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The Influence of *In Situ* Modification of Silica on Filler Network and Dynamic Mechanical Properties of Silica-Filled Solution Styrene–Butadiene Rubber

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Received 20 September 2006; accepted 1 May 2007

DOI 10.1002/app.26843

Published online 27 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The influence of *in situ* modification of silica with bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) on filler network in silica filled solution SBR compound was investigated. *In situ* modification greatly increased the bound rubber content. TEM observation of silica gel showed that bridging and interlocking of adsorbed chains on the surface of silica particles formed the filler network. Rubber processing analyzer (RPA) was used to characterize the filler network and interaction between silica and rubber by strain and temperature sweeps. *In situ* modification improved the dispersion of silica, and in the meantime, the chemical bonds were formed between silica and rubber, which conferred the stability of silica dispersion during the

processing. Compared to the compound without *in situ* modification, the compound with *in situ* modification of silica exhibited higher $\tan \delta$ at low strains and lower $\tan \delta$ at high strains, which can be explained in terms of filler network in the compounds. After *in situ* modification, DMTA results showed silica-filled SSBR vulcanizate exhibited higher $\tan \delta$ in the temperature range of -30 to 10°C , and RPA results showed that it had lower $\tan \delta$ at 60°C when the strain was more than 3%. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 112–118, 2008

Key words: solution SBR; silica; *in situ* modification; filler network; hysteresis

INTRODUCTION

Over the last 10 years, the silica–silane system has widely been applied in the passenger car tires to lower the rolling resistance and improve the wet grip. The modification of silica with a bifunctional silane during the mixing operation is often called *in situ* modification.^{1,2} *In situ* modification with silane-coupling agent is a effective method to improve silica dispersion and reduce agglomeration of silica particles by chemical interfacial interactions. The most widely used silane-coupling agent is bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT).^{3–8} Complete silanization reaction between silanes and silica during the mixing process without unwanted pre-crosslinking of rubber matrix is the key to prepare

silica-filled rubber compounds. For silica-filled rubber systems, extensive works have been carried out for the bound rubber,^{6,9,10} Payne effect,^{11–13} filler flocculation,^{14,15} interfacial effects on viscoelastic behavior,^{9,16,17} and mechanical properties of silica filled styrene–butadiene rubber (SBR) systems.^{18,19} According to the process of measuring bound rubber by extraction method, connective rubber filaments should be needed to ensure the coherence of the swollen rubber–filler gel.^{20,21} That is, to say, in uncured filled rubber compound, when the filler level is high enough, i.e., higher than or close to the so-called percolation level, there is a three-dimensional rubber–filler network, which is named the filler network in this article. Thus, in filler network, there are two kinds of contacts: flexible filler–rubber–filler (FRF) contacts and rigid filler–filler (FF) contacts. The ratio of FRF to FF contacts is closely related to surface characteristics of filler, level of filler dispersion, interactions between filler and rubber, etc. So, it will be interesting to investigate the filler network in filled rubber.

In this article, the influence of *in situ* modification on filler network in silica filled solution SBR (SSBR) compounds was investigated by the rubber processing analyzer (RPA) and dynamic viscoelastic proper-

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50303002.

Contract grant sponsor: Tenth-Five-Year Plan Project; contract grant number: 2004BA310A41.

Contract grant sponsor: Beijing New Star Plan Project; contract grant number: 2004A14.

ties of the compounds were explained in terms of the filler network, and the effects of the temperature on the stability of silica dispersion were studied. Finally, the structure and dynamic properties of the vulcanizates were also investigated.

EXPERIMENTAL

Materials

SSBR-2305 was kindly provided by Yanshan Petrochemical (Beijing, China). Precipitated silica Hi-sil 255N was brought from Jiangxi Nanji Chemical Industry (China). Silane-coupling agent TESPT was purchased from Nanjing Shuguang Chemical (China).

