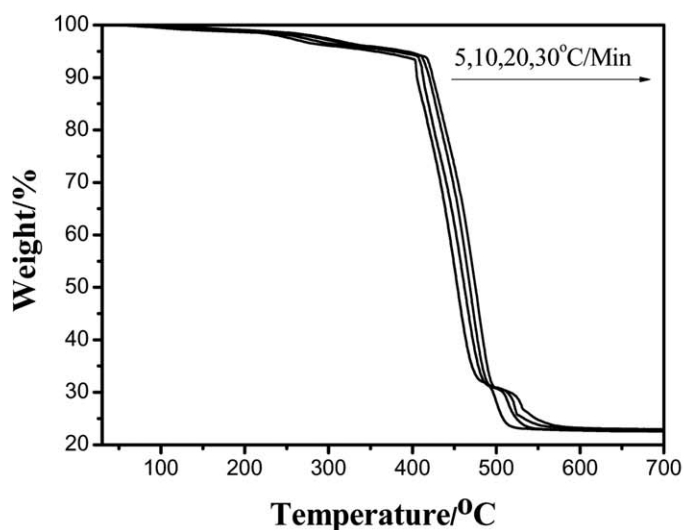


Figure 5. TGA curves of the SBR vulcanizates with supported antioxidant SiO₂-2246 under different heating rates and the corresponding plots of lgβ vs. T⁻¹.

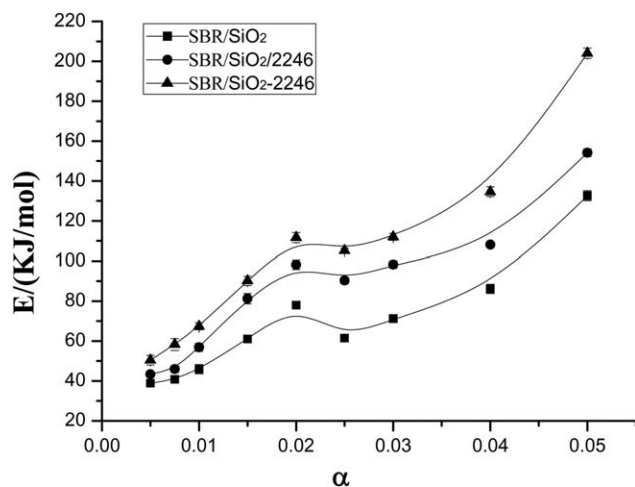


Figure 6. Plots of apparent activation energy E vs. fractional mass loss α .

Figure 6 shows the apparent activation energy (E) changes of the SBR vulcanizates with the increasing of mass conversion rate (α). From Figure 6 thermo-oxidative degradations of the SBR vulcanizates might be carried out in three stages. The first stages of the thermo-oxidative degradations of samples are over a range of α from initiation to 0.02. The apparent activation energy (E) increases with increasing α in this stage; the second stages are over a range of α from 0.02 to 0.025. The apparent activation energy (E) decreases with increasing α , which corresponds to the autocatalytic oxidation; the third stages are over a range of α larger than 0.025. The apparent activation energy increases gradually again, which corresponds to the decomposition of oxidation products and the deepened process of aging.²¹

It is showed that the activation energies of the SBR composite with SiO₂-2246 are higher than those of the SBR composites without antioxidant and with unmodified SiO₂/2246 mixture, indicating that the thermo-oxidation resistance effect of the SiO₂-2246 in SBR is superior to the unmodified SiO₂/2246 mixture.

ATR-FTIR Analyses

Figure 7 presents the ATR-FTIR spectra of the SBR vulcanizates with different antioxidants aged at 100°C for different days.

