

Thiol-Containing Ionic Liquid for the Modification of Styrene–Butadiene Rubber/Silica Composites

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ABSTRACT: To introduce thiol–ene chemistry in the modification of composites by ionic liquid (IL), a novel functional IL, 1-methylimidazolium mercaptopropionate (MimMP), was synthesized and investigated as a modifier for styrene–butadiene rubber/silica composites. MimMP could be hydrogen-bonded with silica and react with the double bonds of rubber chains via thiol–ene chemistry. The filler networking, curing behavior, filler dispersion, cross-link density, and mechanical performance were fully studied. The filler networking in the uncured rubber compounds was effectively restrained. The vulcanization

was largely accelerated by MimMP. The interfacial interaction was quantitatively evaluated and found to consistently increase with increasing MimMP. The mechanical performance and abrasion resistance of the modified vulcanizates improved considerably. The remarkable improvements were mainly ascribed to the improved interfacial structure comprised of MimMP–silica hydrogen bonding and MimMP–rubber covalent bonds via thiol–ene chemistry. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1252–1260, 2012

Key words: interfaces; modification; rubber; silicas

INTRODUCTION

The surface chemistry of silica has been studied extensively by polymer researchers, especially by those people involved in rubber reinforcement.^{1–4} Although the silanol group on the silica surface is of great essence for its reinforcement of rubbers, the simultaneous tough problem is the unsatisfied dispersion and poor interfacial bonding due to its limited compatibility with rubbers.^{5,6} Therefore, the surface chemistry of silica must be tailored to meet the higher requirements of rubber reinforcement. Conventionally, various silanes, such as bis[3-(triethoxysilyl)–propyl] tetrasulfide,^{7,8} bis[3-(triethoxysilyl)–propyl] disulfide,⁹ (3-mercaptopropyl) trimethoxy silane,¹⁰ (3-mercaptopropyl) triethoxy silane,¹¹ and (3-aminopropyl) triethoxy silane,^{12,13} have been employed as modifiers for silica. In most cases, both improved filler dispersion and

changed interfacial structure were always simultaneously highlighted, but rarely has there been any intentional discussion on which one dominates over another. However, according to a recent work of Dohi and Horiuchi,¹⁴ the interfacial structure may play a more important role than the filler dispersion.

As one kind of versatile agent, ionic liquid (IL) has been demonstrated to be highly affinitive toward numerous fillers, such as carbon nanotubes,^{15–20} silica,^{21,22} and clays.²¹ The related interactions, including cation– π interactions,^{15–20,23} van der Waal forces,¹⁷ delocalized electron interactions,²⁴ and hydrogen bonding,^{21,22} have been well studied, and numerous applications have been explored extensively on the basis of these interactions.^{21,24–29}

The design of ILs with functional groups has been expected for tailoring the interface of polymer composites. Having been previously investigated by our group, the introduction of functional groups, such as double bonds, into IL has been highlighted for improving the performance of styrene–butadiene rubber (SBR)–silica composites.^{30,31} Recently, the thiol–ene chemistry has been widely focused for its mild reaction conditions, high reactivity, and excellent yielding. This chemistry has been extensively investigated in the technology of photocrosslinking^{32,33} and in the fabrication of functional materials.^{33–38} In this work, a thiol group was introduced into IL. The functional IL, 1-methylimidazolium mercaptopropionate (MimMP), was synthesized and investigated as a modifier for tailoring the interfacial structure of SBR–silica

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composites. The influences of MimMP on the filler networking, vulcanization behavior, mechanical performance, and morphology were fully studied. Interfacial interactions induced by MimMP were uncovered and correlated to changes in the rubber performance. In comparison to previous protic ILs,^{30,31} MimMP was found to be more reactive toward rubber chains via the thiol-ene reaction and to be more effective in improving the mechanical performance of SBR-silica composites.

EXPERIMENTAL

Materials

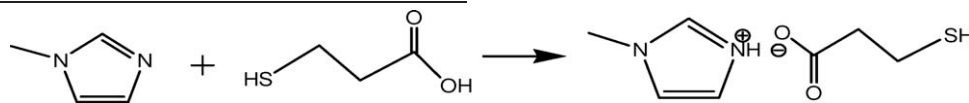
N-Methylimidazole (99% purity) and 3-mercaptopropionic acid (98% purity) were purchased from Alfa Aesar (Tianjin, China). SBR, with the trade name SBR1502 (styrene content = 23.5 wt %), was manufactured by Jilin Chemical Industry Co. (Jilin, China). Precipitated silica, with the trade name WL180, was manufactured by NanPing Jialian Chem., Ltd. (Nanping, China). The Brunauer-Emmett-Teller value of silica was redetermined to

be 200 m²/g by a Micromeritics ASAP 2020 instrument. Other rubber additives were industrial grade and were used as received.

Synthesis of MimMP

As shown later, the dropwise addition of *N*-methylimidazole into 3-mercaptopropionic acid was stoichiometrically carried out with stirring. The reaction was kept in an ice water bath for 1 h. The functional IL (MimMP) was characterized by ¹H-NMR spectroscopy (Bruker Avance Digital NMR spectrometer, 300 MHz; Bruker, Buchen, Germany) and Fourier transform infrared (FTIR) spectroscopy (Vertex 70 FTIR spectrometer, Bruker).