Sample preparation

First, 100 phr SSBR, 50 phr silica, and 3 phr TESPT were mixed uniformly on a two-roll mill at room temperature. Then, the compound was compounded about 6 min at 150°C and a rotor speed of 40 rpm in a Haake mixer (*in situ* modification), and this compound was named S2. As a control, silica-filled SSBR without TESPT was also prepared by the same procedure, and the compound was abbreviated to S1.

Characterization

Contents of bound rubber were determined by extracting the compounds with toluene for 3 days, and the solvent was changed for every 24 h. The remnants after extraction were put into acetone for 1 day to remove residual toluene, and then dried at room temperature for one day and at 50°C in a vacuum oven to constant weight to obtain dried gel. The bound rubber content is calculated by $BdR\% = [(w_0 - (w_1 - w_2))/w_0] \times 100\%$, where w_0 is the weight of rubber in the sample, and w_1 and w_2 the weight of sample before and after extraction, respectively.

Some silica rubber gel is placed in a small test tube containing toluene, and then immersed in the water bath of the ultrasonic unit and agitated for 10 min. A single drop of the dispersion was placed onto a copper specimen grid, and after evaporation of toluene, it was used for transmission electron microscopy (TEM) observation, which was carried out on JEM-3010 of JEOL at an acceleration voltage of 200 kV at room temperature. TEM morphologies of the vulcanizates were taken from ultrathin sections ultramicrotomed under liquid nitrogen cooling using an H-800 TEM (Hitachi, Japan) at an acceleration voltage of 200 kV at room temperature. Before TEM observation, the sample surface was coated a thin carbon film.

The dynamic storage modulus G' and the loss factor $\tan \delta$ of the compounds were measured with a RPA (RPA2000, Alpha Technological). Strain sweep from 0.28% to 100% was operated at 60°C, 1 Hz. Temperature sweep from 60 to 160°C was operated at 1 Hz, 1 or 50% strain.

XL-30 environment scanning electron microscope (ESEM; FEI, USA) was used to observe cryofractured surface of S1 and S2 before or after temperature sweep at 1% strain and 1 Hz. $\tan \delta$ as a function of the temperature of vulcanizates was measured on the (dynamic mechanical thermal analyzer) DMTA V of Rheometrics Science in the tension mode, 1 Hz, and 3°C/min.

RESULTS AND DISCUSSION

Bound rubber

The contents of bound rubber in compounds S1 and S2 are measured. The content of bound rubber in S1 is 9.7%; compared with S1, the content of bound rubber in S2 is markedly enhanced, reaching up to 52.2%, indicating that *in situ* modification greatly improved the dispersion of silica and the interactions between silica and SSBR. Yatsuyanagi et al.¹⁹ suggest that there is an entrapped rubber within the filler agglomerates. To verify the position that the bound rubber in S1 and S2 exists: within the agglomerate or on the surface of silica particles, we carried out TEM observation of bound rubber.

The large scale and small scale TEM photographs of silica gels of S1 and S2 are presented in Figure 1. At low magnification, silica particles in S1 gel are clearer than those in S2 gel; there are large agglomerates in S1 gel, whereas in S2 gel, the size of agglomerates decreases and the dispersion of silica particles is relatively uniform. At high magnification, we can observe that bridging and interlocking of absorbed chains on the surface of agglomerates form the filler network; compared with S1 gel, there are much more absorbed chains and relatively small-sized agglomerates in S2 gel.

Payne effect

In a filled rubber, the amplitude-dependence of the dynamic viscoelastic properties was brought into clear focus by the work of Payne in the 1960s,²² and it is often referred to as the Payne effect. This effect is closely related to the filler dispersion and filler-rubber interactions. The curves of G' versus strain of two compounds S1 and S2 and pure SSBR are presented in Figure 2. At low strains, G' of S1 is much higher than that of S2, which should be attributed to the fact that there are large amounts of direct filler-filler contacts due to the poor dispersion of silica in

