

Studies on Preparation and Properties of Vinyltriethoxysilane-Grafted Styrene-Butadiene Rubber

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ABSTRACT: Graft polymerization of vinyltriethoxysilane (VTES) onto styrene-butadiene rubber (SBR) was carried out in latex using benzoic peroxide (BPO) as an initiator. The concentration of VTES effecting on vulcanization characteristics, mechanical properties and thermal properties of VTES-grafted SBR (SBR-g-VTES) were investigated. The grafting of VTES onto SBR and its pre-crosslinking were confirmed by attenuated total reflectance-Fourier transform infrared reflectance and proton nuclear magnetic resonance. The mechanism of graft polymerization was stud-

ied. The results revealed that the minimum torque, optimum cure time, tensile strength, thermal decomposition temperature, and glass transition temperature (T_g) all increased with the increasing concentration of VTES. But the grafting efficiency of VTES, rate of vulcanization, and elongation at break of the SBR-g-VTES decreased. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2808–2814, 2011

Key words: styrene-butadiene rubber; vinyltriethoxysilane; SBR-g-VTES; graft polymerization

INTRODUCTION

Styrene-butadiene rubber (SBR) is an important synthetic rubber with some good properties such as high strength, outstanding resilience, and high elongation at break. However, SBR is quite sensitive to heat and stress because of the presence of the double bond on its backbone chains. These inherent drawbacks of SBR have limited its application in industry.¹ So as to extend its use, physical mixing and chemical grafting methods have been developed to improve its properties. The chemical grafting of SBR can be carried out in latex,^{2,3} solution,⁴ or solid phase.⁵ Meanwhile, chemical grafting method provides a potential route for significantly altering the mechanical properties and thermal stabilities of SBR.^{6,7}

Recently, many studies^{8–12} have shown that the vinyl monomers grafted onto SBR can provide the compatibility to the polymer matrix. However, researches on the mechanical properties and thermal stabilities of the grafted SBR are seldom reported. As demonstrated by literatures,^{13–15} rubbers grafted by organofunctional silane followed by its condensation reaction in hot latex can improve the mechanical properties and thermal stabilities, finally to improve its processing behavior.

In this study, graft polymerization of vinyltriethoxysilane (VTES) onto SBR was carried out in latex using benzoic peroxide (BPO) as an initiator. The concentration of VTES effecting on vulcanization characteristics, mechanical properties and thermal properties of VTES-grafted SBR (SBR-g-VTES) were investigated. The grafting of VTES onto SBR and its pre-crosslinking were confirmed by attenuated total reflectance-Fourier transform infrared reflectance (ATR-FTIR) and proton nuclear magnetic resonance (¹H-NMR). Finally, the grafting mechanism was also investigated.

EXPERIMENTAL

Materials

The SBR latex (SBRL1721, 25.9 wt % solid element, 60% butadiene content, 18.7% *cis*-1,4-polybutadiene, 32.9% *trans*-1,4-polybutadiene, 8.4% 1,2-polybutadiene content, 3% gel content, ML(Mooney viscosity)₍₁₊₄₎ of 55.73 at 100°C, $M_w = 3.568 \times 10^5$, the medium particle size is 79.13 nm.) was received from LAN Zhou Petroleum Chemical Industrial (LAN Zhou, China). VTES (A-151) was provided by Shandong Nan duo Silicone (Shandong, China). BPO (CP) was supplied by Shan Pu Chemical (Tianjin, China). Toluene was received from Tianjin Fuyu Chemical (Tianjin, China). The blends of *N*-octyl-*N*-Phenyl- ρ -phenylenediamine and 2,2,4-trimethyl-1,2-dihydroquinoline (8PPD), methyl trialkyl ammonium chloride (AM-2) and the condensation product

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TABLE I
Recipe for Preparation of SBR-g-VTES

Recipe	4%	8%	10%	12%	14%
SBR latex (g)	380.00	380.00	380.00	380.00	380.00
VTES (g)	4.11	8.57	10.96	13.45	16.05
BPO (g)	0.15	0.15	0.15	0.15	0.15
Parameter and reaction conditions					
Monomer: DRC ratio (wt %)	4 : 96	8 : 92	10 : 90	12 : 88	14 : 86

on dicyandiamide and formaldehyde (TXD), were supplied by LAN Zhou Petroleum Chemical Industrial (LAN Zhou, China). Zinc oxide (ZnO), stearic acid (SA), sulfur (S), and *N*-terebutyl-2-benzothiazolesulfenamide (TBBS) were commercial products used as received.

