

Prompt Modification of Styrene-Butadiene Rubber Surface with Trichloroisocyanuric Acid by Increasing Chlorination Temperature

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ABSTRACT: In this article, the surface of styrene-butadiene rubber (SBR) was brushed with trichloroisocyanuric acid (TCI) (1 or 2 wt % in ethyl acetate) and then thermally treated under different conditions. The chemical modification was characterized by contact angle measurement and surface energy, ATR-FTIR spectroscopy, scanning electron microscopy (SEM), and single-lap shear test.

The results revealed that the increase of the chlorination temperature was very effective for SBR surface modification by TCI, leading to enhanced surface wettability and shear strength within several minutes. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 661–668, 2012

Key words: surfaces modification; shear; adhesion

INTRODUCTION

Thanks to its excellent resistance to abrasion, tear, and aging, the synthetic vulcanized styrene-butadiene rubber (SBR) is widely applied in the industries of tire, footwear, electric power, automotive, and so on. However, due to poor wettability and adhesion of SBR surfaces, a surface treatment should be carried out to create surface heterogeneities, enhance the chemical activity, and increase surface energy for better mechanical bonding to adhesives. Many surface modification techniques are exploited to enhance the rubber bonding to different substrates by chemical and topographic surface modifications, including plasma,^{1–4} corona discharge or ultraviolet radiation,⁵ acid treatment,^{6–9} and halogenation.^{10–17} For example, Tyczkowski et al.² modified SBR surfaces by plasma treatment with trichloromethane (CHCl₃), tetrachloromethane (CCl₄), and chlorine (Cl₂) as chlorine precursors, respectively, and found that the T-peel strength of SBR surfaces treated by CCl₄ plasma at 35 W was about two times higher than that of nontreated surfaces. Ramesan and Alex¹¹ prepared dichlorocarbene by the alkaline hydrolysis of CHCl₃, and indicated that the chlorine content increased with reaction temperature during

dichlorocarbene modification of SBR. The modified rubber with excellent solvent resistance exhibited higher tensile strength and hardness than those of unmodified SBR. Hong et al.¹⁸ synthesized new types of water soluble adhesion activators which consisted of lithium (sodium) chlorohexylisocyanurate and lithium (sodium) dichloroisocyanurate to improve the adhesion between SBR and polyurethane. It was revealed that the water contact angle (CA) of treated SBR surfaces decreased noticeably while tear resistance values of joints increased because of the creation of polar groups.

Among these approaches, one of the common and effective methods is the chemical chlorination of the SBR surfaces with halogenating agents in organic solutions such as trichloroisocyanuric acid (TCI) feeding in ethyl acetate. Pastor-Blas et al. did a series of studies on TCI modification of SBR surfaces, and suggested that some vital experimental parameters dramatically affected the performance of halogenation treatment, such as the nature and formulation of SBR,¹² the chlorine content in the TCI solution,¹³ the solvent species,¹⁴ the application procedure before chlorination, and durability of the halogenation.¹⁵ However, it had been confirmed that a minimum of 6 h was required to achieve a good adhesiveness for the chlorination of SBR at room temperature.¹⁶ Furthermore, some of the chlorination processes might last several weeks¹³ or even longer.¹⁵ The purpose of this article is to explore the prompt surface modification of SBR by TCI. It was

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found that the increase in the chlorination temperature was very effective for SBR surface modification by TCI solution. After brushed with 1 or 2 wt % TCI solutions in ethyl acetate, the SBR samples were put in the oven at 23°C, 50°C, or 65°C for different chlorination time. The influence of the processing conditions on surface wettability, composition, morphology, and adhesion properties has been discussed to evaluate the effectiveness of chemical chlorination on SBR surfaces. The method proposed here reduces the chlorination time of SBR to a minimum of 10 min with satisfactory modification effect.

EXPERIMENTAL

Materials

The composition of synthetic sulfur-vulcanized SBR used in this study is given in Table I. SBR 1502 (Jilin Petrochemical Company, Ltd., China) is a cold polymerized emulsion SBR, exhibiting the superior tensile strength, flexibility, and recovery properties. The rubber contains carbon black and SiO₂ as fillers and *N-tert*-butylbenzothiazole-2-sulfenamide (TBBS) as a vulcanization accelerator. Zinc oxide and stearic acid react to produce zinc stearate during vulcanization. The components were well mixed by a three-roll calender, and cured at 150°C for 35 min. TCI (NKC-690, Nanjing K.K. Chemical Engineering Corp., China), acetone (A.R., Nanjing Chemical Reagent Co. Ltd., China), ethyl acetate (EA, A.R., Nanjing Chemical Reagent Co. Ltd., China), and distilled water were used as received.