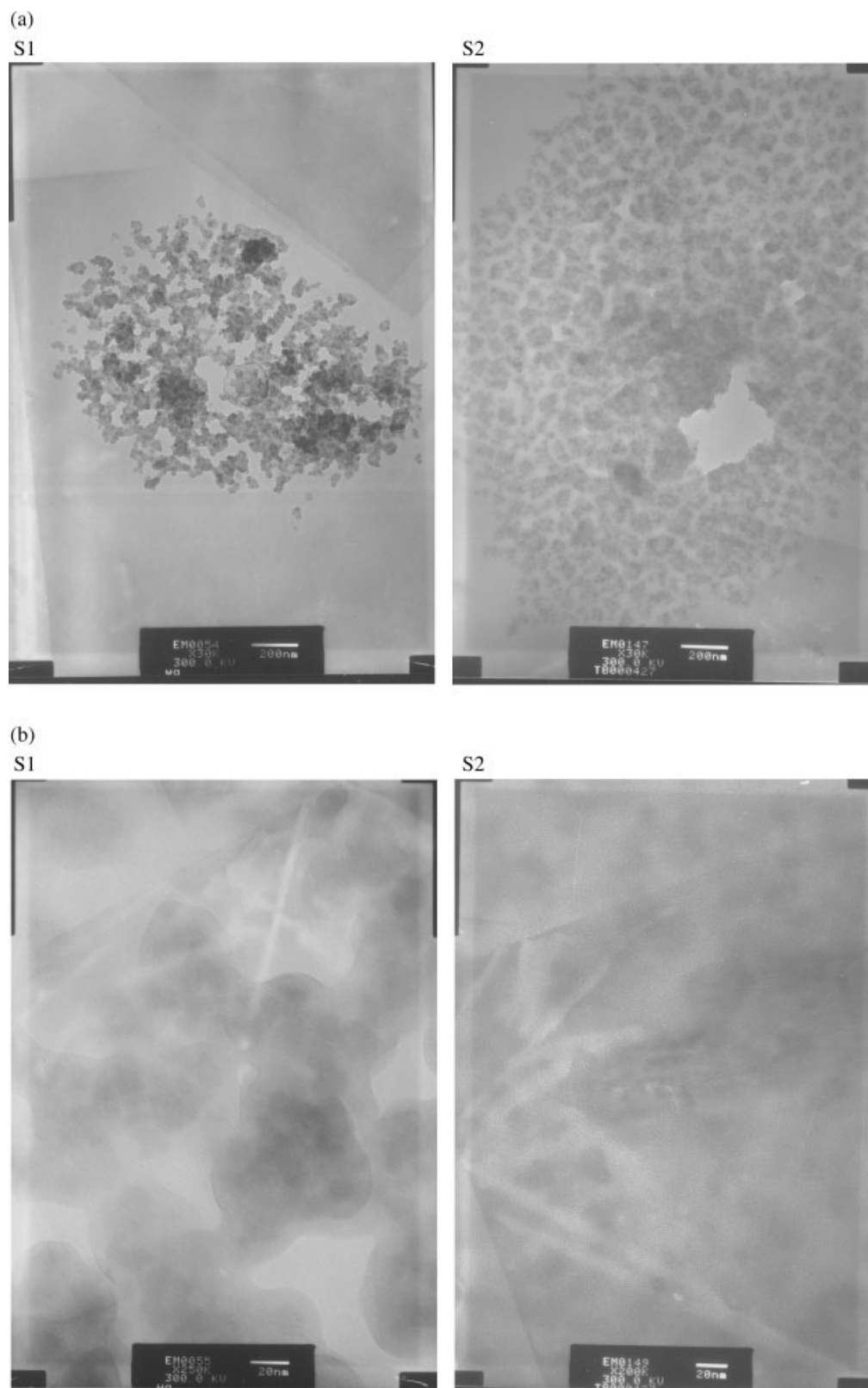


Figure 1 TEM photographs of silica gels of S1 and S2 at two different magnifications: (a) at low scale; (b) at large scale.