Preparation of grafted SBR

The SBR latex was stirred for 30 min in 500 mL flask under N₂ atmosphere, followed by heating to 68–70°C. The BPO and the VTES with required amount were added into the reactor, stirring for 6h to finish reaction. The SBR-g-VTES latex were agglomerated by coagulants (8PPD, AM-2 and TXD), washed several times with water, and finally dried in a vacuum oven to remove water at 60°C for 24 h. The recipes for the preparation of SBR-g-VTES are shown in Table I.

Preparation of the vulcanized SBR-g-VTES

The curing agents and SBR-g-VTES were mixed with appropriate proportion to get homogeneous blends using two roll mills, and then the mixtures were put into a stainless steel mould and hot pressed at 160°C, 10 MPa to prepare the vulcanized SBR-g-VTES. Table II shows the compounding recipe of SBR or SBR-g-VTES.

Measurement and characterization

Ungrafted SBR was washed out in a soxhlet extractor with 60–80°C boiling point petroleum ether for 24 h, and then the residue was extracted in an acetone for 24 h to remove the free polymer of VTES.

The grafting efficiency of VTES (GE)¹⁶ = practical content of silica (w_2)/theoretical content of silica

(w_1), where $w_1 = (m_2 \times 60/190)/m_1$ and $w_2 = m_4/m_3$, m_1 , m_2 represents the total mass of the VTES-g-SBR and VTES, respectively; m_3 denotes the mass of SBR-g-VTES for muffle furnace burning; m_4 denotes the mass of the ashes (the residue of SBR-g-VTES in muffle furnace under 800°C for 24 h, washed by diluted hydrochloric acid and water for three times, respectively); 60 and 190 are the molecular weight of SiO₂ and VTES, respectively. The grafting ratio of SBR¹⁷ = weight of SBR-g-VTES/total weight of SBR formed.

The ATR-FTIR of SBR and SBR-g-VTES was verified by Fourier transform infrared (Bruker model Tensor 27, German). ¹H-NMR spectra was obtained on Bruker AC 250 MHz NMR, and grafted SBR was swollen with CDCl₃.¹⁸

Thermogravimetric studies were carried out on DSC-TGA Q600 (TA, American) from 25–750°C, under nitrogen, at a heating rate of 10°C/min. Differential scanning calorimeter (DSC) studies were carried out on instrument-2910 DSC (TA, American) from –60 to 60°C, under nitrogen, at a heating rate of 10°C/min.

The corresponding vulcanization characteristics were studied using a Moving Die Rhometer (JC-2000E) at 160°C according to ASTM D 2084-95. Tensile strength was measured using Electron Omnipotence Experiment Machine SANS-CMT5105

TABLE II
Compounding Recipe of SBR/SBR-g-VTES

Materials	Content (g)
SBR	100
Zinc oxide	3.00
Steric acid	1.00
Sulfur	1.75
TBBS	1.00

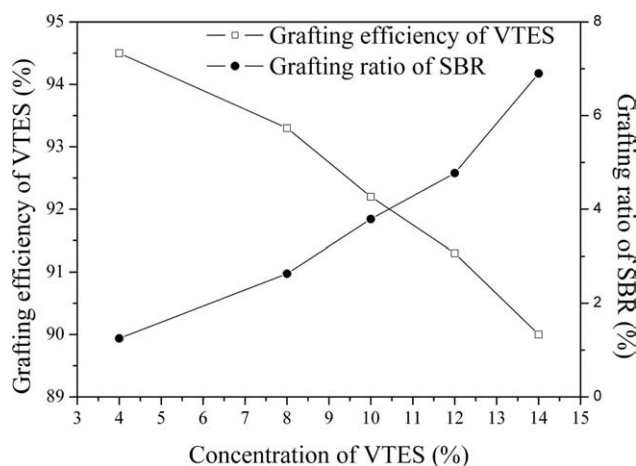


Figure 1 Effect of concentration of VTES on grafted efficiency of VTES and grafted ratio of SBR.