Sample preparation

The SBR samples in dimensions of 12.5 mm × 25 mm × 2 mm were wiped by acetone, and dried at 23°C for 30 min. A paintbrush was dipped into a freshly prepared TCI/EA solution (1 or 2 wt %) and then applied to the SBR surface. The brushing procedure was carried out with 3–4 brush coatings, and the dosage of each coating was 100 ± 10 mL/m². After that, the treated samples were placed in the oven at 23°C, 50°C, or 65°C for different chlorination time, respectively. After reaching the anticipated reaction time, the residual TCI on the rubber surface was rapidly wiped with acetone to prevent further chlorination.

Characterization

The static CAs were evaluated after 1 min (equilibrium time) of a 5 μL distilled water or methylene iodide (CH₂I₂) droplet that was syringed on the rubber surfaces according to the Sessile-Drop Method at 23°C using an optical angle meter (Cam 200, KSV Instrument Ltd., Finland). All the data reported

TABLE I
Formulation of Vulcanized Synthetic Styrene-Butadiene Rubber

Components	Contents (wt %)
SBR 1502	62.6
Carbon black	31.3
SiO ₂	1.9
Zinc oxide	1.9
Stearic acid	0.6
Sulfur	1.1
TBBS	0.6

TBBS: *N-tert*-butylbenzothiazole-2-sulphenamide.

were the average value of five original measurements on different points of the sample surface.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed on the as-received and treated SBR surfaces with a Nexus 870 FTIR spectrometer (Nicolet Co., Fitchburg, MA) ranging from 4000 to 680 cm⁻¹. A Ge element with an incidence angle of 45° provides a sufficient number of reflections. The scanning number is set as 64 at a resolution of 4 cm⁻¹.

The topography of the treated samples was observed by a field-emission scanning electron microscopy (SEM, Hitachi S-4800, Japan). All SEM samples were sputter-coated with 20 nm of gold before observation.

The adhesive shear strength of the SBR samples was examined by Instron 4466 Universal Materials Testing Machine (Instron Co., Binghamton, NY) in accordance with GB/T 13936-1992 (National Standard of China). The crosshead speed was 50 mm/min and testing temperature was maintained at (23 ± 2)°C. The form and dimensions of specimens for single-lap shear test are shown in Figure 1. The stainless steel in size of 100 mm × 25 mm × 2 mm was used as a metal substrate. A rubber sample was bonded to two pieces of metal substrates by an epoxy and polyamide adhesive to create a metal/adhesive/rubber/adhesive/metal sandwich configuration with the thickness of 2.0 ± 0.1 mm. The overlap length was 12.5 ± 0.2 mm. The specimens were cured at 23°C for 5 days before testing. Each result was obtained by the test repetition with five specimens.

RESULTS AND DISCUSSION

Contact angle and surface free energy

Presented in Figure 2 is water CA on the SBR surfaces before and after modification. It was found that the CA values of untreated samples were 92° on average, but they rapidly declined after chlorination. The 0 min sample, which was prepared by brushing with 2 wt % TCI solution immediately followed by wiping with acetone, has a CA that fell to about 84°,