S1. This is consistent with the results of bound rubber. With the increase in strain, the filler network starts to be broken, and G' decreases. It can be noticed that G' of S1 begin to decrease at lower

strains than that of S2. The reason should be that the direct FF contacts are more rigid than the FRF contacts, and they are broken down at lower strains. Owing to the increased content of bound rubber in

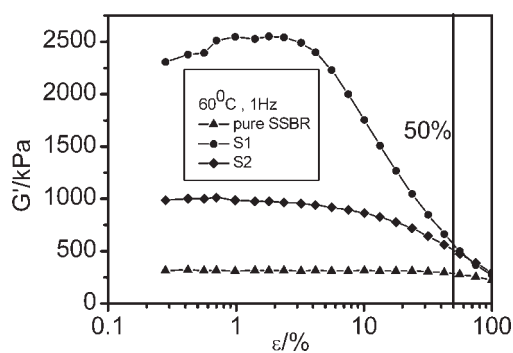


Figure 2 Curves of storage modulus versus strain of S1, S2, and pure SSBR.

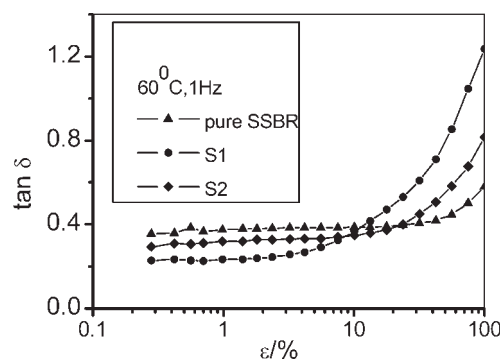
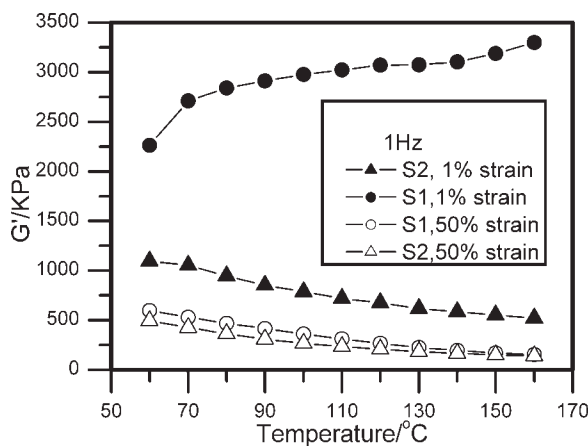


Figure 3 Curves of $\tan \delta$ versus strain of S1, S2, and pure SSBR.

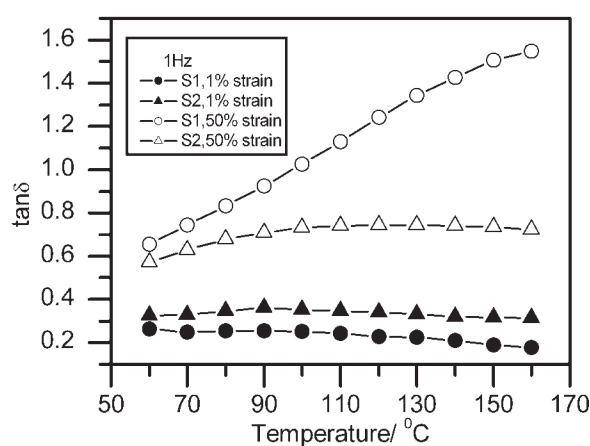
S2 by *in situ* modification, at high strains, S2 exhibits little higher modulus than S1. That is, at low strains, filler–filler contacts contribute much more to G' than filler–rubber–filler contacts. In addition, Payne effect of pure SSBR is not evident.

Loss factors $\tan \delta$ of S1, S2, and pure SSBR as a function of strain are presented in Figure 3. From Figure 3, at low strains ($< 10\%$), the order of $\tan \delta$ is pure SSBR $>$ S2 $>$ S1, whereas at high strains ($> 10\%$), this trend completely reverses. The cause should be attributed to the different modes of energy dissipation at low and high strain regions. At low strains ($< 10\%$), filler network is almost not destroyed, and the viscous nature of rubber would mainly be responsible for the energy dissipation. Without the restriction of filler, pure SSBR exhibits the highest $\tan \delta$. S1 shows the lowest $\tan \delta$, which may be interpreted in terms of a reduction in deformable rubber fraction. Compared to S2, the dispersion of silica in S1 is poorer, and accordingly the number of filler clusters formed by direct FF contacts is more.

