# Contribution of silica-rubber interactions on viscoelastic behaviors of modified solution polymerized styrene butadiene rubbers (M-S-SBRs) filled by silica

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**ABSTRACT：** A series of modified solution-polymerized styrene butadiene rubbers (M-S-SBRs) with different molar contents of polar groups were prepared through grafting 3-mercaptopropionic acid into solution-polymerized styrene butadiene rubber (S-SBR) chains and the molar contents of the polar groups in M-S-SBR were calculated by the use of $^1$H nuclear magnetic resonance ($^1$H NMR) spectra. The thermodynamic analytical methods including surface energy of M-S-SBR and filler flocculation manifest that the introduction of polar groups increases the work of adhesion of filler-rubber ($W_{rf}$), which is an indicator for the compatibility of the filler with rubber. The thermodynamic results can be further proved by TEM micrographs. Strain sweep experiments were carried out to investigate the temperature dependent nonlinear strain-dependence of elastic moduli, referred as Payne effect. The filler-filler network and interfacial strength was studied in terms of critical strain $\gamma_c$ and activation energy $E_a$. Dynamic mechanical measurements present that a combination of higher energy dissipation in low temperature range and higher elasticity at high temperature region was achieved for M-S-SBR/Silica compared with non-modified counterpart.

## Introduction

In the rubber science and technology, reinforcement of rubbers by fillers is of practical and technical importance to improve final performance and hence has continuously been in research focus. Carbon black (CB) was the first commercial filler in rubber industry. Precipitated silica has been proved to be the filler of choice for the manufacture of high performance pneumatic passenger car tires since the introduction of the so-called “Green tire” by Michelin in the 1990s.[1,2] Technological

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development of changing the active filler from carbon black to precipitated silica in rubber compound and some related studies of reinforcing mechanism have attracted considerable interest in both industrial and academic fields. Silica as a reinforcement agent provides a combination of good mechanical properties, high resilience, excellent rolling resistance and low heat build-up. [3-7]

Although the above mentioned successes have been achieved, a major problem in implementation of silica is the poor dispersion in rubber matrix, which is caused by the great difference in surface polarity between silica and rubber. [8,9] So far the most successful effort to enhance the filler dispersion is the introduction of silane coupling agents. [10,11] In addition, surface modification of silica [12-14] and the development of new highly dispersed silica [15-18] have also been subjects of interest in recent years.

As a matter of fact, the macro-properties of filled rubber are not only affected by filler structure, surface chemistry and particle size, what are also important are the characteristics of rubber such as chemical composition, chain microstructure including molecular weight and molecular weight distribution, configuration, stereoregularity, monomer unit distribution and sequence, and their functionality. Therefore, modification of rubber which has a potential to cover the gap between surface characteristics of rubber and filler tends to be an effective way to improve filler dispersion and enhance interfacial strength. Recently, some efforts have been devoted to introducing functional groups, such as –COOH, –OH and $–NH_2$, into rubber molecules[19-21] and obtained some exciting results in dynamic mechanical properties. To our knowledge, such research works mostly focus on preparations of modified rubber and some characterizations of macro-properties. However, few literatures have been published related to the rubber-filler interaction and nonlinear viscoelastic behavior of functional rubber filled by silica.

Hereby, in the present paper a series of modified solution-polymerized styrene butadiene rubbers (M-S-SBRs) with different molar contents of polar groups were synthesized and the study is an attempt to investigate the contribution of filler-rubber interactions on viscoelasticities of M-S-SBRs filled by silica. The surface energies of M-S-SBRs and the work of adhesion value between M-S-SBRs and silica were calculated, which are good indicator for the compatibility of the filler with rubber. Strain sweep experiments were carried out to investigate the temperature dependent nonlinear strain-dependence of elastic moduli, referred as Payne effect. The filler-

filler, filler-rubber network and interfacial strength was studied in terms of critical strain $\gamma_c$ and activation energy $E_a$. In the dynamic mechanical measurements, viscoelastic behaviors of filled M-S-SBRs were investigated by linking with the filler/polymer interactions, which would help us to understand how to tailor the interfacial properties of filled rubber for a desired performance.

## Experimental

### Materials

Commercial S-SBR2506 (styrene content = 21±2wt%, vinyl content = 60±2wt%, $SiCl_4$ coupled, ML1+4 100°C = 60±5) was purchased from Yanshan Petrochemical Co. Sinopec. (Beijing, P.R.C.). Cyclohexane was commercially available from Beijing Chemical Reagents Company. The modification agent and initiator were 3-mercaptopropionic acid (99%, Aldrich) and azobisisobutyronitrile (AIBN) (99%, Aldrich ). The precipitated silica (Ultrasil VN3) with specific surface area of 175 $m^2/g$ and pH of 6.2 was kindly provided by Degussa. Silane coupling agent bis-(triethoxysilylpropyl)-tetrasulfide (TESPT) was product of Nanjing Shuguang Chemical Group Co., P.R.C. The curing accelerators were diphenylguanidine (DPG) (>97%, Aladdin, Shanghai, P.R.C.) and n-cyclohexyl-2-benzothiazolesulfenamide (CBS) (>97%, Puyang Willing Chemicals.Co., Henan, P.R.C.).

### Preparation of modified solution-polymerized styrene butadiene rubbers (M-S-SBRs )

S-SBR2506 was firstly dissolved in cyclohexane with a concentration of 10g/100ml. The mixture was stirred for 24 hours at 50°C and became homogeneous. Predetermined amount of 3-mercaptopropionic acid was loaded in the S-SBR solution. The reaction was initiated by AIBN at an elevated temperature. The mixture was kept at 80 °C for 30 minutes with stirring for the completion of reaction. Most of the solvents were evaporated at 50°C while keeping stirring. Subsequently, the resulting polymer solution was placed in a vacuum oven at 55 °C for two days to remove the residual solvents.

### Preparation and vulcanization of the compounds

The formulations of compounds are listed in Table 1. Silica and TESPT were mixed in rubber on a two-roll mill at room temperature. Afterwards, the compounds were transferred to internal mixer (Thermo Fisher Scientific, Rheomix 3010 OS, Banbury rotors). The temperature was held for 7 min in the range of 155 $^{o}$C at rotor speed of 35rpm to ensure the reaction of silane with silica surface. The curing package consists of 1.4 phr sulfur, 1.5 phr DPG and 1.4 phr CBS. The cure time was determined using an oscillating disc rheometer (ODR) at 150 $^{o}$C.