TABLE III
Effect of Concentration of VTES on Particle Properties of SBR Latex

Concentration of VTES (wt %)	Mean value (nm)	Standard deviation(S.D)
0	79.90	0.019
4	79.98	0.019
8	80.45	0.020
10	81.03	0.021
12	81.18	0.025
14	81.93	0.028

(Shenzhen New Sansi, China) according to standard ASTM D 3185-1999.

The particle sizes and particle size distributions were studied using a Laser Diffraction Particle Analyzer (LS 13 320, BECKMAN COULTER).

RESULTS AND DISCUSSIONS

Grafting efficiency of the VTES

Figure 1 shows the effects of concentration of VTES on the grafting efficiency of VTES and the grafting ratio of SBR.

It can be seen that the grafting efficiency of VTES decreases with the increasing concentration of VTES. The grafting ratio of SBR increases with the increasing concentration of VTES. It is due to that the grafting reaction occurs mainly on the surface of the SBR latex. As grafting processed and a certain thickness of the polymer of VTES is reached on the surface of SBR, the contact area between VTES and SBR decreased. The analysis of particle sizes is used to confirm this result. Table III shows the effects of concentration of VTES on the particle properties of SBR latex. The particle size increases slightly with the increasing concentration of VTES. The similar results have been reported by Merkel.¹⁹ Therefore, it is more difficult for graft polymerization

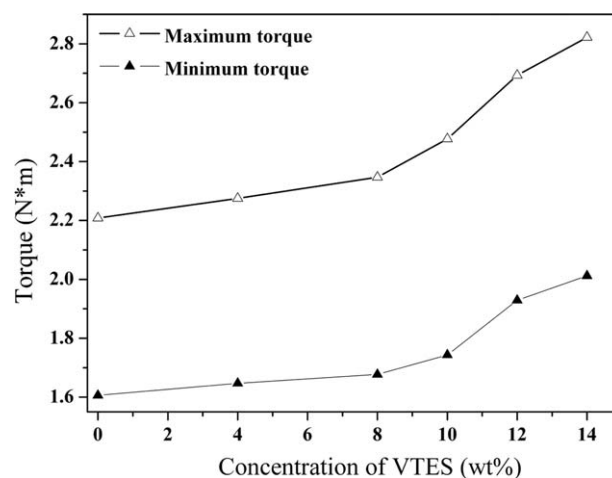
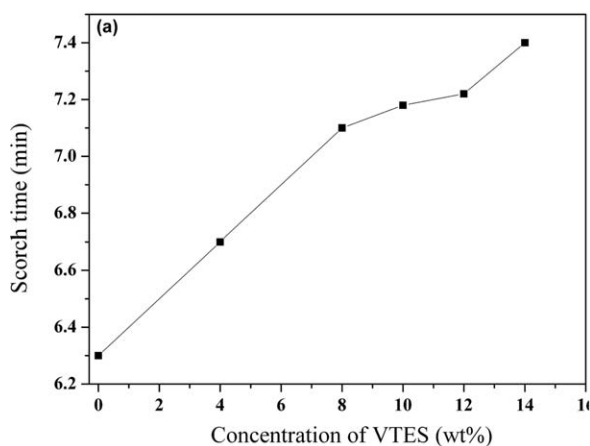


Figure 2 Effect of concentration of VTES on T_{\min} and T_{\max} of the SBR-g-VTES.

of VTES onto the surface of SBR than that of homopolymerization.²⁰

Vulcanization characteristics of SBR-g-VTES

Torque of the SBR-g-VTES

Figure 2 shows the effects of concentration of VTES on the minimum and maximum torque (T_{\min} and T_{\max} , respectively) of the SBR-g-VTES.

Both the T_{\min} and T_{\max} of the SBR-g-VTES increase with the increasing concentration of VTES. The increase of T_{\min} is due to the stronger rubber-rubber interaction of SBR-g-VTES, the $-\text{Si}-\text{O}-\text{Si}-$ bond can be formed successfully by the hydrolysis and condensation of alkoxy silyl ($-\text{Si}(\text{OC}_2\text{H}_5)_3$) groups in the SBR-g-VTES, and it causes stronger intermolecular interactions of SBR-g-VTES. In addition, the increase of T_{\max} is due to the increase of crosslink density of the vulcanized SBR-g-VTES. Meanwhile, the $-\text{Si}-\text{O}-\text{Si}-$ bond can also improve