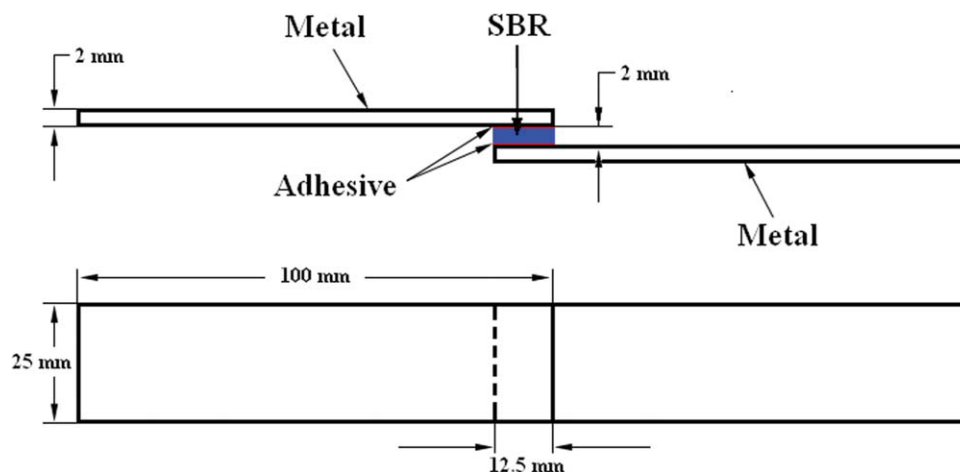


Figure 1 Schematic of the form and dimensions of single-lap shear test specimen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

demonstrating effectiveness of fast halogenation treatment. After this TCI coated sample was heated in the oven at 50°C for 10 min, the CA sharply dropped to $(68.3 \pm 2.1)^\circ$ and almost remained constant even if the SBR surface had been further heated for 6 h. Although halogenation treatment at 23°C could also decrease the CA values to the similar level, which would be consistent with previously reported results,^{13–15} the chlorination time would be prolonged to 1 h or even longer. When the SBR surface was treated with 1 wt % TCI solution (Fig. 3), similar CA results could be obtained. The time when the CA reached the expected value was 1 h, 30 min, and 20 min for the chlorination temperature of 23°C, 50°C, and 65°C, respectively. Previous studies¹⁷ demonstrated that chlorination was an effective reaction and required only a small amount of TCI (0.5–2 wt %) to produce enough chemical modifica-

tions (oxidation and chlorination of the rubber surface). In this experiment, a higher chlorination temperature (50°C or higher) favors the reaction of TCI with the rubber. Compared with the reported results, the chlorination time can be significantly shortened to 10 min when the rubber is treated with 2 wt % TCI solution.

The solid surface energy was calculated by evaluating the CA of water and methylene iodide, based on the equation suggested by Owens and Wendt¹⁹ and Wynne and Ho.²⁰

$$1 + \cos \theta = 2\sqrt{\gamma_s^d} \left(\sqrt{\gamma_l^d / \gamma_l} \right) + 2\sqrt{\gamma_s^h} \left(\sqrt{\gamma_l^h / \gamma_l} \right) \quad (1)$$

$$\gamma_l = \gamma_l^d + \gamma_l^h \quad (2)$$

$$\gamma_s = \gamma_s^d + \gamma_s^h \quad (3)$$

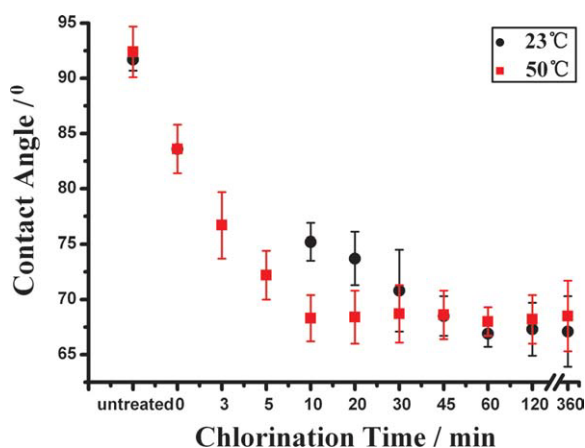


Figure 2 Water contact angle of 2 wt % TCI solution treated SBR surfaces at chlorination temperature of 23°C and 50°C for different chlorination time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

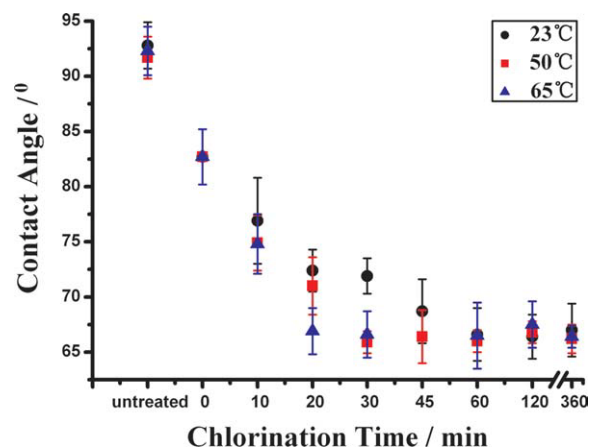


Figure 3 Water contact angle of 1 wt % TCI solution treated SBR surfaces at chlorination temperature of 23°C, 50°C, and 65°C for different chlorination time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Surface Energy of 2 wt % TCI Solution Treated SBR at the Chlorination Temperature of 50 °C for Different Chlorination Time