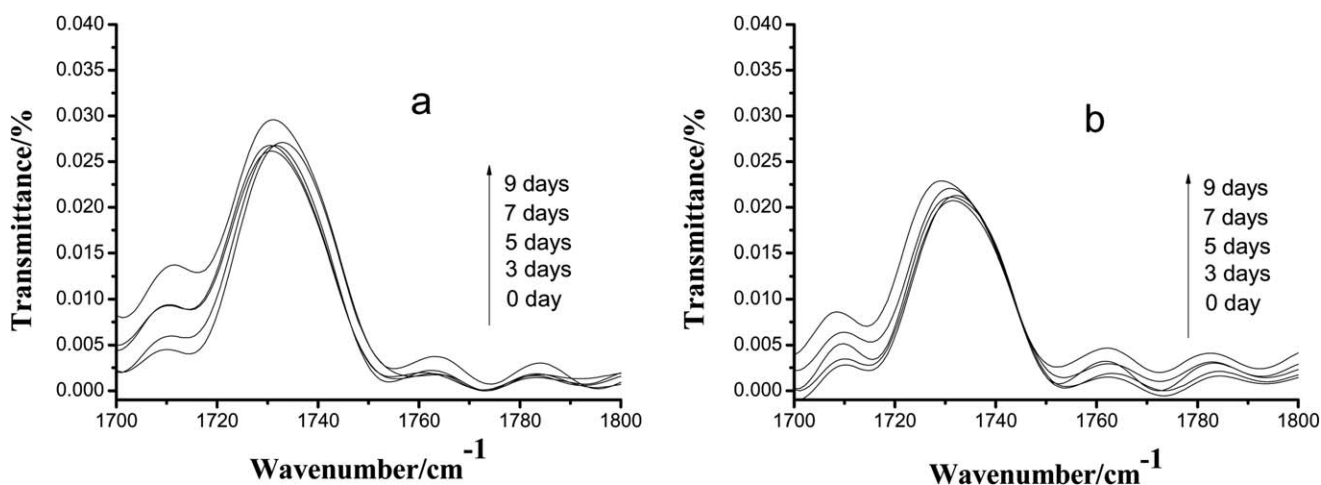


Figure 7. ATR-FTIR spectra of the SBR composites with different kinds of antioxidants after aging at 100°C: (a) SBR/SiO₂/2246, (b) SBR/SiO₂-2246.

The ATR-FTIR spectra show significant characteristic absorption bands after aging. It is known that in the process of rubber aging, the rubber surface will be oxidized at first and the main productions are carbonyl compounds, with the increase of aging time, the area of the absorbance bands will be increased. This assesses the intensity of the peaks in the range 1800–1700 cm⁻¹, thus reflecting the formation of carboxylic acids (1710 cm⁻¹) and esters (1730 cm⁻¹) in the course of degradation. Figure 7 shows that the absorbance bands of two composites, SBR/SiO₂/2246 and SBR/SiO₂-2246, have increased with increasing aging times due to the oxidation of SBR composites. Furthermore, the absorbance bands of the composite with SiO₂-2246 are weaker than those of the composite with the unmodified SiO₂/2246, indicating that the silica-supported 2246 exhibits improved antioxidative efficiency.

Morphology of SiO₂-2246 in SBR Composites

SEM is an important tool for investigating the morphology of materials.^{22,23} The dispersion state of supported antioxidant SiO₂-2246 and SiO₂/2246 mixture in SBR matrix are shown in Figure 8.

As shown in Figure 8(a), SiO₂/2246 is not evenly dispersed in the SBR matrix as large agglomerates because of the formation of hydrogen bonds^{24,25} between the hydroxyl groups on the surface of the SiO₂ and the phenolic hydroxyl groups in 2246 or between the SiO₂ particles themselves. However, for SiO₂-2246, the hydroxyl groups on SiO₂ surface have reacted with the phenolic hydroxyl groups of 2246 and hence resulted in the decrease of hydroxyl groups on SiO₂ surface, thus the agglomerates of the silica particles were reduced and silica became more compatible with the SBR matrix, which allows the SiO₂-2246 to be well-dispersed in the SBR matrix, as shown in Figure 8(b). The antioxidative efficiency of the antioxidants has been reported to be related to the dispersion state of the antioxidant in the polymer matrix.²⁶ Hence, SiO₂-2246 should exhibit higher antioxidant efficiency than SiO₂/2246 in the SBR matrix.

Mechanical Properties Retentions in Thermo-Oxidative Aging Process

Thermo-oxidative aging test is indispensable for studying the properties of vulcanizates. The SBR/SiO₂-2246 and SBR/