¹H-NMR (300 MHz, CDCl₃):³⁹⁻⁴¹ 14.10 (s, 1H, N-H), 7.72 (s, 1H, N-CH=N), 7.08-7.09 (t, 1H, C=N-CH=C, *J*₁ = 1.2 Hz), 6.87-6.88 (t, 1H, =N-C=CH-N-, *J* = 1.3 Hz), 3.71 (s, 3H, N-CH₃), 2.75-2.79 (t, 2H, -CH₂-COO, *J* = 6.4 Hz), 2.62-2.67 (m, 2H, S-CH₂-C), 1.680 (s, 1H, S-H). FTIR (Bruker Vertex, KBr):⁴²⁻⁴⁴ 3410 (N-H), 3131 (imidazolium-H), 2947 (CH₂), 2557 (S-H), 1707 (C=O), 1525, 1570 (imidazole conjugate).



Affinity of MimMP toward silica and its reactivity with SBR chains

Interactions between MimMP and silica were determined by X-ray photoelectron spectroscopy (XPS; Axis Ultra DLD; Kratos Analytical, Eppstein, Germany). A monochromated Al K α source (1486.6 eV) was used, and all XPS spectra were individually calibrated to its reference C1s component at 285.0 eV.⁴⁵ Shirley background and Gaussian function were employed in the fitting program. After MimMP-silica (1/10 w/w) was mixed in a solution of acetone, the silica-MimMP sample used for the XPS experiment was obtained after sonication, centrifugation, and vacuum drying.

To verify the reactivity of MimMP toward rubber chains, a model compound was prepared by grafting copolymerization in a toluene solution of SBR. The reaction of SBR-MimMP-2,2'-azobisisobutyronitrile (1/4/0.2 w/w/w) was performed at 65°C for 24 h. The crude product was first extracted by water for 2 days. After it was vacuum-dried at 80°C, the graft product (SBR-g-MimMP) was characterized by FTIR spectroscopy.

Preparation of the SBR-silica compounds and characterizations

SBR and other additives were mixed on an open two mill. The composition was as follows: SBR, 100

phr; silica, 40 phr; zinc oxide, 5 phr; stearic acid, 1 phr; *N*-cyclohexyl-2-benzothiazole sulfenamide, 1.5 phr; dibenzothiazole disulfide, 0.5 phr; 2-mercaptobenzoimidazole, 1.5 phr; sulfur, 1.5 phr; and MimMP, variable. In the following text, R_xMimMP indicates the rubber sample with *x* parts per hundred rubber MimMP. To make a comparison with a commercial coupling agent, bis(γ -triethoxysilylpropyl)-tetrasulfide (Si69) was used. Another rubber compound with the addition of 2 phr Si69 was prepared on the basis of the same composition and identified as R2Si69 to ease the following discussion. All of the compounding was performed at about 25°C and lasted for about 12 min. The dependence of shear modulus (*G'*) on the strains of the uncured rubber compounds was measured with a viscoelastography rubber processing analyzer (Göttfert-Werkstoff-Prüfmaschinen GmbH, Germany). The temperature and frequency were set to be 100°C and 1 Hz, respectively. The content of bound rubber in the uncured rubber compounds was determined by extraction of the sample with toluene on a Soxhlet extractor for 3 days. The Mooney viscosity of the uncured rubber compound without sulfur was determined according to ISO standard 289-2005 at 100°C.

The curing characteristics of the rubber compounds were determined with a UR-2030 vulcameter (U-CAN, Nantou, Taiwan) at 150°C. The rubber compounds were vulcanized at 150°C × scorching time (Tc90). Tensile, tear, and hardness tests of the vulcanizates were performed according to ISO 37-2005, ISO 34-2004, and ISO 7619-2004, respectively. The abrasion resistance of the vulcanizates was determined by the volume loss according to GB/T 1689-1998 (China).

The crosslink density (V_e) of the vulcanizates was determined by the equilibrium swelling method.⁴⁶ The specimens of the vulcanizates were ultramicrotomed into thin pieces of about 300 nm in thickness with a Leica EMUC6 instrument (Leica, Wetzlar, Germany) in liquid nitrogen. The transmission electron microscopy (TEM) observations were done with a Philips Tecnai 12 transmission electron microscope (Philips, Eindhoven, Netherlands) with an accelerating voltage of 30 kV.

RESULTS AND DISCUSSION

Reactivity of MimMP toward the SBR chains

The thiol-ene reaction is considered to be highly reactive in photocrosslinking elastomers and tailoring structures for functional materials.^{32,37,47} The reactivity of MimMP toward rubber chains was studied by FTIR spectroscopy of the model copolymer (SBR-g-MimMP) and SBR, as shown in Figure 1. The aromatic hydrogen (3025 and 3061 cm^{-1}), CH_2 (2917 and 2847 cm^{-1}), *trans*- $\text{CH}=\text{CH}$ - (965 cm^{-1}), vinyl ($\text{C}=\text{CH}_2$; 913 cm^{-1}), and phenyl (699 cm^{-1}) could be assigned to the SBR backbone.^{48,49} In the lower curve, the presence of characteristic groups of MimMP, such as carbonyl (1708 cm^{-1}), $\text{C}=\text{N}$ (1553 cm^{-1}), and