Table 1 Formulations of the S-SBR/Silica compounds

| Ingredients | Amount ( phr[a] ) |
|---|---|
| S-SBR | 100 |
| Silica | 50 |
| TESPT | 4 |
| Stearic acid | 1 |
| ZnO | 2.5 |
| CBS | 1.4 |
| DPG | 1.5 |
| Sulfur | 1.4 |

a. The number of rubber, filler and additives in phr ( parts by weight per hundred parts of rubber )

## Measurements and characterization

The molar contents of 3-mercaptopropionic acid grafted in S-SBR and structural units of all samples, including styrene units and vinyl contents from 1,2-polybutadiene and 1,4-polybutadiene, were calculated from the $^{1}$H Nuclear Magnetic Resonance ($^{1}$H NMR) spectra acquiring on a BRUKER AMX 600-MHz spectrometer. The chemical shifts are given relative to tetramethylsilane (TMS) internal reference. Integrals on the proton spectra were obtained directly on concentrated solutions in 1,1,1,2-tetrachloroethane-d2. It is noted that all M-S-SBR samples were extracted by ethanol for 24 hours to remove the unreacted chemicals and then dried in vacuum at 40 $^{o}$C for 12 hours.

Gel permeation chromatography (GPC) analyses of the M-S-SBR molecular weight and its distribution were performed on a Alliance2690 system (Waters, U.S.A.) consisting of a 5μm and 7.5mm×300mm PLgel Mixed-C column and a refractive-index detector. The eluting solvent was tetrahydrofuran at a flow rate of 1.0 mL/min. The retention times were calibrated against polystyrene standards.

Sessile drop contact angle measurements of uncured M-S-SBR were conducted with DSA100 drop shape analyze (KRÜSS, Germany). The test liquids with different surface tension were deionized water (Sigma-Aldrich), ethylene glycol (spectrophotometric grade, ≥99%, Sigma-Aldrich), ethanol (≥99.5%, Sigma-Aldrich) and formamide (spectrophotometric grade, ≥99%, Sigma-Aldrich). The uncured raw rubber films with 1mm in thickness were obtained by compression molding at 100 °C having a PTFE surface to minimize surface contamination. The surface energy was calculated by fitting Fowkes' equations [22] as described in ref. [23]

The micromorphology of S-SBR/Silica was examined with Transmission Electron Microscopy (TEM). Ultrathin sections of the specimens were prepared at −100 °C using a Leica Ultracut-R ultra-microtome. The thin slices were put on copper grids and then submitted to TEM observation with a JEOL JEM-2010 TEM under an accelerating voltage of 200 kV.

Filler Flocculation was performed on Rubber Processing Analyzer (RPA2000, Alpha, U.S.A.) at 0.7% strain during 100 °C for 20 minutes after preheating for 1 minute. According to Mihara et al, [24] the flocculation rate constant ($k_a$) can be calculated by:

$$k_a = \frac{\ln(1-x_1) - \ln(1-x_2)}{t_2 - t_1} \tag{1}$$

Where x is the degree of flocculation; t is the heating time; the subscribe 1 and 2 refer to different heating time t. x is defined as:

$$x = \frac{G'(t) - G'(i)}{G'(f) - G'(i)} \tag{2}$$

Where G'( $t$ ) is the storage modulus at 0.7% strain after heating time t; G' ( $I$ ) is the initial storage modulus after preheating for 1 minute; G'( $f$ ) is the final storage modulus.

Strain sweep of the silica filled rubber was conducted on Rubber Process Analyzer RPA2000 (Alpha, U.S.A.) at 70 °C in the dynamic strain range of 0.7-100%. The tests were carried out at a frequency of 1Hz. For studying the effect of temperature on Payne effect, the temperature were chosen as 60 °C, 80 °C, 100 °C and 120 °C and dynamic strain range is from 0.5% to 35%.

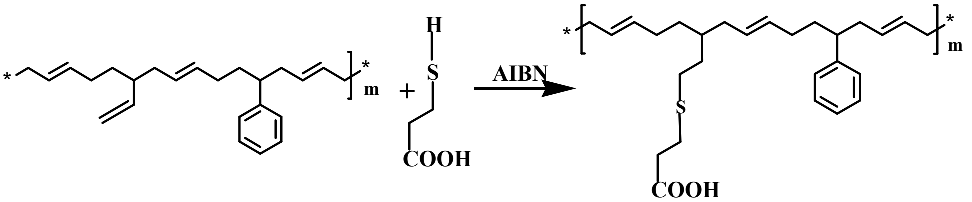
Viscoelastic properties of all samples were measured on EPLEXOR-500N Dynamic Mechanical Analyzer (Gabo, Ahlden, Germany). The samples were trimmed to the following dimensions: 35.0 mm in length, 8.0 mm in width, and 1.0 mm in thickness. The properties were measured by using tension clamp in the temperature range from -80 $^{o}$C to 80 $^{o}$C at a heating rate of 3$^{o}$C/min. The tests were carried out at a frequency of 10Hz. For the measurement of the complex modulus G*, a static load of 1.0% prestrain was applied, and then the samples were oscillated to a dynamic load of 0.25% strain.

The Differential Scanning Calorimeter (DSC) measurements were carried out on a Q100 (TA Instruments, U.S.A.) in temperature range of -100 $^{o}$C to 50 $^{o}$C for all samples under a nitrogen atmosphere. The scanning rate was chosen as 10 $^{o}$C /min.

## Results and discussion

### Preparation of M-S-SBR

A series of M-S-SBRs were prepared through the addition reaction between the vinyl groups in S-SBR and the sulfydryl groups from 3-mercaptopropionic acid (referred to as modification agent). [19] As can be seen in Figure 1 the addition reaction can be identified by the appearance of characteristics peak of 3-mercaptopropionic acid in M-S-SBRs after extraction in $^{1}$H NMR spectrum, such as $–SCH_2–$ at chemical shift of 2.75ppm. Two kinds of vinyl groups exist in polybutadiene units in S-SBR molecular structure, i.e the ones in the backbone from 1,4-polybutadiene and the ones in the side-chains from 1,2-polybutadiene. Which kind of vinyl groups react with the sulfydryl group from 3-mercaptopropionic acid was firstly determined by $^{1}$H NMR spectrum. The molar contents of structural units were given in Table 2, in which the unmodified S-SBR denoted as M0 is given for comparison. As can be seen in Table 2, the molar contents of 1,2-polybutadiene units go down with increasing modification agents, while the molar contents of 1,4-polybutadiene units remain unchangeable, suggesting of an addition reaction between vinyl groups from 1,2-polybutadiene and the sulfydryl groups. The addition reactions were carried out as follows:



The molar contents of 3-mercaptopropionic acid grafting on S-SBR and molecular weights of all samples were listed in Table 2. It is obvious that the molecular weights almost keep constant after modification and the slight fluctuation can be regarded as within the detection errors of devices.