Chlorination time (min)	θ	θ	γ_s^d (mJ/m ²)	γ_s^h (mJ/m ²)	γ_s (mJ/m ²)
	H ₂ O (°)	CH ₂ I ₂ (°)			
–	92.2	57.6	28.6	1.7	30.3
0	84.5	50.5	31.8	3.2	35.0
3	76.7	44.3	34.2	5.3	39.4
5	72.2	41.8	34.9	6.9	41.7
10	68.3	37.5	36.5	8.1	44.6
30	68.7	38.2	36.2	8.0	44.2
60	68.0	36.9	36.8	8.1	44.9
360	68.5	36.8	36.9	7.9	44.8

where θ stands for the CA, γ_l and γ_s for the surface energy of the liquid and solid respectively, γ_l^d and γ_s^d for the components due to dispersion forces, and γ_l^h and γ_s^h for the components due to hydrogen bonding and dipole–dipole interactions. In this work, the surface energy of water and methylene iodide can be obtained from the literature¹⁹: for water, $\gamma_l^d = 21.8$ mJ/m² and $\gamma_l^h = 51.0$ mJ/m², and for methylene iodide, $\gamma_l^d = 49.5$ mJ/m² and $\gamma_l^h = 1.3$ mJ/m².

Table II displays changes of surface energy of 2 wt % TCI solution treated SBR at the chlorination temperature of 50°C as a function of the chlorination time. The surface free energy of SBR remained at a relatively low level of 30.3 mJ/m². With the increase of chlorination time, the surface energy was gradually enhanced to an average value of 44.6 mJ/m² within 10 min. The increase of the surface energy was attributed to the polar groups produced on the modified surface as a result of chlorination action. As revealed in Table III, the surface energy of the rubber after chlorination at 50°C for 1 h increased to 45.2 mJ/m², which was slightly higher than that of 23°C for 1 h (42.5 mJ/m²). The results reveal that increasing temperature can strikingly accelerate the rate of halogenation on the SBR surface and shorten the chlorination time to 10 min (2 wt % TCI solution with chlorination temperature of 50°C).

Surface morphology

The topographic characteristics of the SBR surface before and after modification was examined using

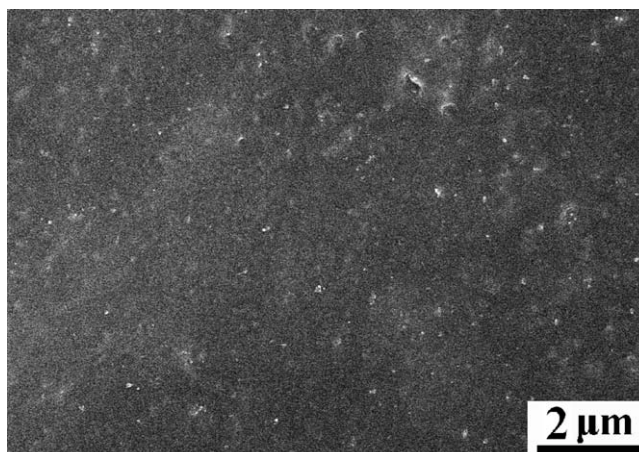


Figure 4 SEM image of the as-received SBR surface.