Thus, in S1, the rubber fraction entrapped within filler clusters (occluded rubber) is larger, which is shielded from deformation, leading to the reduced deformable rubber fraction. At high strains ($> 10\%$), the filler network was gradually destroyed, and the hysteresis was mainly from FF friction due to the destruction of filler clusters. In addition, the interfacial friction between filler and rubber, and the viscous characteristic of rubber fraction released from within filler clusters also contributed to the hysteresis. Concerning S1, the breakdown of filler clusters increased filler–filler friction, and in the meantime the weaker interfacial interaction also increased the interfacial friction between filler and rubber. Therefore, S1 shows the highest $\tan \delta$ at high strains. By contrast, due to the improved dispersion of silica and chemical interfacial interaction, S2 exhibits higher $\tan \delta$ at low strains and lower $\tan \delta$ at high strains relative to S1. This phenomenon is completely different from that of carbon black-filled rubber compound, in which $\tan \delta$ exhibited a peak at 1–10% strain.¹³



(a)



(b)

Figure 4 Temperature sweep curves of S1 and S2 at two different strains of 1 and 50%: (a) curves of G' versus temperature; (b) curves of $\tan \delta$ versus temperature.

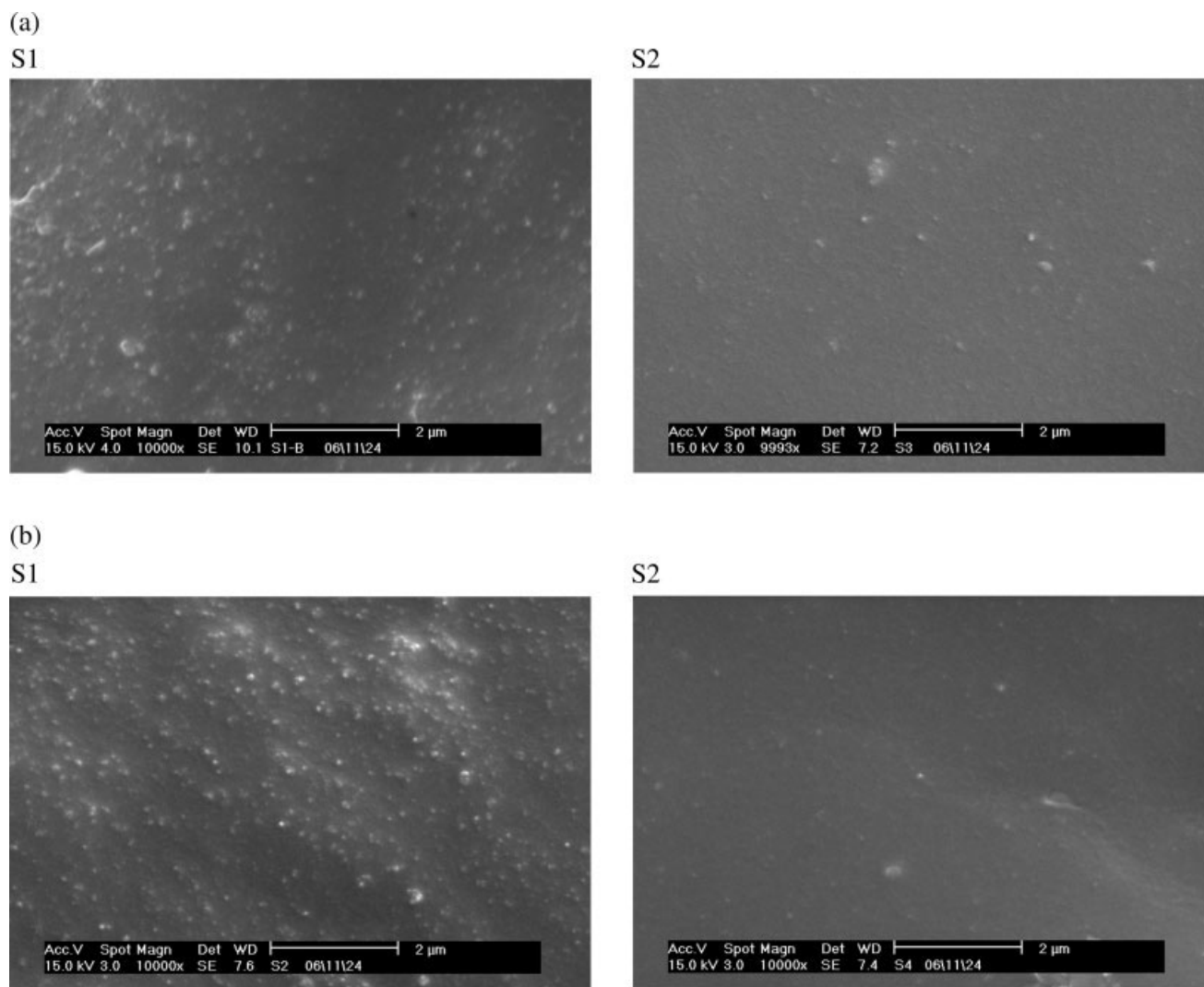


Figure 5 SEM photographs of S1 and S2 before and after temperature sweep at 1% strain: (a) before temperature sweep; (b) after temperature sweep.

Stability of silica dispersion