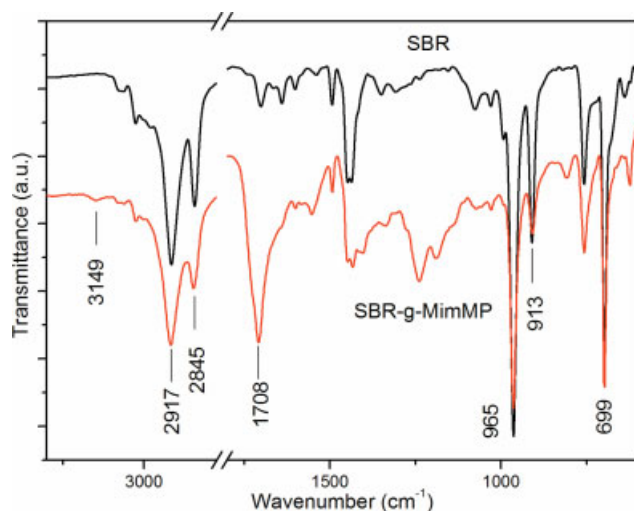


Figure 1 FTIR spectrum of SBR and SBR-g-MimMP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

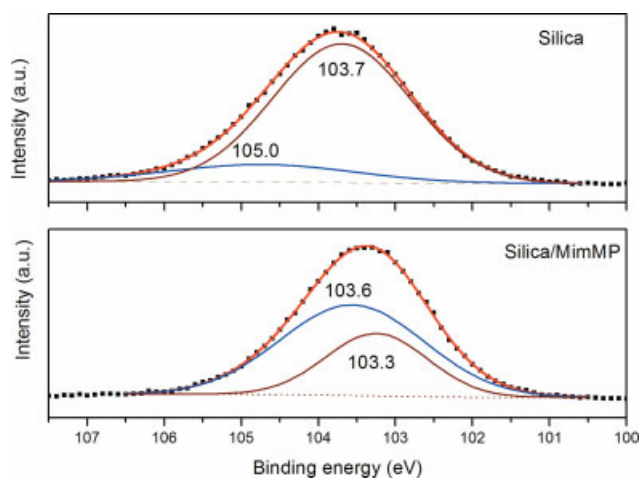


Figure 2 XPS spectra of silica and silica-MimMP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$\text{C}=\text{CH}$ (3149 cm^{-1}) in the imidazolium cation,^{44,50} indicated its successful grafting onto the SBR chains. The integration area of certain peaks may provide more information about the possible mechanism. The integration intensity (I) of each group was calculated. According to the integration results, their values of $I_{965}(-\text{C}=\text{CH}-)/I_{699}(\text{phenyl})$ for SBR and SBR-g-MimMP were 1.64 and 1.66, respectively. This means that the $I_{965}(-\text{CH}=\text{CH}-)/I_{699}(\text{phenyl})$ ratios were almost unchanged after the grafting reaction. However, the $I_{913}(-\text{CH}=\text{CH}_2)/I_{699}(\text{phenyl})$ ratio in SBR was 0.63 and that in SBR-g-MimMP was obviously decreased, at 0.55. This indicates that the activity of $-\text{CH}=\text{CH}_2$ toward thiol was much higher, although the content of vinyl was much lower than the other. The thiol-ene reaction may have rendered important influence on the curing behavior and the performance of the cured vulcanizates.³⁷

Compared with other protic ILs synthesized previously,^{30,31} the reactivity of MimMP toward rubber chains was estimated to be higher. The experimental evidence was that the ratios of the peak area, $I(\text{C}=\text{O})/I(\text{phenyl})$, were different from each other. The integration peak ratio $I(\text{C}=\text{O})/I(\text{phenyl})$ in SBR-g-methylimidazolium sorbate was 0.6 and that in SBR-g-methylimidazolium methyl methacrylate was 2.7. Both were smaller than that in SBR-g-MimMP (3.6). It could be concluded that the reactivity of MimMP was higher than the previous ones. It may have been related to the existence of imidazolium cation and initiated radicals.^{32,35}

MimMP-silica interaction and its influence on the Payne effect

To detect the possible interactions between MimMP and silica, a peak fitting program on the XPS spectra