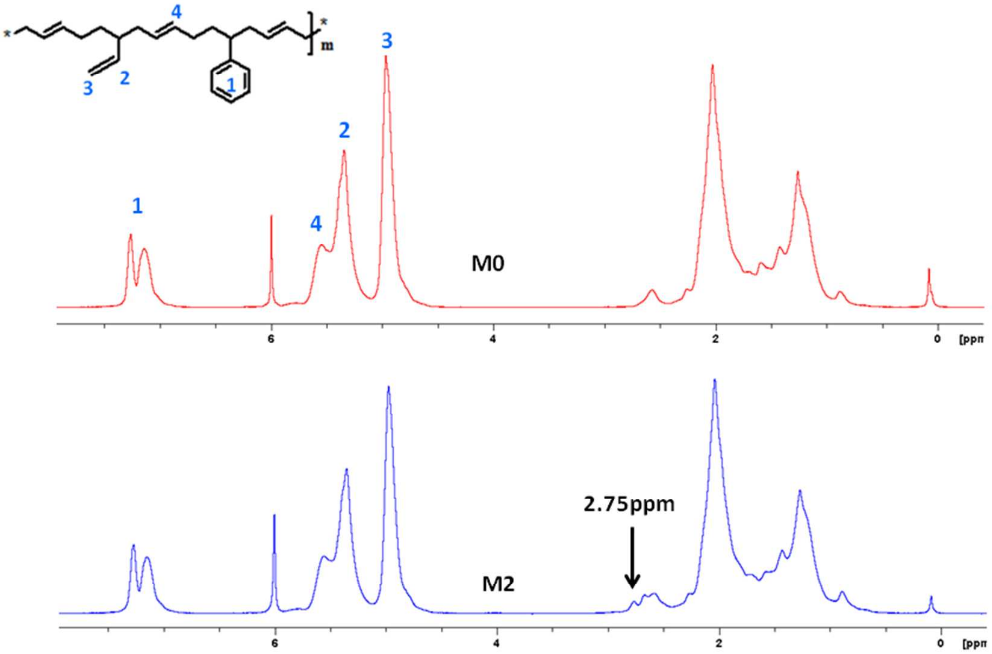


Figure 1 $^{1}$H NMR spectra of M0 and M2. The signal assignments are indicated.

Table 2 Molecular weights and weight contents of modifier and structural unit of M0 and M-S-SBRs

| Sample code | Styrene units (wt%) | 1,2-polybutadiene units (wt%) | 1,4-polybutadiene units (wt%) | modification agent (wt%) | Mn×$10^{-4}$ (g/mol) | Mw/Mn |
|---|---|---|---|---|---|---|
| M0 | 21.0 | 47.4 | 31.6 | 0 | 20.66 | 1.33 |
| M1 | 20.7 | 45.6 | 31.3 | 2.4 | 21.47 | 1.41 |
| M2 | 20.4 | 44.2 | 31.2 | 4.2 | 20.02 | 1.34 |
| M3 | 20.1 | 40.2 | 30.1 | 9.6 | 22.56 | 1.44 |

**Surface energies of M-S-SBR**

It is well accepted that the mechanical property and viscoelasticity of filled rubber remarkably depends on state of filler dispersion, filler structure and rubber-filler interactions. From the thermodynamic standpoints, the interfacial strength between filler and rubber and filler flocculation are influenced by the surface energies of filler particles and polymer. In the present study, the carboxyl groups in the modification agents are designed to be the functional groups for increase the surface polarity of S-SBR. Therefore, in order to study the adhesion between M-S-SBR and silica and further prove the modifications of rubber are favorable for improving the filler dispersion, the contact angle measurements of M0 and M-S-SBR were performed by means of sessile drop method. The dispersive ($r_p^d$) and polar ($r_p^p$) parts of rubber are calculated by fitting Fowkes' equation and are listed in Table 3. The $r_p^d$ and $r_p^p$ for silica Ultrasil VN3 is 19.7mJ/m$^2$ and 15.2 mJ/m$^2$ according to ref.[23] It can be seen that the M-S-SBR exhibits an increasing trend for both polar part and total surface energies compared with M0. More precisely, the polarity is monotonically increasing with modification content. i.e. the contents of polar groups in molecules.

Table 3 Surface energies of S-SBR and M-S-SBR

| Rubber code | Dispersive part $r_P^d$/ mJ/m$^2$ | Polar part $r_P^p$/ mJ/m$^2$ | Total $r_P$/ mJ/m$^2$ |
|---|---|---|---|
| M0 | 24.7 | 0.9 | 25.6 |
| M1 | 25.9 | 1.2 | 27.1 |
| M2 | 25.4 | 2.3 | 27.7 |
| M3 | 27.3 | 4.8 | 32.1 |

The possible interactions between two materials are determined by their surface energies. Therefore, the adhesive energy ($W_{rf}$) between silica and rubber according to Fowkes' model is given by:

$$W_{rf} = 2\left(\sqrt{r_r^{\,d} r_f^{\,d}} + \sqrt{r_r^{\,p} r_f^{\,p}}\right) \qquad (3)$$

Where the rubber and filler are denoted by r and f, respectively.

According to Wang's model,[25] $\Delta W$ described as the change in adhesive energy in the filler agglomeration process is given by:

$$\Delta W = 2\left(\sqrt{r_f^{\,d}} - \sqrt{r_r^{\,d}}\right)^2 + 2\left(\sqrt{r_f^{\,p}} - \sqrt{r_r^{\,p}}\right)^2 \qquad (4)$$

From the thermodynamic point of view, $\Delta W$ is the driving force of filler flocculation. When $\Delta W$ tends to zero, the filler and rubber have the similar surface property, leading to the consequence that the filler does not tend to flocculate. On the contrary, the larger the difference of surface characteristics lies between filler and rubber, the higher is the tendency for filler self-association.

Table 4 shows the thermodynamic parameters for filler-rubber adhesion and filler flocculation rate constant. Rubber containing higher content of polar groups has stronger adhesive strength with silica and the filler exhibits decreasing $\Delta W$ and $k_a$ values with increasing polarity of M-S-SBR, indicating that the introduction of polar groups into rubber can improve the stability of silica particles in rubber matrix.