To evaluate the stability of silica dispersion after *in situ* modification, we carried out temperature sweep measurement at two different strains: 1% low strain and 50% high strain. The results are presented in Figure 4. From Figure 4(a), at 1% strain, with increasing temperature, G' of S1 increases evidently, whereas G' of S2 decreases. These results should be originated from different filler–rubber interaction. Without TESPT, interactions between silica particles in S1 are stronger compared with that between silica and SSBR. With the increase in temperature, the viscosity of rubber matrix reduces, and thus flocculation of silica particles occurs, which result in the improved G' . For S2, due to the coupling reaction of TESPT with silica and SSBR, the chemical bonds between rubber and silica greatly prevent the occurrence of flocculation of silica particles; in the meantime, G' of rubber matrix decreases with the increase

in temperature. Combining the two effects, G' of S2 shows the reverse trend relative to S1. At 50% high strain, with increasing temperature, G' of S1 and S2 decreased. This is due to the destruction of filler network at 50% (see Fig. 2).

From Figure 4(b), at 1% low strain, $\tan \delta$ of S1 is lower than that of S2, and $\tan \delta$ of S1 and S2 changes little with increasing temperature; at 50% high strain, $\tan \delta$ of S1 increased linearly with the increase in temperature, whereas $\tan \delta$ of S2 increased slightly with the increase in temperature. This can be explained in terms of filler network. At 1% strain, filler network is not destroyed, and as the above explanation, the viscous nature of deformable rubber mainly contributes to the hysteresis. Thus, $\tan \delta$ of S1 at 1% strain is lower than that of S2, which is consistent with the results shown in Figure 3. At 50% strain, most of filler network is destroyed. For S1, with increase in temperature, the filler–rubber friction