SEM. The surface of the unmodified SBR was relatively flat and homogeneous (Fig. 4). Small and slender holes were observed on the surface after brushed with 2 wt % TCI solution [Fig. 5(a)] as a result of fast chlorination. Surface micro-roughness began to appear on 2 wt % TCI treated SBR surface after it was heated at 50°C for 3 min [Fig. 5(b)] and became quite distinct for 5 min [Fig. 5(c)]. The μ -degree crevices created on the outermost rubber surface clearly showed the effectiveness of chlorination by prolonged chlorination time to 10 min [Fig. 5(d)]. With the increase of the reaction time, the chlorinating agent penetrated into a deeper position to create a thicker rubber layer [Fig. 5(e)] in accordance with the previous study.¹⁷ When the treated SBR was heated for 60 min, the cracks and wrinkles became more obvious in a deeper and wider range, and most of the rubber surface was roughened [Fig. 5(f)]. Additionally, it was found that the surface roughness created from the treatment at 23°C for 60 min [Fig. 6(a)] was similar to that at 50°C for 10 min [Fig. 5(d)]. Even if chlorination time is prolonged to 360 min at 23°C [Fig. 6(b)], the chlorination seemed still less aggressive than that at 50°C for 60 min [Fig. 5(f)]. Several literatures have also shown that less micro-roughness would be produced when the chlorine concentration was decreased.^{13,17} The SEM images of SBR surfaces treated with 1 wt % TCI solution were shown in Figure 7. The topography of

TABLE III
Surface Energy of 1 wt% TCI Solution Treated SBR at Different Chlorination Temperatures for 60 min

Chlorination temperature (°C)	θ H ₂ O (°)	θ CH ₂ I ₂ (°)	γ_s^d (mJ/m ²)	γ_s^h (mJ/m ²)	γ_s (mJ/m ²)
23	66.6	45.0	32.3	10.2	42.5
50	66.0	38.1	35.9	9.3	45.2
65	66.5	38.2	35.9	9.1	45.0