Table 4 Thermodynamic parameters for filler-rubber adhesion and filler flocculation rate constant

| | M0/Silica | M1/Silica | M2/Silica | M3/Silica |
|---|---|---|---|---|
| $W_{rf}$/ mJ/m$^2$ | 51.2 | 53.3 | 55.8 | 62.1 |
| $\Delta W$/ mJ/m$^2$ | 13.0 | 11.8 | 8.1 | 4.6 |
| $k_a \times 10^{-3}$ / S$^{-1}$ | 3.98 | 3.56 | 3.12 | 2.82 |

**Non-linear behaviors of M-S-SBR/Silica**

Strain sweep measurements have been carried out to study the rubber-filler and filler-filler interactions and the results are presented in Figure 2. The filled polymers present nonlinear rheological amplitude dependency, which is known as Payne effect. The storage modulus is the highest at small strain (referred to as $G'_0$) and rapidly decreases to a low value (referred to as $G'\infty$). Due to the limitation of the instrument, the plateau at high amplitude is not reached. The magnitude of Payne effect ($G'_0 - G'\infty$) is reduced with increasing modification agent. The $G'_0$ values display more differences among the samples than the $G'\infty$ values. The first derivative, $dG'/d\gamma$, is used to denote the dependence of G′ on the strain (Figure 3). It is indicated that G′ is less dependent on the strain for M-S-SBR and the inflection point shifts toward high strain. The inflection point can be regarded as the strain where G′ drops rapidly.

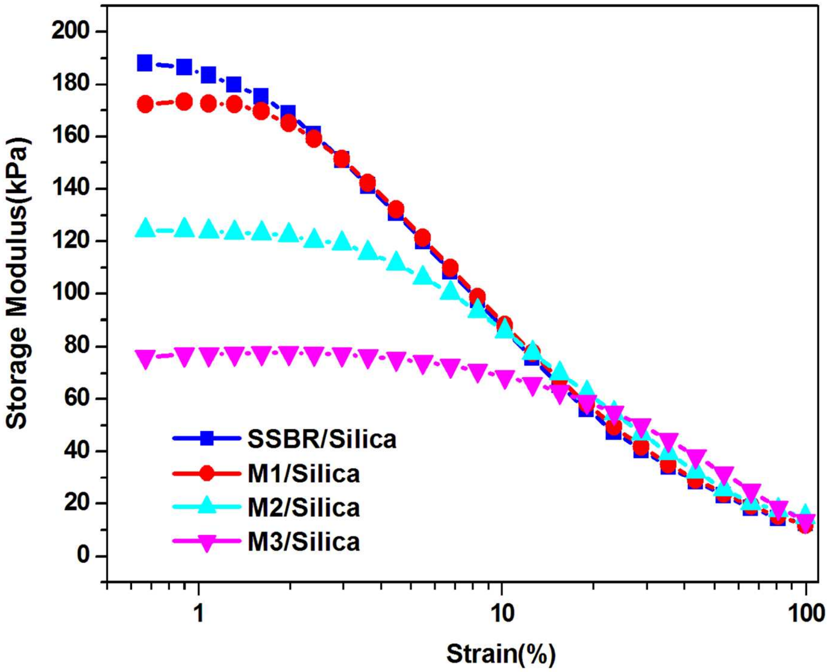


Figure 2 Dependence of storage modulus on strain of M-S-SBR/Silica at 70 °C

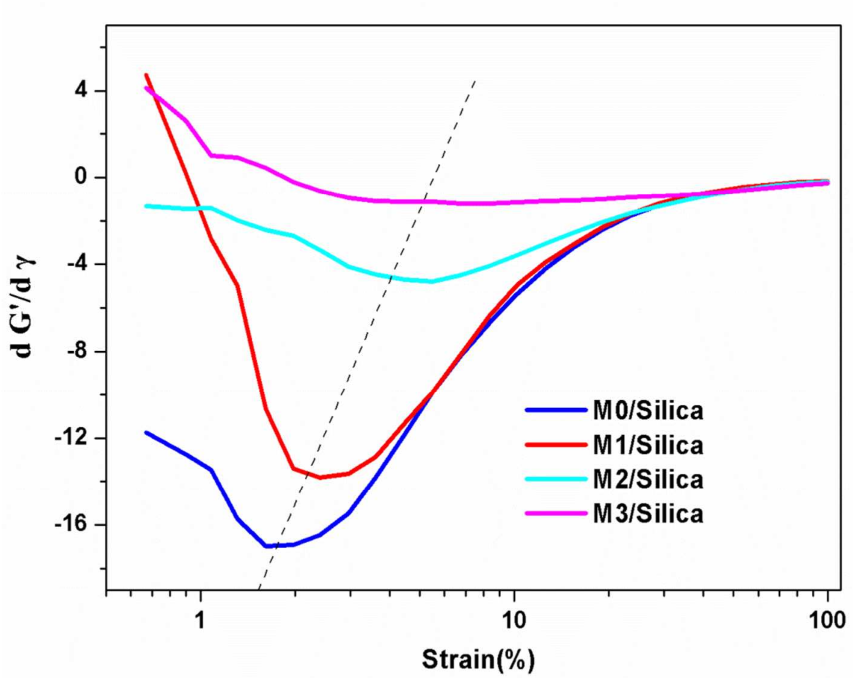


Figure 3 First derivative of M-S-SBR/Silica curves of storage modulus vs. strain

The influences of temperature on the Payne effect for all samples have been investigated in the range from 60 °C to 120 °C and M0/Silica is given in Figure 4 as an example. A decrease of the magnitude of Payne effect with increasing temperature can be observed, in which the decrease of modulus at low strain is larger than that at high strain. This is consistent with the results in the literatures. [26, 27]

In order to parameterize the nonlinear behavior of M-S-SBR/Silica system, the phenomenological quantitative Kraus [28, 29] model has been adopted, which is based on the assumption of an agglomeration/deagglomeration mechanism of filler agglomerates:

$$G'(\gamma) = G'_{\infty} + \frac{G'_0 - G'_{\infty}}{1+(\gamma/\gamma_c)^{2m}} \qquad (5)$$

Where $G'_\infty$ is the value of $G'(\gamma)$ at very large strain; $G'_0$ is equal to the value of $G'(\gamma)$ at very small strain; $\gamma_c$ is the critical strain where the $G'(\gamma)$ reach the half-value of $G'_0 - G'_\infty$; m is the shear strain sensitivity of the mechanism of filler-filler contact breakage and defines the shape of the $G'(\gamma)$ curve. In this paper, the $G'_\infty$ was calculated based on the Guth-Gold equation: $G' = G'_{uf}(1+2.5\Phi+14.1\Phi^2)$. [30,31]