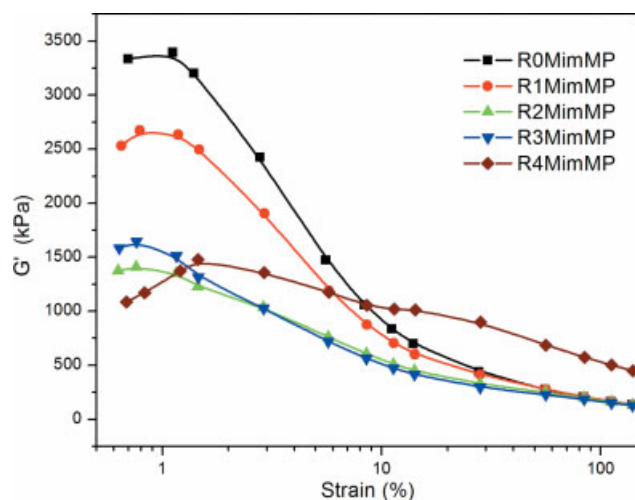


Figure 3 Dependence of G' on strains of the SBR-silica uncured rubber compounds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of silica and silica-MimMP was performed.⁵¹ As shown in the upper curve in Figure 2, the binding energies of silicon in the silanol group (Si-OH) and in the silicon-oxygen bond (Si-O-Si) were located at 105.0 and 103.7 eV, respectively.⁵² Once silica was treated with MimMP, two phenomena were observed. First, Si-OH could not be distinguished by the fitting program; this indicated a strong interaction between Si-OH and MimMP. The interaction was possibly due to the hydrogen bond between Si-OH and the anion of MimMP.^{22,30} Second, the environment of silicon in Si-O-Si seemed to be divided into two components: one was located at 103.6 eV, and the other was at 103.3 eV. A shift of binding energy value for Si atoms from 103.7 to 103.3 eV indicated that there was another strong interaction between Si-O-Si and MimMP. This may have resulted from the hydrogen bond between the Si-O-Si and the imidazolium cation. However, the peak at 103.6 eV may have been assigned to the region that was geometrically unavailable for the Si-O-Si/MimMP interaction.

Generally speaking, filler-filler and polymer-filler interactions can exert significant influences on the Payne effect. The shear modulus discrepancy ($\Delta G'$) between G' at small strain ($\sim 0.5\%$) and G' at large strain ($\sim 100\%$) was employed in monitoring the filler network in the uncured rubber compounds. As shown in Figure 3, with increasing loading of MimMP (<3 phr), $\Delta G'$ gradually decreased; this indicated that the Payne effect was gradually restrained and that the silica networking was effectively alleviated. The restrained Payne effect may have been due to the weakened interaction among silica particles due to the hydrogen bond,³⁰ as sub-

stantiated previously. Interestingly, when the loading of MimMP was higher (>4 phr), the dependence of G' on strains did not have a normal pattern similar to others but had first an increased and then a decreased pattern with increasing strains. Because of the high reactivity of the thiol-ene chemistry,^{32,37} which could be further activated by quaternary ammonium salt,³⁵ the compound with such a high concentration of MimMP may have been premature at 100°C . Consequently, when MimMP was gradually grafted onto the SBR chains, the value of G' initially increased, even with increasing strains. However, when the grafting at 100°C was completed, the dependence of G' on the strains was as simple as the others. The prematurity of the sample with higher content of MimMP was unfavorable to the processing, which is discussed later.

Bound rubber analysis

The contents of bound rubber of the uncured samples were determined by Soxhlet extraction. Their values with incorporations of 0, 1, 2, 3, and 4 phr MimMP were 18, 13, 11, 8, and 90%, respectively. Interestingly, after an extraction with toluene for 3 days, the R4MimMP sample still had in a gel-like appearance, whereas all of the others were white powder just like a pile of silica. For the R1MimMP, R2MimMP, and R3MimMP samples, the surface of silica was coated by MimMP because of hydrogen bonding. At the same time, the grafting of MimMP onto rubber chain was quite limited because of the limited concentration of MimMP. So, the bound rubber contents, which could reveal the interaction between the silica and rubber chains, gradually decreased. However, when the concentration of MimMP was high, up to 4 phr, both the MimMP-silica hydrogen bonding and MimMP-rubber reactions were possibly responsible. During the extraction, scorching took place. The precrosslinking of the uncured compounds resulted in microgels with embedded silica particles because of the substantiated hydrogen bonding. So, the abnormal value of bound rubber content for R4MimMP could be treated as an overestimated one. This result was very consistent with the observed phenomenon in the Payne effect testing.

The Mooney viscosity for the rubber compounds without sulfur was determined to evaluate their processability. When the addition of MimMP was 0, 1, 2, 3, and 4 phr, their Mooney viscosity values were 78.1, 75.1, 68.3, 80.5, and 84.2, respectively. With increasing loading of MimMP, the viscosity took a minimum value. Two reasons should be considered. On the one hand, the restrained filler networking, as substantiated in Figure 3, could have improved the processability by lowering the

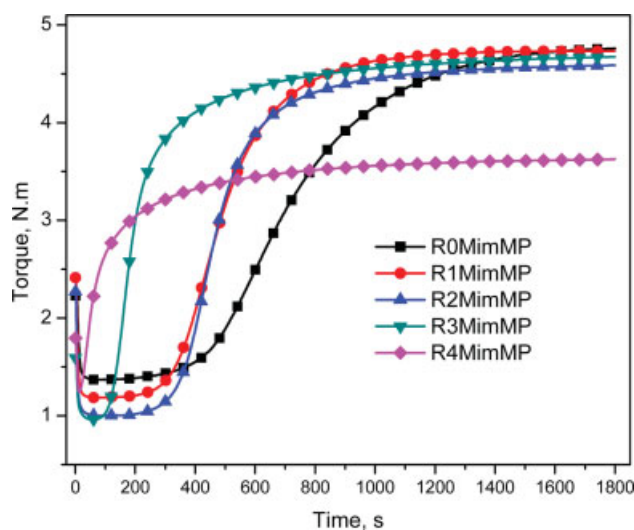


Figure 4 Curing curves of the SBR–silica rubber compounds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

effective volume of the filler. On the other hand, the thiol–ene reaction was initiated at a higher temperature, such as at 100°C, for a high loading of MimMP (>3 phr). With the generated SBR-g-MimMP, the interfacial interactions between silica and rubber chains may have promoted the value of torque. Consequently, the Mooney viscosity of the uncured rubber compound with a higher loading of MimMP (4 phr) took a higher value.