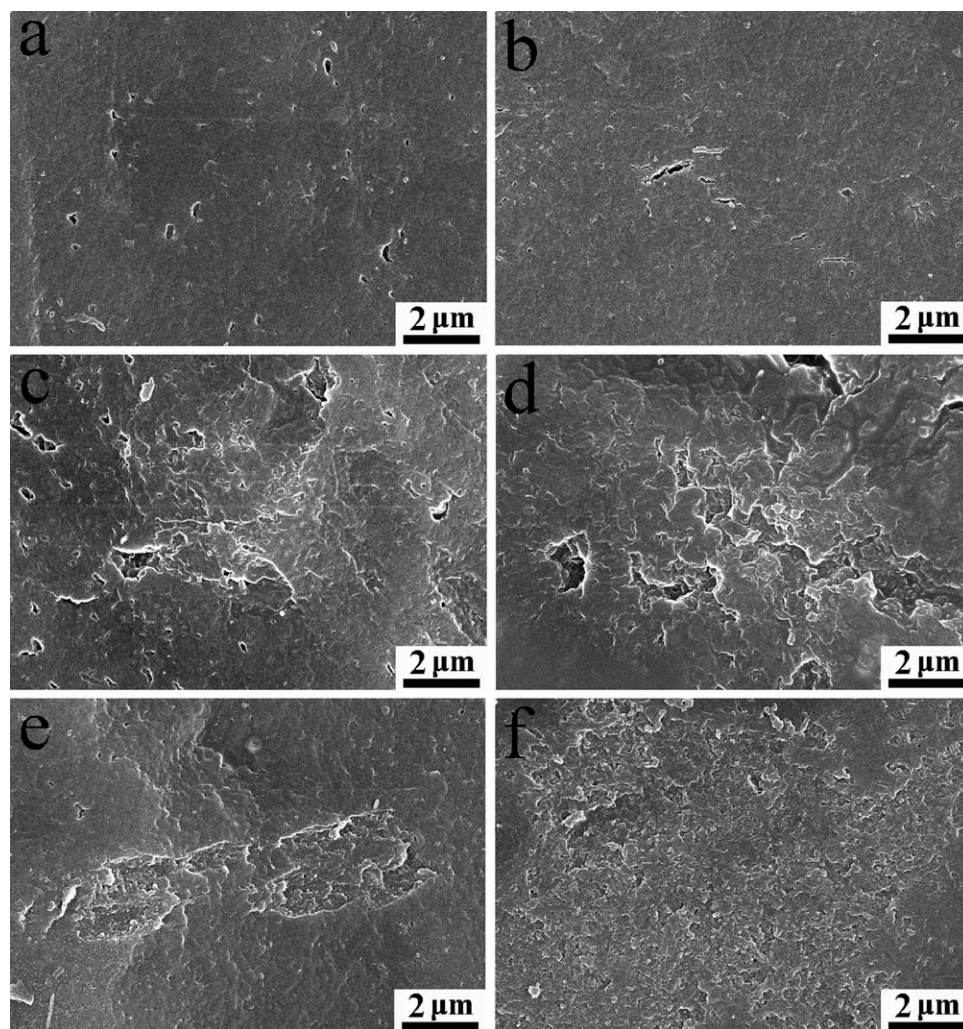


Figure 5 SEM images of 2 wt % TCI solution treated SBR surfaces at the chlorination temperature of 50°C for (a) 0 min; (b) 3 min; (c) 5 min; (d) 10 min; (e) 30 min; (f) 60 min.

the surface changed little after it had been heated at 23°C for 60 min [Fig. 7(a)]. With the same concentration of TCI and reaction time, the formation of crevices and wrinkles was accelerated at the chlorination temperature of 50°C [Fig. 7(b)]. When the temperature further increased to 65°C, more prominent

roughness was observed on the surface due to a higher degree of halogenation [Fig. 7(c)]. It is revealed that the effect of chlorination will be enhanced by the increase of the chlorine concentration or chlorination temperature, fast surface modification can be expected.

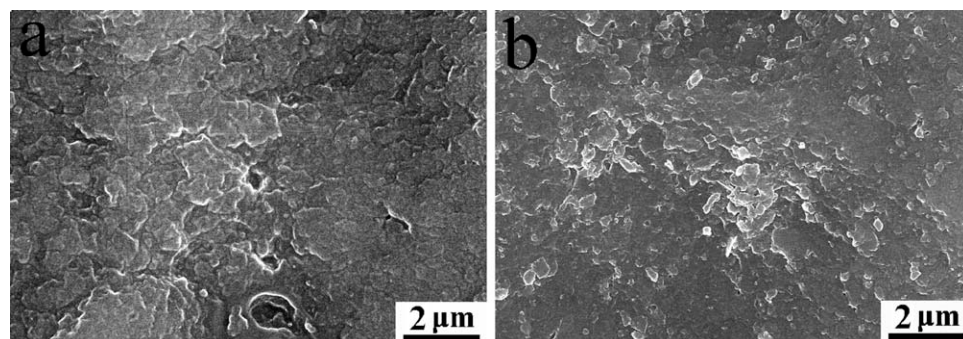


Figure 6 SEM images of 2 wt % TCI solution treated SBR surfaces at the chlorination temperature of 23°C for (a) 60 min; (b) 360 min.

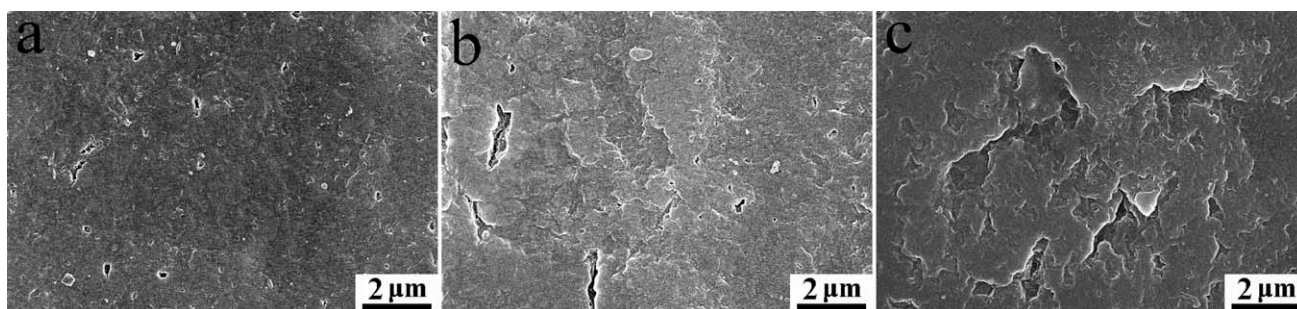


Figure 7 SEM images of 1 wt % TCI solution treated SBR surfaces at the chlorination temperature of (a) 23°C; (b) 50°C; (c) 65°C for 60 min.