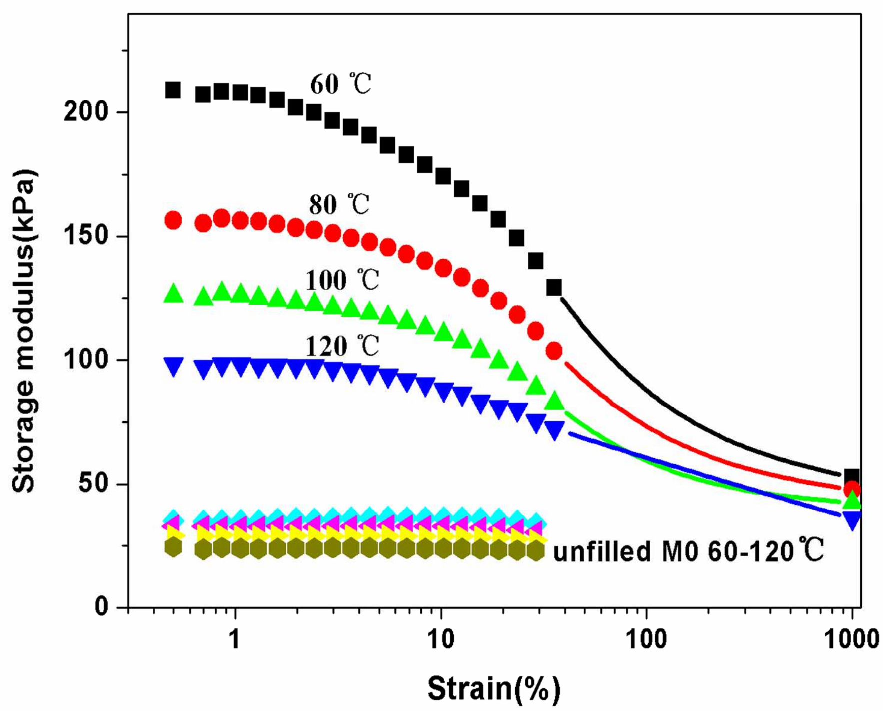


Figure 4 Payne effect of M0/Silica at different temperatures

Temperature dependence of the critical strain $\gamma_c$ shows in Figure 5. We can observe that $\gamma_c$ values depend greatly on temperature and modification agent. The larger $\gamma_c$ means that filler agglomerates are broken down at higher strain, implying weak strength between fillers. This phenomenon is discussed in depth in K.W. Stöckelhuber's literature.[26] By means of the Arrhenius plot of the temperature dependency of $\gamma_c$ (Figure 6), the activation energy $E_a$ is obtained by multiplying the slopes of 1/T versus $\ln\gamma_c$ plot with gas constant, $R=8.314 \times 10^{-3}$ kJ•mol$^{-1}$• K$^{-1}$. Table 5 gives the variations of $E_a$ values for all samples with different modification agent. The changes manifest that $E_a$ goes up with modification agent.

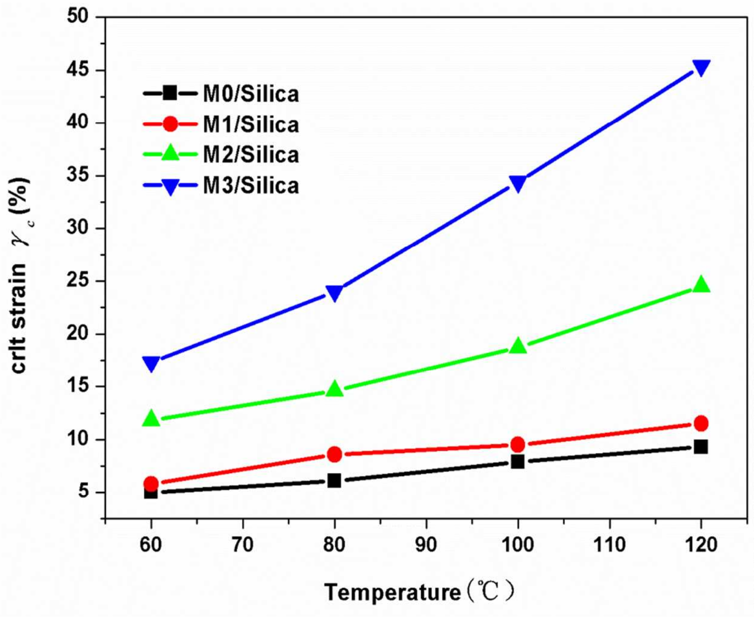


Figure 5 Temperature dependence of the critical strain $\gamma_c$

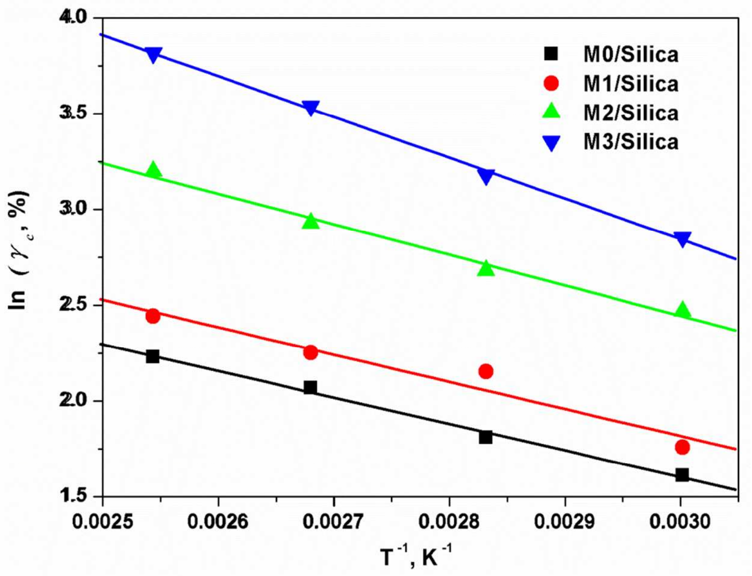


Figure 6 Arrhenius plot of the temperature dependency of the critical strain $\gamma_c$

As can be seen in Figure 7, the sketch of the dispersion of silica in M-S-SBR and unmodified S-SBR, the high magnitude of Payne effect for unmodified S-SBR/Silica is caused by filler agglomerates, but this kind of filler network is less stable, which is easy to be broken down upon strain. This is why the activation energy of M0/Silica is the lowest among the samples. When carboxyl groups are grafted on rubber chains, the difference in surface polarity of rubber and silica decreases, and the rubber-filler interaction is enhanced through the hydrogen bonds between carboxyl groups of rubber and silanol groups on the surface of silica. This contributes to the better and fine dispersion of silica. For a filler well-dispersed rubber compound, the amount of filler particles which can interact with rubber chains is larger. Therefore, in M-S-SBR/Silica compound, the filler network is not filler-filler association any more, but changes into filler-rubber-filler linkage. This kind of interaction is much more stable than the one in unmodified S-SBR/Silica, resulting in higher activation energy and decreased magnitude of Payne effect. This observation supports the results from the filler flocculation experiments.