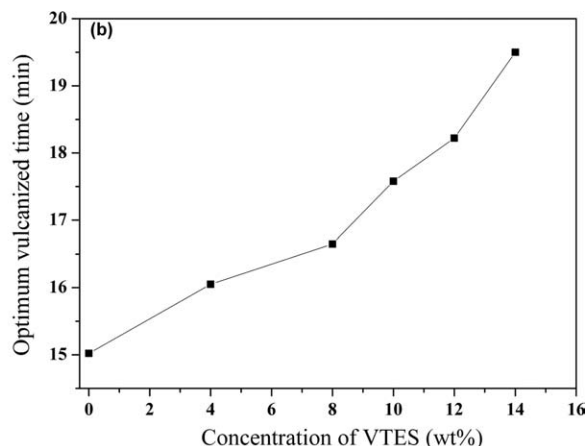


Figure 3 Effect of concentration of VTES on t_{s1} and the t_{90} of the SBR-g-VTES.

TABLE IV
The Vulcanized Reaction Kinetic Parameters of the SBR-g-VTES

Concentration of VTES (wt %)	k_r (min^{-1})	n	t_0 (min)	t_{20} (min)	t_{50} (min)
0	0.513	0.609	6.30	6.50	8.25
4	0.461	0.641	6.70	6.95	8.87
8	0.415	0.697	7.12	7.45	9.53
10	0.365	0.739	7.18	7.60	9.92
12	0.333	0.748	7.22	7.80	10.22
14	0.260	0.807	7.33	8.02	11.17

rubber-rubber interaction of the vulcanized SBR-g-VTES.

Vulcanized time of the SBR-g-VTES

The effects of concentration of VTES on the scorch time (t_{s1}) and the optimum vulcanized time (t_{90}) of the SBR-g-VTES are shown in Figure 3.

It can be seen that both t_{s1} and t_{90} of the SBR-g-VTES increase with the increasing concentration of VTES. The results are due to the reduction in the rate of vulcanization of SBR after grafted by VTES. The rate of vulcanization is being discussed below.

The kinetic parameters are obtained from the normalized torque θ curves according to the isothermal vulcanized model proposed by Kamal and Sourour²¹:

$$\theta = \{k_r(t - t_0)^n / \{1 + (k_r(t - t_0))^n\}\}$$

where θ is considered the state of the vulcanization, k_r is the reaction rate, n is the reaction order, and t_0 is the scorch time.

The corresponding vulcanized reaction kinetic parameters are indicated in Table IV. As expected, the parameters show that SBR-g-VTES makes the rate of

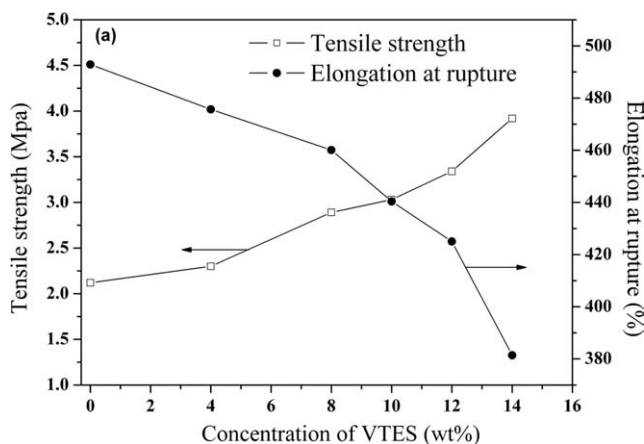


Figure 4 Effect of concentration of VTES on mechanical properties of SBR-g-VTES.

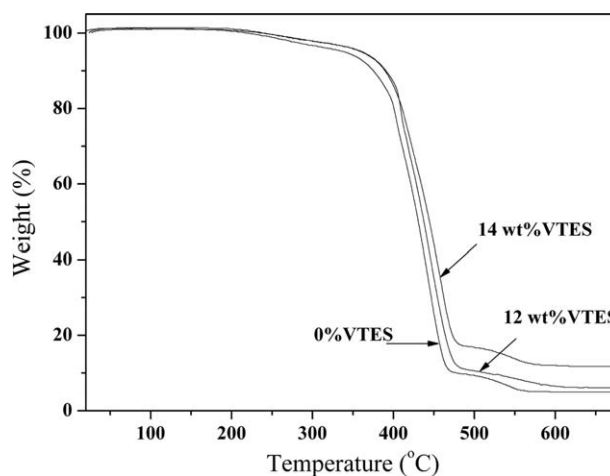


Figure 5 TGA curves of SBR and SBR-g-VTES.

vulcanization decrease, but the reaction order of vulcanization increase. The decrease of reaction rate is due to the lower concentration of double bonds in SBR-g-VTES. Additionally, the formation of steady $-\text{Si}-\text{O}-\text{Si}-$ linkage through hydrolysis of alkoxy-silyl ($-\text{Si}(\text{OC}_2\text{H}_5)_3$) groups may increase the reaction order.