Vulcanization behavior of the SBR–silica rubber compounds

The vulcanization behavior of the SBR–silica rubber compounds was studied, and their curing curves and characteristics are shown in Figure 4 and Table I, respectively. Without any MimMP (R0MimMP), a long marching cure was observed, which was possibly related to the acidity of silica and its high adsorption ability toward rubber additives.⁵³ Once MimMP was loaded, scorch time (T_{s2}) was cut down and consistently decreased with increasing loading of MimMP. Two possible reasons are proposed. First, the thiol group may have largely acti-

vated the vulcanization via effectively lowering the corresponding activation energy of rubber vulcanization.⁵⁴ Second, the high active thiol–ene reaction led to the grafting of MimMP onto the rubber chains. The ions in SBR-g-MimMP could have interacted with silica and accelerated the increasing trend of the torque. As thiol–ene addition could have been activated when the thiol substance bore a catalyzing group, such as the imidazolium cation,^{32,35} the reactivity of MimMP was considerably high enough to exert profound effects on the vulcanization.

From the curing data, we could also see changes in the minimum torque (T_{min}) and maximum torque (T_{max}) during vulcanization. T_{min} was gradually reduced at first and then increased a little. As substantiated in bound rubber analysis, the incorporation of MimMP at lower loading could effectively restrain the network formation of silica. Then, the effective volume of silica may have been lowered. So a decreased T_{min} was observed when a low loading of MimMP (<3 phr) was used. When the loading of MimMP was higher (>4 phr), the increased T_{min} was possibly due to the prematurity of the rubber matrix.

T_{max} was mainly dependent on the rubber network, filler networking, and filler–rubber interfacial interaction in the vulcanizate at its vulcanization temperature (150°C). For the different torque values at the onset of vulcanization, the difference between T_{max} and T_{min} (ΔT) could have been a good indicator for the crosslink formation. According to the data in Table I, when the content of MimMP was lower than 3 phr, ΔT slightly increased. However, ΔT was considerably lowered at higher loading (4 phr). It seemed to be contradictory with the bound rubber analysis, as described previously. It was possibly due to the scorch shown in Figure 4. This means that the T_{min} value for R4MimMP, obtained from the curing curves, was largely overestimated. Also importantly, the T_{max} value for R4MimMP was further underestimated because the physical interfacial interaction, such as hydrogen bonding, was thermally sensitive, which could be easily destroyed during vulcanization.

TABLE I
Curing Characteristics of the SBR–Silica Rubber Compounds

	T_{s2} (min)	T_{10} (min)	T_{90} (min)	T_{min} (N m)	T_{max} (N m)	ΔT (N m)	CRI (N m/min)
R0MimMP	6.87	7.65	19.16	1.37	4.76	3.39	0.28
R1MimMP	5.17	5.65	12.73	1.18	4.73	3.55	0.47
R2MimMP	5.30	5.81	12.29	1.00	4.59	3.59	0.51
R3MimMP	1.97	2.15	8.99	0.96	4.67	3.71	0.53
R4MimMP	0.48	0.50	8.21	1.25	3.63	2.38	0.31

T_{10} AND T_{90} are the time with a torque value of $T_{min} + (T_{max} - T_{min}) \times 10\%$ and $T_{min} + (T_{max} - T_{min}) \times 90\%$, respectively. Curing rate index (CRI) is calculated by $\Delta T / (T_{90} - T_{10})$.

TABLE II
Mechanical Properties of the MimMP-Modified SBR–Silica Vulcanizates

	R0MimMP	R1MimMP	R2MimMP	R3MimMP	R4MimMP	R2Si69
Stress at 100% (MPa)	1.0 ± 0.1	1.5 ± 0.1	1.8 ± 0.1	2.0 ± 0.1	2.6 ± 0.1	2.0 ± 0.1
Stress at 300% (MPa)	1.3 ± 0.1	2.5 ± 0.1	3.5 ± 0.1	4.1 ± 0.2	8.0 ± 0.5	6.7 ± 0.5
Stress at 500% (MPa)	2.2 ± 0.1	4.5 ± 0.1	6.6 ± 0.2	7.8 ± 0.2	15.9 ± 0.4	17.0 ± 0.7
E_b (%)	1182 ± 12	860 ± 10	760 ± 11	735 ± 15	588 ± 10	584 ± 17
Tensile stress (MPa)	13.9 ± 1.1	18.6 ± 1.5	25.0 ± 0.9	24.4 ± 0.9	23.4 ± 0.7	24.0 ± 0.8
Tear strength (kN/m)	34.8 ± 1.5	35.4 ± 1.1	43.5 ± 1.5	49.3 ± 1.6	60.0 ± 0.9	52.1 ± 1.7
Tensile permanent set (%)	70	28	20	30	20	15
Shore A hardness	59	57	62	64	70	65
Volume loss (cm ³ /1.61 km)	2.49	1.86	1.57	1.43	1.06	0.71