ATR-FTIR spectra

Figure 8 shows the ATR-FTIR spectra of SBR surfaces modified by 2 wt % TCI solution and heated at 50°C for different time. From Figure 8, it can be seen that the typical butadiene absorptions of C—H stretching (2840, 2910 cm^{-1}), $-\text{CH}_2$ twisting (1447 cm^{-1}) and *trans*-1,4-C=C (962 cm^{-1}) appear in untreated SBR surface. The C—H offplane vibration of vinyl (705, 761, and 907 cm^{-1}) and aromatic C—C stretching (1600 cm^{-1}) of styrene are also found. The chemical composition of the SBR surface was changed after chlorination with 2 wt % TCI solution. The C—H stretching (2840, 2910 cm^{-1}) and C=C (962 cm^{-1}) bonds are reduced markedly even after chlorination of 3 min; however, the C—H offplane vibrations at 705 and 761 cm^{-1} seem unaffected after reaction. This is attributed to the formation of chlorinated hydrocarbon (1230, 1369 cm^{-1}) in butadiene groups. In addition, a broad peak of C=O bond (1707 cm^{-1}) also occurs due to the oxidation on the rubber surface. The intensity of Si—O bond (1090 cm^{-1}) and zinc stearate (1440, 1600 cm^{-1}) decreases strongly, demonstrating the presence of a nonrubber layer. However, with more chlorination time (10 min or 60 min), there is no further visible change in ATR-FTIR spectra. To better understand the reaction between SBR and TCI, the chlorination mechanism is schematized in Figure 9.²¹ Although the ATR-FTIR spectra provide chemical information of treated surfaces, it does not seem sensitive enough to distinguish the diversity of samples modified by TCI solution with different chlorine concentrations or at different chlorination temperatures.

Adhesive property

The adhesive behavior was characterized by shear strength test. Presented in Figure 10 are the results of the lap shear test as a function of chlorination time at 23°C and 50°C, respectively. The shear strength of untreated SBR was only 2 ± 0.4 MPa. The fracture appeared entirely between the interface of the rubber and adhesive. After the sample was

brushed with 2 wt % TCI solution with 0 min of chlorination, the shear strength increased rapidly to about 4 MPa, which was in accordance with the change of surface wettability and morphology. In this situation, the failure of adhered joints occurred (30 ± 5)% inside the rubber (cohesive failure) and (70 ± 5)% at the rubber–adhesive interface. From Figure 10, it is also shown that the shear strength exhibits a continuous increase in the first few minutes of chlorination, and the diversity of surface modification at different chlorination temperature is more remarkable before the reaction lasts for 10 min. It is noted that the shear strength reached 9–10 MPa after chlorination at 50°C for 10–360 min, confirming prompt modification effect. In these instances, the cohesive fracture of the broken lap shear samples exceeded 90%, and the bulk tensile strength of the rubber was considered to be the main factor responsible for adhesion, as stress–strain analysis proved that the tensile strength of SBR before and after

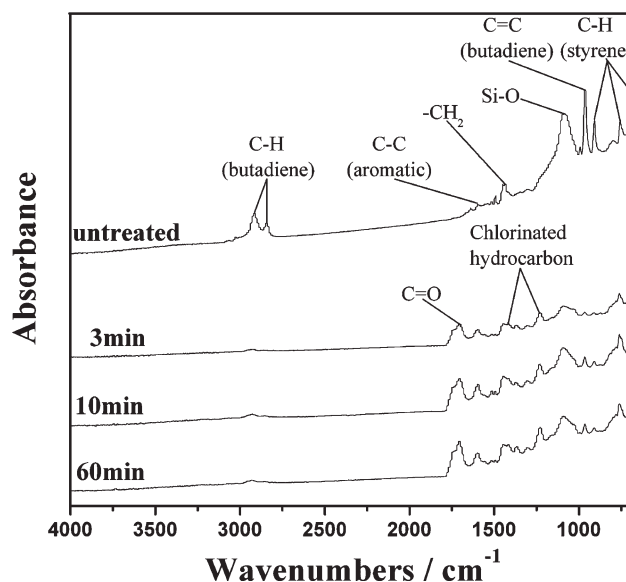


Figure 8 ATR-FTIR spectra of 2 wt % TCI solution treated SBR surfaces at the chlorination temperature of 50°C for different time.