Mechanical properties

Figure 4 shows the effects of concentration of VTES on the mechanical properties of the vulcanized SBR-g-VTES.

The tensile strength of the SBR-g-VTES increases with the increasing concentration of VTES, but the elongation at break decreases. The tensile strength of the SBR-g-VTES reaches to 3.92 MPa with 14% VTES. The increase of tensile strength can be explained by the increased reinforcement and crosslink density, which is agreed with the results of torque. The decrease of elongation at break is due to the formation of complex network structures for increased crosslink density.

Thermal properties

The TGA curves of ungrafted SBR and SBR-g-VTES are presented in Figure 5. Table V shows the temperature at 5, 10, 30, and 50% weight loss for the SBR and SBR-g-VTES samples.

TABLE V
Analysis on Thermogravimetric of VTES-Modified SBR

Sample	$T_{5\%}$ ($^{\circ}\text{C}$)	$T_{10\%}$ ($^{\circ}\text{C}$)	$T_{30\%}$ ($^{\circ}\text{C}$)	$T_{50\%}$ ($^{\circ}\text{C}$)
SBR	340.0	375.0	411.0	430.7
VTES/SBR-g-VTES = 0.17	361.3	390.7	418.1	437.8
VTES/SBR-g-VTES = 0.19	361.3	390.7	422.9	444.5

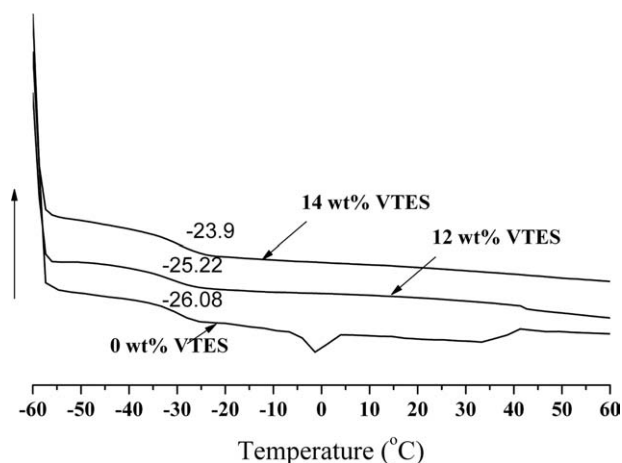


Figure 6 DSC curves of SBR and SBR-g-VTES.

It can be seen that there is no difference between SBR and VTES-g-SBR at the beginning stage. The moment is mostly due to the degradation of ungrafted SBR chains. When the temperature increases to above 300°C, the temperature of VTES-g-SBR is higher than that of ungrafted SBR at the same weight loss, which reveals that thermal stability of SBR has been improved after grafting.

Meantime, the thermal decomposition temperature increases with the increasing concentration of VTES. It reveals that the thermal stability of SBR improves after grafting. It is attributed to the presence of the remaining silanol groups in the SBR-g-VTES network.²² The thermal stability of silanol groups is better than hydrocarbon groups.

The DSC curves of SBR and SBR-g-VTES are presented in Figure 6. The corresponding glass transi-

TABLE VI
The Enthalpies and T_g of SBR and SBR-g-VTES

Concentration of VTES (wt %)	ΔH (J/g)	T_g (°C)
0	0.70	-26.08
12	0.85	-25.22
14	0.94	-23.9

tion temperature (T_g) and the enthalpies are listed in Table VI. It can be seen that the T_g increases with the increasing concentration of VTES. The results are ascribed to the formation of steady $-\text{Si}-\text{O}-\text{Si}-$ bond. The presence of $-\text{Si}-\text{O}-\text{Si}-$ bond can impose restrictions on the molecular motions between the SBR-g-VTES chains, and finally to make the T_g increase.