The values of V_e of R0MimMP to R4MimMP were 0.71, 1.37, 1.84, 1.80, and 2.34×10^{-4} mol/cm³, respectively. The increased V_e may have been due to the following reasons. First, the crosslinking efficiency of the rubber ingredients was enhanced by the restraint of their adsorption onto the silica surface. Second, the initiated thiyls and their intermediate radicals could have increased the crosslinks. Last, the imidazolium cation and the radicals could have catalyzed the thiol–ene reaction and the vulcanization. The V_e value for R2Si69 was 3.02×10^{-4} mol/cm³, which was much higher than those discussed previously. We ascribed this to the extra donated sulfur from Si69 molecules and to the covalent bonding between silica and Si69.

Mechanical performance and interfacial interaction of the modified SBR–silica vulcanizate

The mechanical properties of the SBR–silica vulcanizate are included in Table II. Due to the addition of MimMP, the mechanical properties were greatly changed. The main observations are as follows. In comparison to R2MimMP, R2Si69 exhibited a higher stress at 300%. It was ascribed to its higher V_e and the covalent bonding between the silica and rubber chains. However, for the R4MimMP sample, the stress at 300% was higher than that of R2Si69 and reached up to a value of 8.0 MPa. With the increasing loading of MimMP, the elongation at break (E_b) consistently decreased from 1181 to 588%. The tensile strength took a maximum value of 25.0 MPa at R2MimMP, which was even higher than that of R2Si69 (24.0 MPa). However, the tensile permanent set of all of the MimMP modified vulcanizates was larger than that of R2Si69. The tear strength gradually increased from 34.8 kN/m for R0MimMP to 60.0 kN/m for R4MimMP. The tear strength of R4MimMP was slightly higher than that of R2Si69 (54.0 kN/m). Several possible reasons are proposed to explain these phenomena. First, the increased V_e , which was one of the factors determining the deformability of the rubber network, was responsi-

ble for the increased modulus and the decreased E_b . Second and more importantly, the interfacial structure in the modified SBR–silica vulcanizates may have been strengthened by the hydrogen bonding and the intermediate SBR–g–MimMP induced by thiol–ene chemistry, as substantiated previously and further examined later. Last, the interfacial structure functionalized via physical interactions (introduced by MimMP) may have increased the slippage at the interface, and therefore, the tensile permanent set was higher than that of interfacial structure composed via chemical bonding (introduced by Si69).

The abrasion resistance was also evaluated, and the results are shown in Table II. It can be seen that R2Si69 had the best abrasion resistance. This was possibly due to the covalent bonding between the silica and rubber chains. For MimMP-modified samples, the abrasion resistance consistently improved with increasing addition of MimMP. The abrasion volume for the R4MimMa dropped considerably to 1.06 cm³/1.61 km, which was even less than a half of the control one (2.49 cm³/1.61 km). Although the abrasion resistance performance could have been directly related to the mechanical properties, such as tensile strength, tear strength, and hardness of the vulcanizates, the polymer–filler interfacial structure was also essential in determining the abrasion resistance.⁵⁵ The largely improved abrasion resistance of the modified SBR–silica vulcanizates may have mainly originated from the modified interfacial structure. In comparison to the previous IL,³¹ MimMP exhibited a higher efficiency on improving abrasion resistance, which possibly originated from the high reactivity of the thiol–ene reaction, substantiated previously.

As the dispersion of filler and filler–rubber interaction were two critical factors in governing the ultimate performance of the rubber vulcanizates, the dispersion of silica in this systems was examined by TEM observations. As shown in Figure 5, the silica in these two vulcanizates was finely dispersed in the rubber matrix. Even with careful observation, there was no practical difference found between the silica dispersion in R0MimMP [Fig. 5(a,b)] and that in