Table 5 Activation energies of M-S-SBR/Silica for nonlinear behaviors

| Sample code | $E_a$(kJ mol$^{-1}$) |
|---|---|
| M0/Silica | 11.3 |
| M1/Silica | 12.8 |
| M2/Silica | 14.2 |
| M3/Silica | 17.7 |

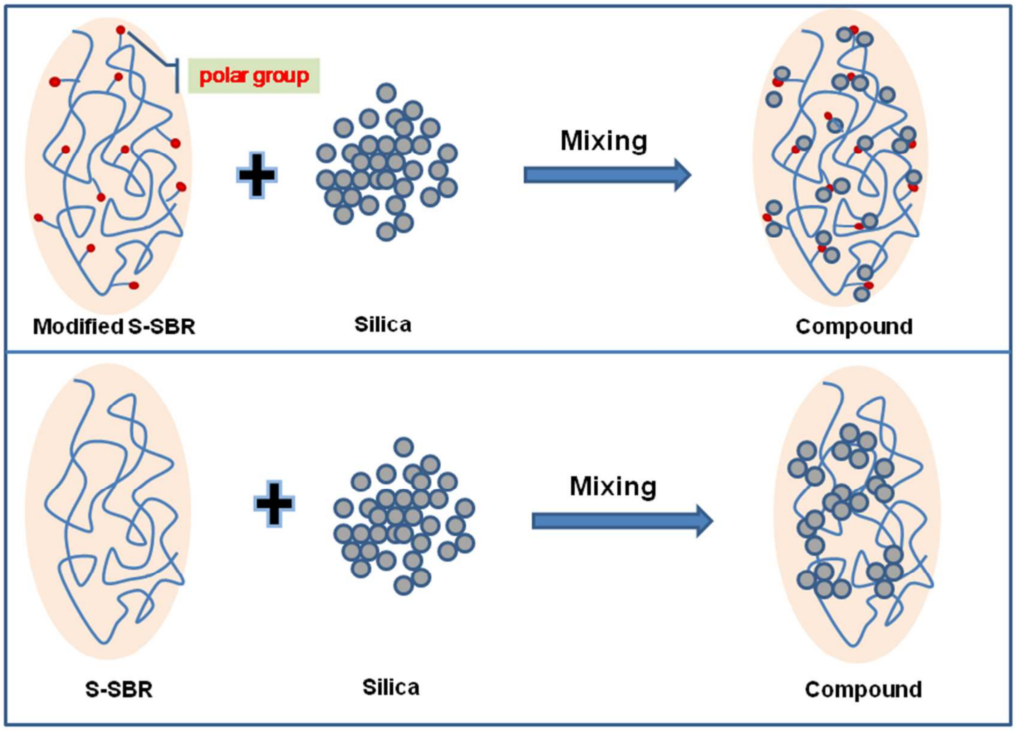


Figure 7 Sketch of the dispersion of silica in M-S-SBR and unmodified S-SBR

## Morphology of M-S-SBR/Silica

TEM micrographs support the results from thermodynamic analysis and strain sweep measurement. TEM images of M-S-SBR/Silica are displayed in Figure 8. It is evident that large silica agglomerates embed in S-SBR/Silica without modification, indicating relatively poor filler-rubber interactions. When 2.4wt mol% modification agent is grafted on S-SBR, the dispersion state of silica is somewhat improved. As far as M3 with content of modification agent up to 9.6wt% is concerned, silica presents relatively uniform and homogeneous dispersion and has a relatively narrow distribution.

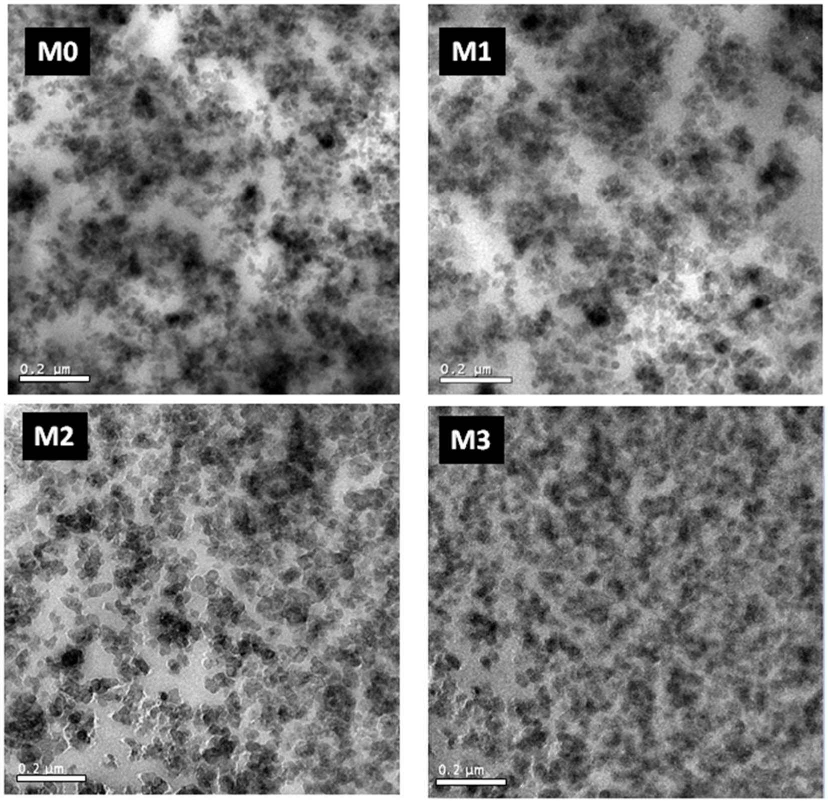


Figure 8 TEM images of M0/Silica and M-S-SBR/Silica fractions

**Viscoelastic behavior of M-S-SBR/Silica**

It has been proved that controlling the structure of S-SBR is a promising method to balance the grip and fuel efficiency performance for silica compounds used in passenger tire treads, i.e. lower elasticity at low temperature region (-10～10 $^{o}$C) and lower energy dissipation at relative high temperature range (50～80 $^{o}$C), to a high level. Figure 9 presents tan δ curves obtained for M-S-SBR/Silica vulcanizates and the $T_g$, taken as the temperature of maximum tan δ, together with maximum tan δ (tan $\delta_{max}$) are collected in TABLE 6. From the DMA measurements, we detected the changes in relaxation behaviors with contents of modification agents. An exciting result in the dynamic behavior is that intensity of $T_g$ relaxation increases with modification agent, i.e. M3/Silica gives the highest energy dissipation in this temperature range, whereas this sample exhibits the lowest tan δ in temperature region of 50～80 $^{o}$C (see Figure 9). The loss modulus (G”) data in Figure 10 shows that the lower and lower G” with contents of modification agents is also indicative of the decreased energy dissipation.