Mechanism of graft polymerization

The overall graft polymerization for SBR may involve two steps and is (i) the VTES grafted onto SBR, (ii) the formation of steady $-\text{Si}-\text{O}-\text{Si}-$ linkage through hydrolysis of alkoxyethyl ($-\text{Si}(\text{OC}_2\text{H}_5)_3$) groups in the hot SBR latex. The tentative schematic grafting mechanism and pre-crosslinking of SBR are presented in Figure 7. The similar results have been reported by Azanam and Alagar.^{23,24} The ATR-FTIR and $^1\text{H-NMR}$ analysis are used to confirm the mechanism of grafting reaction between SBR and VTES.

The ATR-FTIR spectra of SBR, SBR-g-VTES, and the corresponding ashes are shown in Figure 8.

Compared with the ungrafted SBR, the new peaks of organofunctional silane groups occur in the SBR-

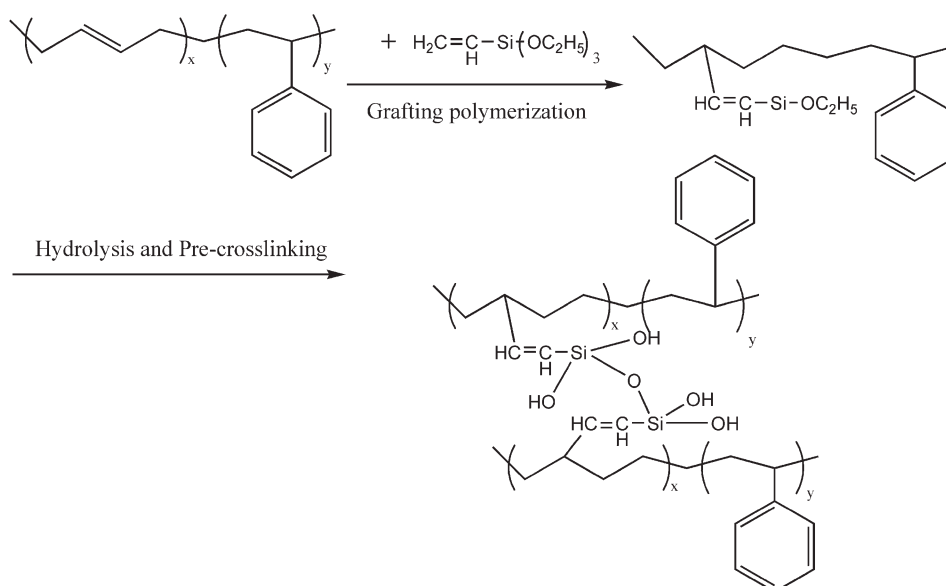


Figure 7 Schematic representation of grafting and pre-crosslinking for SBR.

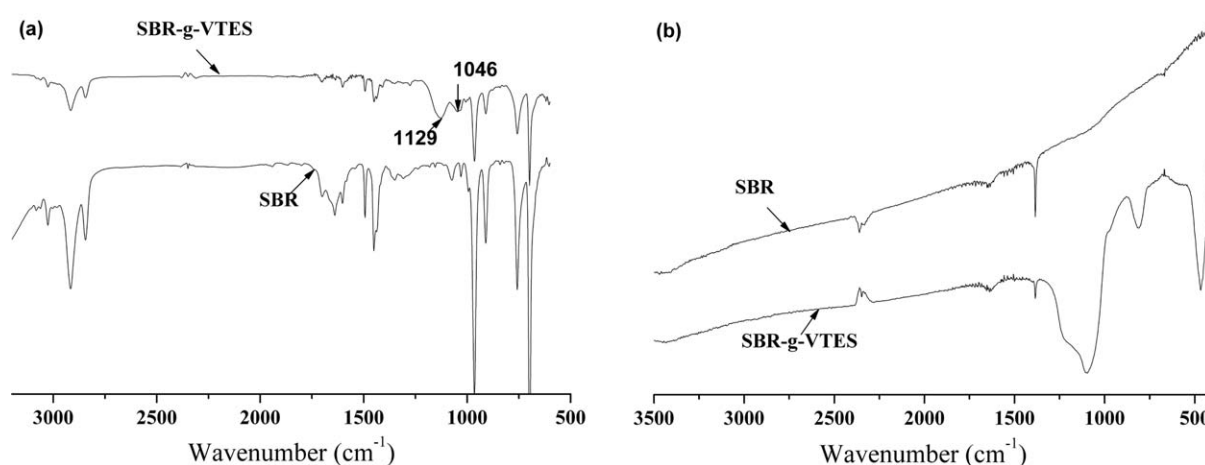


Figure 8 ATR-FTIR spectra of SBR, SBR-g-VTES, and the ashes.