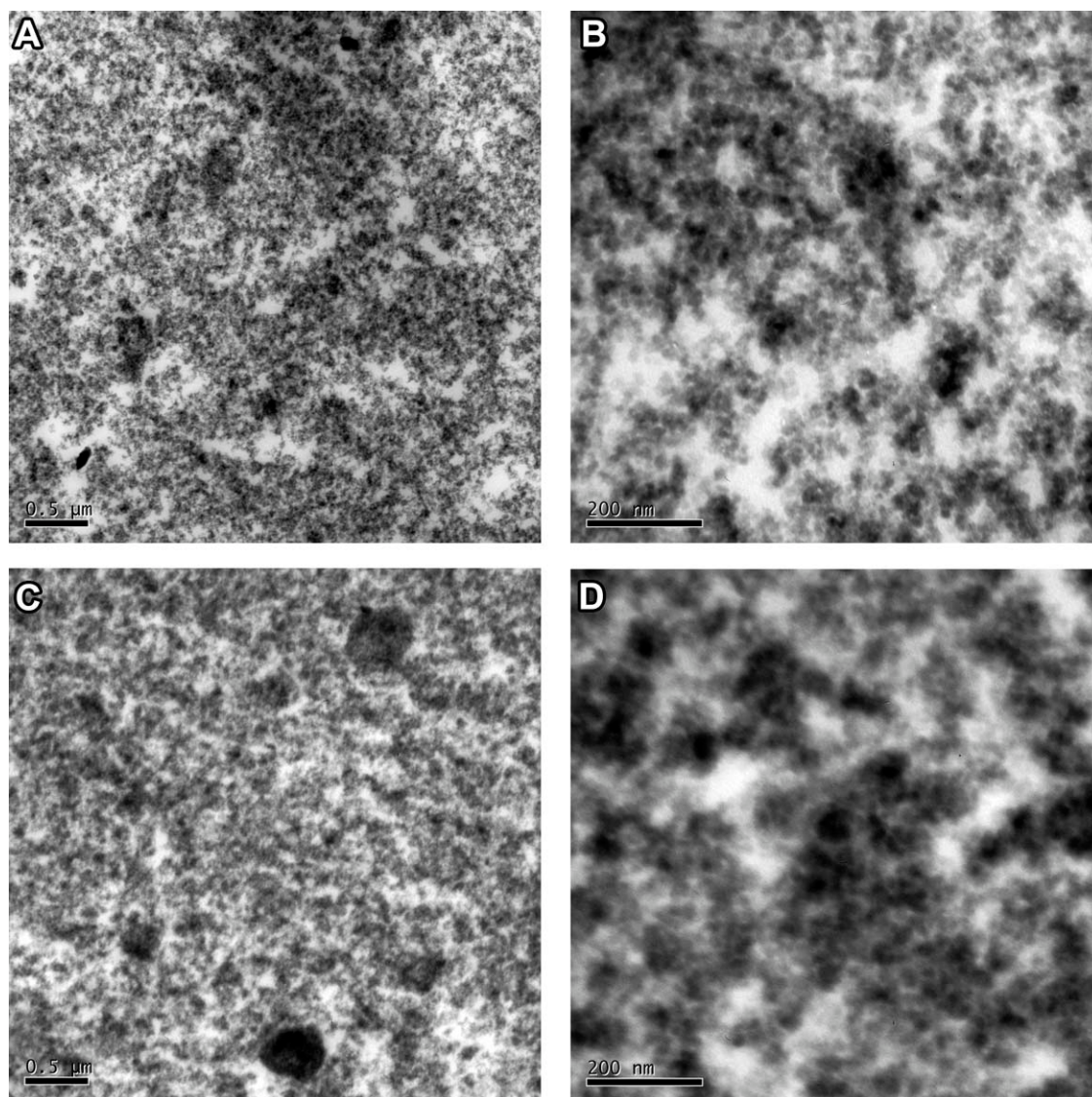


Figure 5 TEM photos for (a,b) R0MimMp and (c,d) R4MimMp.

R4MimMP [Fig. 5(c,d)]. However, the filler dispersion, just as one of the most important factors, could not solely determine the performance of the vulcanizates. The interfacial structure was also important and was even considered to be more important than the filler dispersion.¹⁴ For this point, the interfacial interaction should be quantitatively compared among these samples.

The dependence of the stress on the strains of the vulcanizates is shown in Figure 6. The highest value of E_b , up to 1180%, was obtained for R0MimMP; this indicated the easiest deformability for its rubber network. This may have been due to the lowest V_e of the rubber network and the poor interfacial bonding between the rubber matrix and silica. With increasing loading of MimMP, the E_b values gradually decreased. The increased V_e in the rubber network and the improved interfacial bonding structure may

have been responsible. Within various methods for evaluating the interfacial interactions with the stress-strain curve, the slopes at certain strains and/or certain ranges of strains were used. However, the reasonability of this method should be strictly criticized for it ignores the significant impact from V_e of the rubber network.^{56–58} A quantitative method was proposed to evaluate the interfacial interaction, in which the effect of the crosslinking density of the rubber matrix was excluded.³¹ The rubber-polymer interfacial interaction (F_{int}) could be expressed as follows:

$$F_{\text{int}} = \frac{\sigma_{\text{com}}}{RT(\lambda - \lambda^{-2})} - \frac{3}{2}V_e \quad (1)$$

where σ_{com} is the stress for the filled vulcanizates, V_e is the crosslink density of the rubber matrix, λ is the tensile ratio of the sample, R is the universal gas

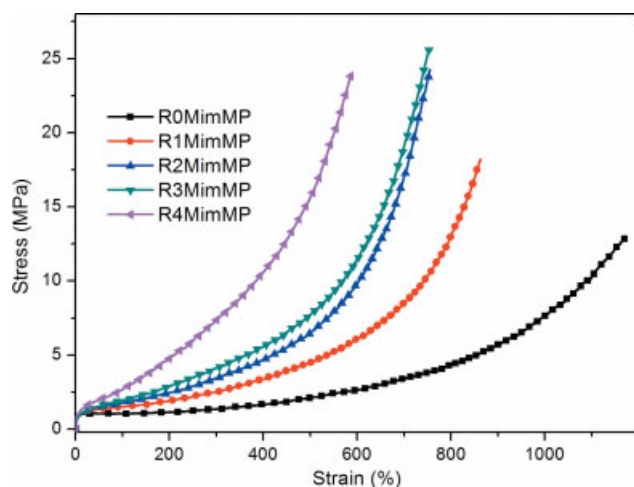


Figure 6 Dependence of the stress on the strains of the SBR-silica vulcanizates. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

constant, and T is the absolute temperature. However, because the chemical bonding between the silica and rubber chains led to an overestimated V_e , this equation could not be roughly adapted to the R2Si69 sample, and the related discussion about interfacial bonding is not included here.