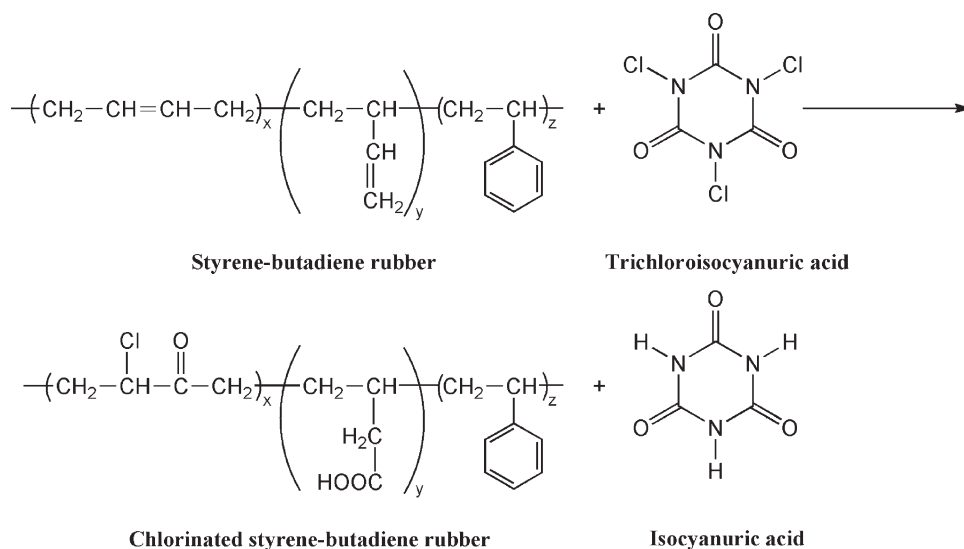


Figure 9 The chlorination reaction between styrene-butadiene rubber and trichloroisocyanuric acid.²¹

modification varied little. However, for the same chlorination time, a slower increase of the shear strength was observed when the samples were heated at 23°C. The test values of the shear strength reached to 9.3 MPa after 360 min as a result of complete halogenation. The shear strength of 1 wt % TCI solution treated SBR with different chlorination time at 23°C, 50°C, and 65°C was also tested. The results revealed that the chlorination time for achieving the shear strength of 9 MPa was over 360 min for 23°C, 30 min for 50°C and 65°C, respectively. In summary, the increase of the chlorination temperature or chlorine concentration effectively accelerates chlorination process on SBR surfaces treated by TCI, and the aim of fast surface modification of SBR with satisfactory shear strength can be obtained.

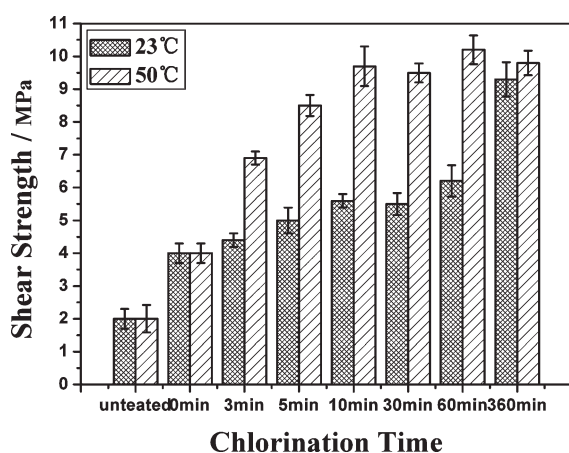


Figure 10 The shear strength of 2 wt % TCI solution treated SBR samples at the chlorination temperature of 23°C and 50°C for different time.

CONCLUSIONS

The chemical chlorination of the SBR with TCI/EA solutions has been performed at different chlorination temperatures to investigate the influence of reaction conditions on the effectiveness of surface modifications. The FTIR spectra only generally characterize the effects of the treatment, showing the rapid creation of chlorinated hydrocarbon and C=O bond between butadiene and TCI on SBR surface. Greater roughness and improved surface wettability are observed by SEM and CA measurement as a result of an effective surface modification at higher chlorination temperatures, which demonstrates that the increase of the heating temperature facilitates chlorination reaction on the SBR surface. The optimization of experimental conditions to obtain better adhesive properties is as follows: SBR is brushed with TCI (2 wt % in EA) and then thermally treated at 50°C for 10 min. The shear strength of the modified SBR can be easily enhanced from 2.0 MPa to 9.7 MPa.

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