g-VTES [Fig. 8(a)]. The bands at 2931 and 1607 cm^{-1} can be assigned to the stretching vibration peaks of C—H and C=C groups, respectively. And the band at 1452 cm^{-1} can be attributed to the rocking vibration of $-\text{CH}_2$. Additionally, the absorption peaks of $-\text{Si}-\text{O}-\text{Si}-$ bond at 1046 cm^{-1} and $-\text{Si}-\text{O}-\text{C}-$ bond at 1129 cm^{-1} appear in the SBR-g-VTES, respectively.

The ashes of the SBR and SBR-g-VTES are shown in Figure 8(b). The appearance of $-\text{Si}-\text{O}-\text{Si}-$ bond at 1095 cm^{-1} shows that SBR-g-VTES contains Si element. It can prove that VTES has been grafted onto the SBR on the other hand.

The $^1\text{H-NMR}$ spectra of SBR and SBR-g-VTES are shown in Figure 9. The peaks at 7.0–7.5 ppm are attributed to the phenyl group. The peaks at 5–5.5 ppm are attributed to $=\text{CH}$. Compared with the ungrafted SBR, the new peaks at 2.5–2.6 ppm

are attributed to Si—OH. The interpretations prove the mechanism of the graft polymerization in latex.

CONCLUSIONS

SBR grafted by VTES was prepared via graft polymerization in SBR latex, using BPO as an initiator. The minimum torque, optimum vulcanized time, tensile strength, thermal decomposition temperature, and the glass transition temperature (T_g) of the SBR-g-VTES increased with the increasing concentration of VTES. But the grafting efficiency of VTES, vulcanized rate, and the elongation at break of SBR-g-VTES decreased. ATR-FTIR and $^1\text{H-NMR}$ analysis proved that the VTES had been successfully grafted onto the SBR.

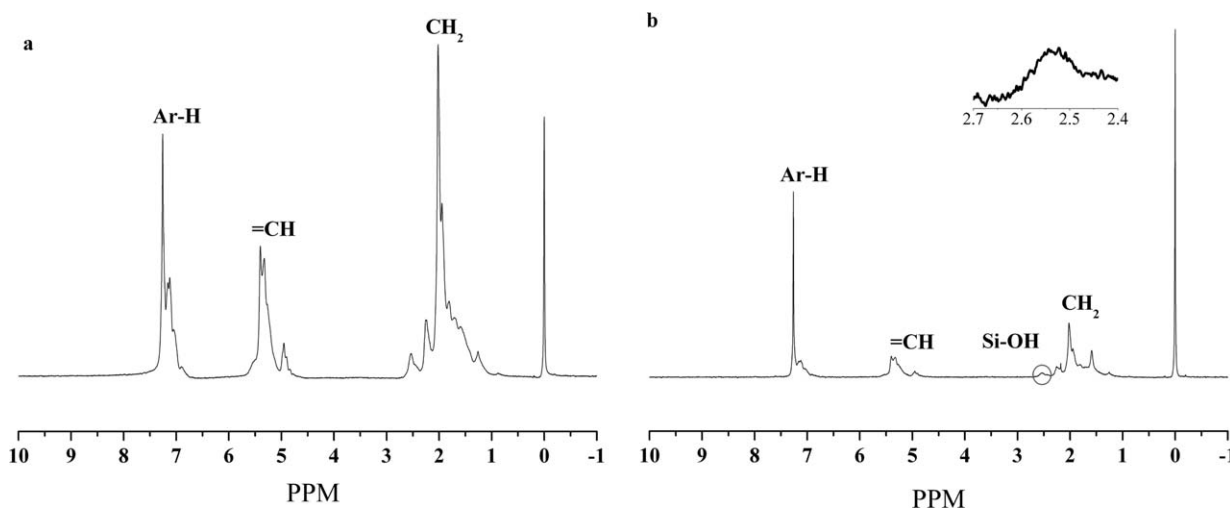


Figure 9 $^1\text{H-NMR}$ spectra of SBR (a) and SBR-g-VTES (b).

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