The curves of F_{int} versus strain of SBR-silica vulcanizates are plotted in Figure 7. Within a range of lower strains (<100%), the unreasonably high value of F_{int} may have been due to the silica network formation, and therefore, they dropped dramatically with increasing strains in the vulcanizates. With increasing concentration of MimMP, the values of F_{int} were first slightly lowered (R1MimMP) and then increased to higher values (R3MimMP and R4MimMP) compared to those of the blank sample. The decrement of F_{int} at lower loadings of MimMP may have been related to the effectively restrained silica networking. The increased F_{int} at higher loadings may have been mainly due to the strengthened interfacial interaction introduced by hydrogen bonding.

In a range of larger strains (>100%), the value of F_{int} gradually increased with increasing strains; this implied that the SBR-silica interaction was dependent on the deformation rubber network and that a stronger interfacial interaction could have been

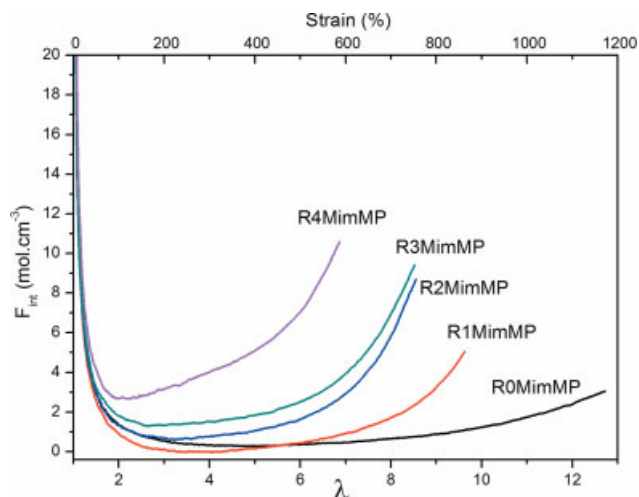


Figure 7 Dependence of F_{int} on the strains of the SBR-silica vulcanizates. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

obtained at a larger strain. From Figure 7, more importantly, F_{int} obviously increased with increasing loading of MimMP. This strongly indicated that the interfacial interaction between rubber and silica was largely improved. It may have been related to the high reactive thiol-ene chemistry and the high affinity between MimMP and silica, as described previously. The hydrogen bonding of SBR-g-MimMP and silica was also responsible for the SBR-silica interaction in the SBR-MimMP vulcanizate.

Proposed modification mechanism

According to the substantiated interactions, a possible mechanism of this modification is proposed and illustrated in Figure 8. Hydrogen bonding between MimMP and silica effectively alleviated the filler networking of silica in the uncured rubber compounds. Once vulcanization was performed, MimMP could have been grafted onto the SBR molecules via thiol-ene chemistry. The intermediate graft product, SBR-g-MimMP, could effectively enhance the compatibility between MimMP and SBR. Together with the hydrogen-bonding interactions, which existed in both the uncured rubber compounds and the rubber vulcanizates, the high reactivity of MimMP to SBR

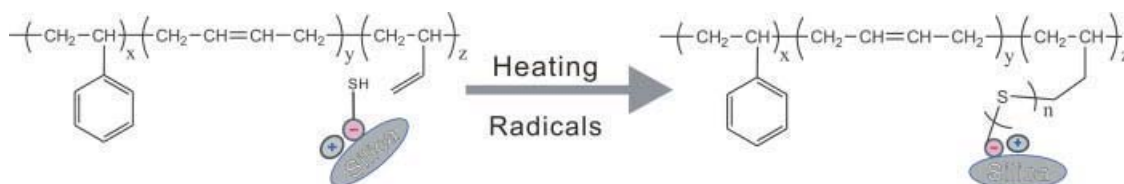


Figure 8 Proposed possible interfacial modification induced by MimMP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

chains not only strengthened the interfacial interactions but also considerably improved the mechanical performance of the modified SBR–silica vulcanizates.

CONCLUSIONS

To introduce thiol–ene chemistry in the modification of rubber composites by ILs, a novel functional IL, MimMP, was synthesized and investigated as an interfacial modifier for SBR–silica composites. The affinities of MimMP toward the silica and rubber chains were substantiated to originate from hydrogen bonding and the high reactive thiol–ene chemistry, respectively. Substantiated hydrogen bonding between the silica and MimMP effectively restrained the silica networking in the rubber matrix. The restrained adsorption of rubber ingredients by silica and the presence of thiol and imidazolium cation groups in MimMP could have been responsible for the promoted vulcanization. The quantitative evaluation of interfacial interaction indicated that the interfacial interaction consistently increased with increasing MimMP. The remarkable improvements in the mechanical properties and abrasion resistance were mainly ascribed to the improved interfacial structure comprised of MimMP–silica hydrogen bonding and intermediate graft (SBR-g-MimMP) induced by the thiol–ene chemistry.

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