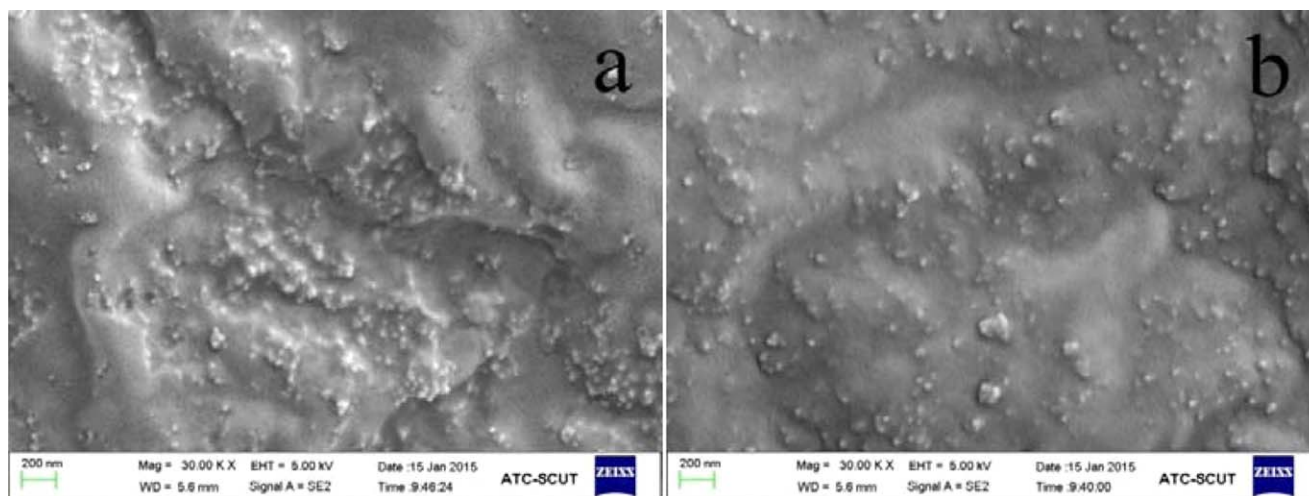


Figure 8. SEM images of (a) SBR/SiO₂/2246 composites and (b) SBR/SiO₂-2246 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SiO₂/2246 composites were subjected to thermal oxidative aging at 100°C for different times. The variations of the mechanical properties retentions are represented in Figure 9. It is clearly shown that the composite with silica-supported antioxidant SiO₂-2246 exhibits better mechanical properties retentions than that with corresponding low-molecular-weight antioxidant 2246 and that without the antioxidant during long-term thermo-oxidative aging. After 3 days of aging, the tensile strength retention and the elongation at break retention are even increased for the silica-supported 2246. The superior anti-aging capability of SiO₂-2246 can be attributed to the immobilization of 2246 via covalent bonds onto the surface of homogeneously dispersed SiO₂, which can simultaneously improve the uniform dispersion of the antioxidant in SBR matrix, enlarge the contact area between the

antioxidant and the rubber matrix, and retard the volatilization and migration of 2246 especially during the long-term accelerated aging.

The excellent retentions of the mechanical properties of the SBR/SiO₂-2246 composite indicate that the supported 2246 exhibits a huge potential to expand the application of antioxidant 2246 for industrial production.

Thermo-oxidative aging of rubbers is believed to occur in two ways: chain scission and chain crosslinking, i.e., degradation and crosslinking.²⁷ The crosslinking of rubber chains dominates the thermal oxidative process of SBR vulcanizates due to the presence of butadiene. Therefore, the crosslinking density can be used to evaluate the extent of the oxidation reaction. The crosslinking densities of the SBR vulcanizates with different