Another point should be noted is that tan δ peaks move to higher temperature monotonically with increasing modification agent. One may wonder that the increase of $T_g$ is simply because of the higher $T_g$ for M-S-SBR or due to the changes of relaxation behaviors by strong interactions between silica and M-S-SBRs. For clarifying this issue, DSC measurements were performed on the M-S-SBR/Silica compounds and DSC curves are shown in Figure 11. The $T_g$ values for M-S-SBR/Silica from DSC were listed in Table 6 and $T_g$ of the raw rubbers were given for comparison. It can be observed that the $T_g$ does not exhibit distinct variation after compounding with silica in comparison with that of the raw rubber. Therefore, it can be concluded that the shifted $T_g$ from DMA with modification agent is due to the raw rubber rather than the interaction between silica and M-S-SBR.

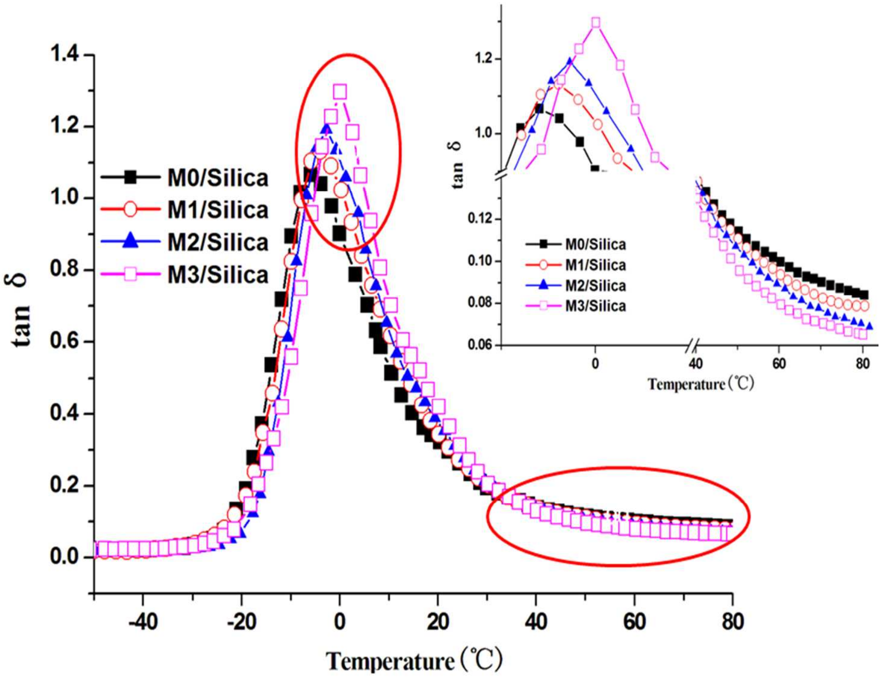


Figure 9 Dynamic mechanical analysis of the M-S-SBR filled with silica: temperature dependence of tan δ

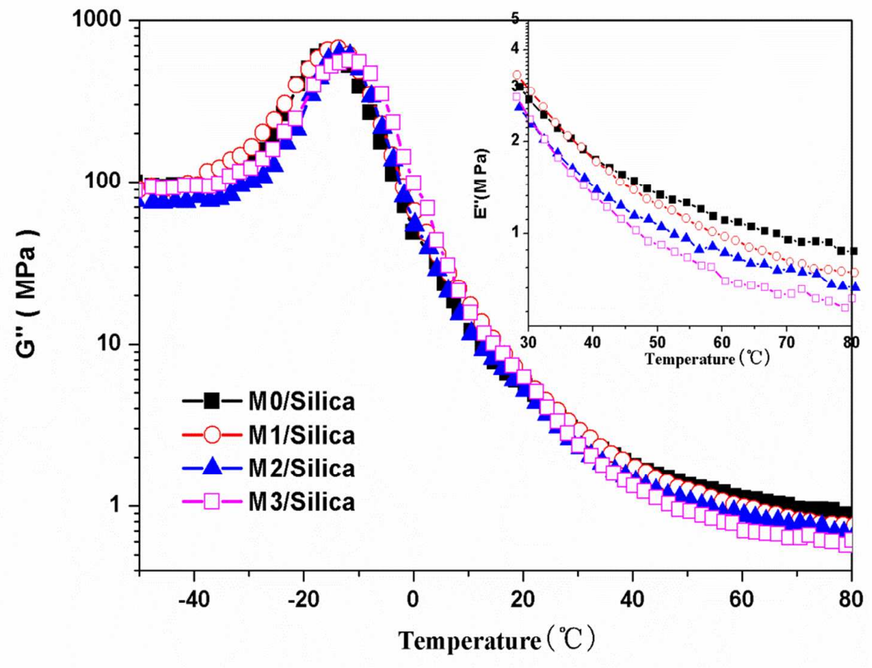


Figure 10 Dynamic mechanical analysis of the M-S-SBR filled with silica: temperature dependence of loss modulus G”

Table 6 Dynamic property parameters and $T_g$ from DSC of M-S-SBR/Silica

| | $T_g$/℃ | tan δ $_{max}$ | $T_g$-c/℃ | $T_g$-r/℃ |
|---|---|---|---|---|
| M0/Silica | -5.9 | 1.07 | -27.2 | -26.8 |
| M1/Silica | -3.9 | 1.11 | -26.7 | -26.4 |
| M2/Silica | -2.7 | 1.19 | -25.4 | -25.8 |
| M3/Silica | 0.1 | 1.30 | -23.9 | -24.4 |

$T_g$-c is the $T_g$ from DSC for M0/Silica and M-S-SBR/Silica
$T_g$-r is the $T_g$ from DSC for M0 and M-S-SBR

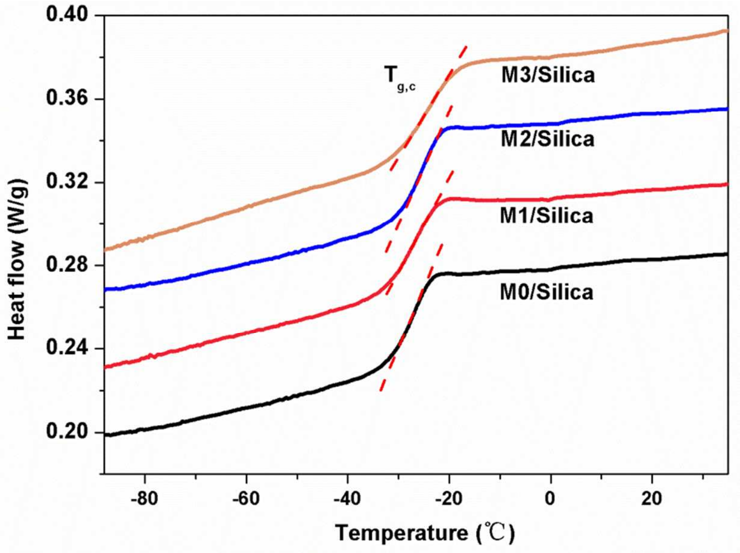


Figure 11 DSC curves of M-S-SBR /Silica

After we verified the filler and rubber adhesions are indeed enhanced by rubber modifications, it is worthwhile to discuss further the interesting dynamic mechanical properties of our system. It is well accepted that the lower elasticity at low temperature and lower energy dissipation at relative high temperature seem to be a pair of contradictions and the synchronous improvements of these are difficult to be established. Nevertheless, the better balance of wet grip and rolling resistance can be obtained by introducing functional groups in S-SBR. As a matter of fact, the energy dissipations at different temperature ranges are governed by different mechanisms. [32] At temperature near tan δ peak in the transition zone, the portion of the filled rubber for energy dissipation is polymer matrix and thus the number of rubber molecular chains which can be involved in the transition dominates the intensity. In the present study, the breakdown of filler network can be excluded due to the relative low strain amplitudes in the DMA measurements. In the filled rubber system with large amount of silica, the filler parameters, such as particles size, structure and surface characteristics, make effective filler volume quite different from real filler volume. Especially for highly polar filler such as silica which has large tendency to agglomerate, chain-like filler structure easily forms via hydrogen bonding. In that case, some polymer chains are supposed to be trapped in the agglomerates which behave as a part of rigid filler rather than polymer matrix [33, 34] (see the schematic diagram in Figure 12). The effective immobilization of the rubber portion increases the effective filler volume beyond the value calculated from the mass and density. As a result, the worse silica disperses in the rubber matrix, the more molecule chains are occluded in the filler agglomerates, thus the less can engage in the transition.

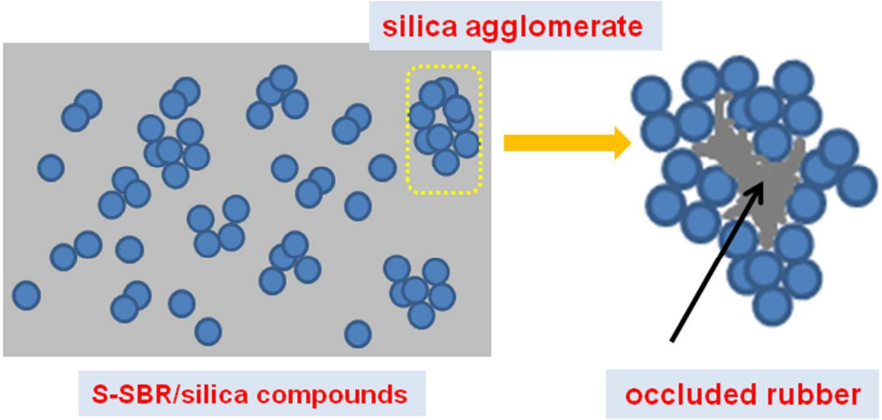


Figure 12 Schematic diagram of occluded rubber in unmodified S-SBR filled by silica

Returning to our system, the interactions between rubber and silica are remarkably improved by introduction of polar groups and thus silica exhibit better dispersion stabilities and finer morphologies as well. This means that less polymer chains are occluded in the filler agglomerates and more can be engaged in $T_g$ transition, which leads to higher tan $\delta_{max}$. Another point should not be ignored here is that the silane coupling agent TESPT is employed when compounding in our system. Based on the model of rubber reinforcement with silica by silane coupling agent proposed by Luginsland, [35] there is a layer of bound rubber chemically bonded to the silica surface by the organosilane coupling agent and this layer is considered to be immobilized. As mentioned above, better dispersion of silica suggests more silica particles can get involved with TESPT, and therefore more chemically bonded rubber forms. But why does the increase in bound rubber result in that more rubber chains can participate in the glass transition? It seems to be contradictory. Here, we detect the heat capacity ($\Delta C_p$) of glass transition for all rubber/Silica compounds by DSC (the DSC curves are shown in Figure 11) and the values are given in Table 7. $\Delta C_p$, which is related to the fraction of the polymer participating in the glass transition and is proportional to the number of internal degree of freedom of molecular motion, [36] shows an increasing tendency with the content of polar groups. It is clear that a higher fraction of polymer chains can be involved in the glass transition in the M-S-SBR/Silica. Therefore, we assume that the amount of rubber chains engaged in the transition for M-S-SBR/Silica system is larger compared with that in M0/Silica probably because the increased amount of molecular chains released from the occluded rubber in M-S-SBR /Silica can compensate the loss in the number of rubber chains due to being chemically bonded to silica surface.

According to the G” and tan δ data mentioned above, M3/Silica presents the lowest energy dissipation in the elastic temperature region. It is can be deduced that energy dissipation is dominated by the interactions between rubber and fillers because the energy dissipation in the elastic state is increased by the frictions between rubber chains and filler particles which are derived from weak interface strength. Conversely, strong rubber-filler interaction is favorable for lower hysteresis in this temperature range.

Table 7 $\Delta C_p$ for all M-S-SBR/Silica compounds

| Sample code | $\Delta C_p$ ( J/g/K ) |
|---|---|
| M0/Silica | 0.23 |
| M1/Silica | 0.24 |
| M2/Silica | 0.26 |
| M3/Silica | 0.29 |

## Conclusion

In the present study, we synthesized a series of modified solution-polymerized styrene butadiene rubbers (M-S-SBRs) with different molar contents of polar groups through grafting 3-mercaptopropionic acid on S-SBR. According to the thermodynamic analysis and strain sweep measurement, the presence of polar groups in S-SBR increase the surface energy, especially the polar part, resulting in the stronger adhesive strength between rubber and silica and thus more stable filler-rubber-filler network compared with unmodified one. TEM photographs support the abovementioned observations. As far as the dynamic mechanical property is concerned, the better dispersion of silica and stronger filler-rubber interaction facilitates the combination the lowest tan δ and G” in higher temperature region of 50～80 $^{o}$C and higher intensity of $T_g$ relaxation.

## Appendix (a list of parameters)

| | |
|---|---|
| $r_p^d$ | dispersive part of surface energy |
| $r_p^p$ | polar part of surface energy |
| $r_P$ | total surface energy |
| $\Delta W$ | the change in adhesive energy in the filler agglomeration process |
| $W_{rf}$ | adhesive energy |
| $G'$ | elastic modulus |
| $G'_0$ | elastic modulus at very small strain |
| $G'\infty$ | elastic modulus at very large strain |
| $G'_{uf}$ | elastic modulus for unfilled rubber |
| G” | loss modulus |
| $\gamma$ | strain |
| $\gamma_c$ | critical strain where |
| $E_a$ | activation energy |
| tan δ | loss factor |
| tan $\delta_{max}$ | maximum tan δ value in the plot of tanδ *vs.* temperature |
| $T_g$ | glass transition temperature |
| $\Delta C_p$ | heat capacity |

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