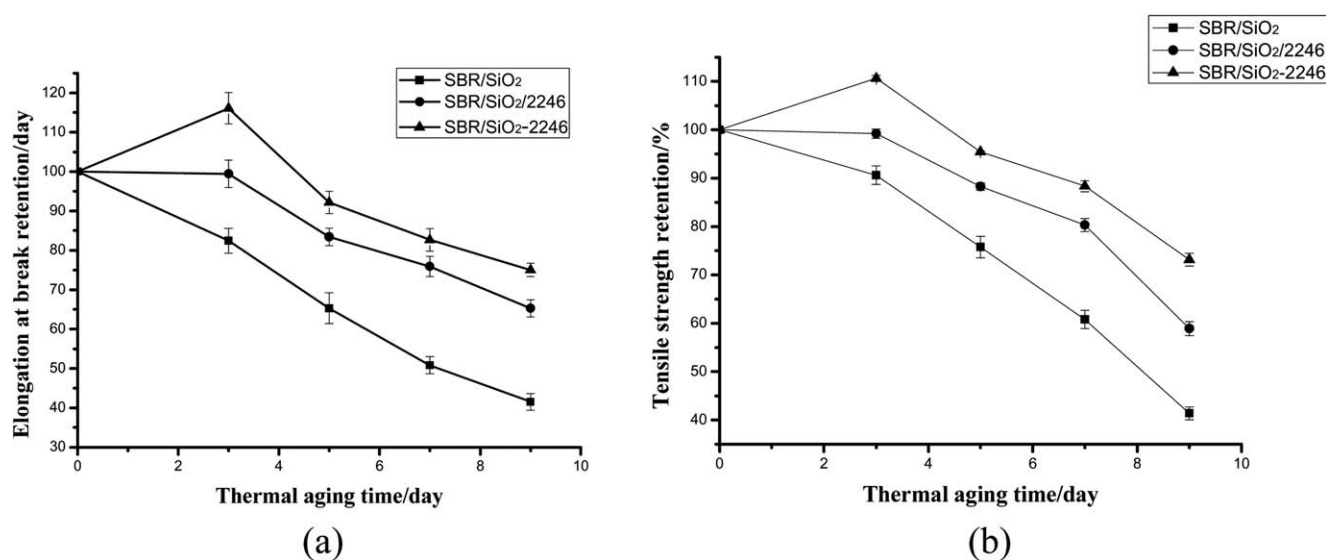


Figure 9. Retentions of the mechanical properties of SBR composites after thermal oxidation aging at 100°C: (a) tensile strength, (b) elongation at the break.

Table II. Crosslinking Densities of SBR Composites before and after Thermo-Oxidative Aging at 100°C

Sample	Crosslinking densities at different aging time (10^{-5} mol cm $^{-3}$)				
	0 day	3 day	5 day	7 day	9 day
SBR/SiO $_2$	7.42 ± 0.03	7.95 ± 0.04	8.69 ± 0.07	9.16 ± 0.05	10.10 ± 0.05
SBR/SiO $_2$ /2246	7.53 ± 0.03	8.02 ± 0.04	8.34 ± 0.04	8.75 ± 0.03	9.19 ± 0.04
SBR/SiO $_2$ -2246	7.94 ± 0.04	8.10 ± 0.04	8.22 ± 0.04	8.43 ± 0.04	8.90 ± 0.04

antioxidants (SiO $_2$ -2246, SiO $_2$ /2246 and SiO $_2$) after aging at 100°C for varying times are shown in Table II. The samples with antioxidants exhibit higher initial crosslinking densities before aging than the sample without the antioxidant. During the first period of thermo-oxidative aging (0–3 days), the crosslinking density of the composite with the silica-supported antioxidant increased with the increase of aging time and is higher than that with SiO $_2$ /2246 and SiO $_2$ because the support of 2246 on SiO $_2$ surface activates the reaction of phenolic hydroxyl groups with the rubber chains and facilitates the increase of crosslinking density. After aging for 3 days, the crosslinking densities of the three composites all increased with the increase of aging time, but the increasing rate of the crosslinking density of SBR/SiO $_2$ -2246 composite is the slowest, indicating that the inhibitory effect of the supported antioxidant SiO $_2$ -2246 on the crosslinking reaction of the SBR composites in aging process is the strongest. Besides, because of the covalent bonds between SiO $_2$ and antioxidant 2246, the migration and volatility of low molecular antioxidant is dramatically reduced, the silica-supported antioxidant has higher antioxidant efficiency, and as a result, the increasing rate of crosslinking density is the slowest. Therefore, it can be concluded that the thermal oxidative resistance of the supported antioxidant SiO $_2$ -2246 is superior to that of the SiO $_2$ /2246 mixture.

CONCLUSIONS

Silica-supported antioxidant SiO $_2$ -2246 was successfully prepared by a solid-phase method. The low molecular antioxidant 2246 was directly immobilized onto the surface of silica particles through covalent bonds. In SBR/SiO $_2$ -2246 vulcanizate, SiO $_2$ -2246 was homogeneously dispersed in SBR matrix. In the process of thermo-oxidative aging, the apparent activation energies and mechanical properties retentions of the SBR composite with SiO $_2$ -2246 were higher than those of the composite with unmodified SiO $_2$ /2246 mixture, and the absorbance bands of the composite with SiO $_2$ -2246 were weaker than those of the composite with the unmodified SiO $_2$ /2246. Therefore, it was concluded that the SiO $_2$ -2246 could significantly improve the thermo-oxidative stability of the SBR vulcanizates compared to the corresponding low-molecular-weight 2246. Additionally, the advantages of the silica-supported 2246 prepared by the solid-phase method also included low migration, low volatility, low pollution, easy operation, and high yield.

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