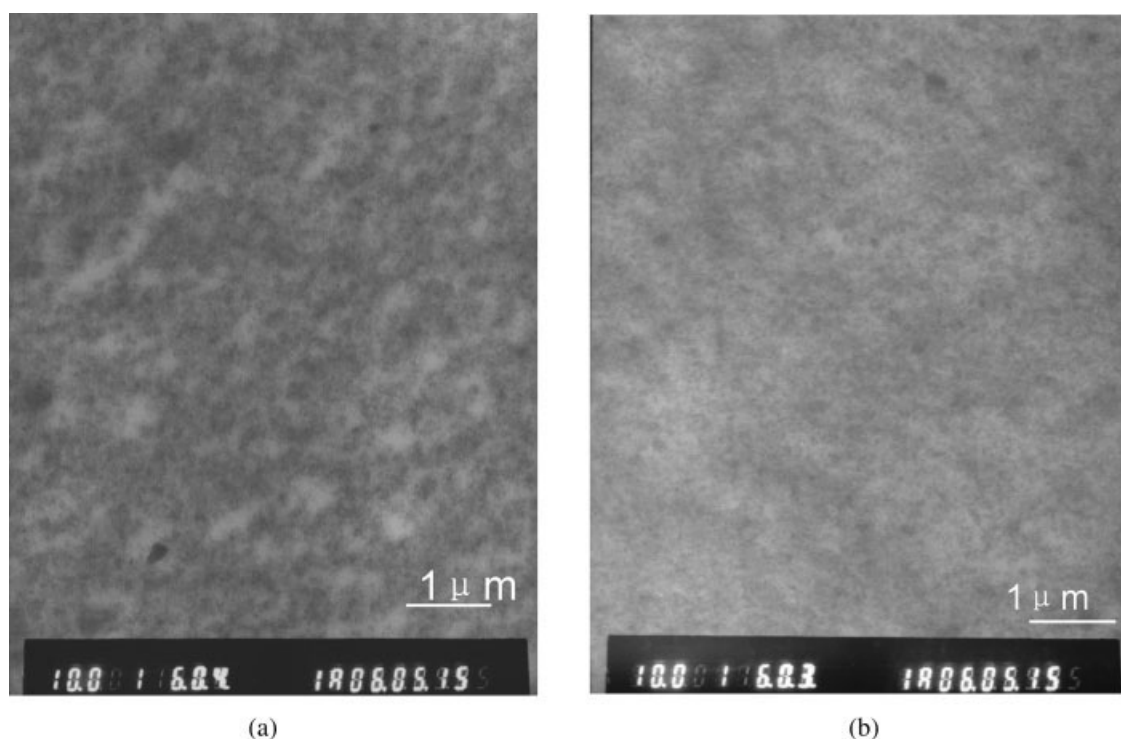


Figure 6 TEM photographs of S1 and S2 vulcanizates (a) S1; (b) S2.

increased due to the decreased physical interactions, and the viscous characteristics of the rubber fraction released from within filler clusters increased. So, for S1, besides the friction of filler–filler, the friction of filler–rubber and viscous characteristics of released rubber also contribute to the increase in the value of $\tan \delta$ with increasing temperature.

To directly observe the agglomerating degree of silica particles during temperature sweep, SEM photographs of S1 and S2 before and after temperature sweep at 1% low strain are shown in Figure 5. Before temperature sweep [Fig. 5(a)], the surface of S1 is much rougher than that of S2, and much more silica particles can be observed clearly in S1, indicating that the dispersion of silica is poorer in S1 than in S2. After temperature sweep, the surface of S1 becomes much rougher, suggesting that silica particles agglomerate during the process of temperature sweep; the surface of S2 is smooth, and silica particles seem to be embedded in matrix. This should be attributed to the stronger interfacial interactions in S2 after high temperature sweep.

On the basis of the above-mentioned facts, the coupling reaction of TESPT with silica and rubber, i.e., *in situ* modification reaction, greatly improved the stability of dispersion of silica particles in rubber matrix.

Structure of S1 and S2 vulcanizates

TEM micrographs of S1 and S2 vulcanizates are shown in Figure 6. As expected, in S1 vulcanizate,

silica agglomerates were observed and the dispersion was poor; in S2 vulcanizate, the dispersion of silica particles was greatly improved. These are consistent with the results shown in Figure 5.

Dynamic mechanical properties of S1 and S2 vulcanizates

The curves of $\tan \delta$ versus temperature of S1 and S2 vulcanizates tested by DMTA are shown in Figure 7. In the temperature range of -30 to 10°C , $\tan \delta$ of S2 was higher than that of S1, indicating that S2 vulcanizate exhibited better wet grip than that of S1. The higher $\tan \delta$ of S2 should be attributed to more rubber frac-

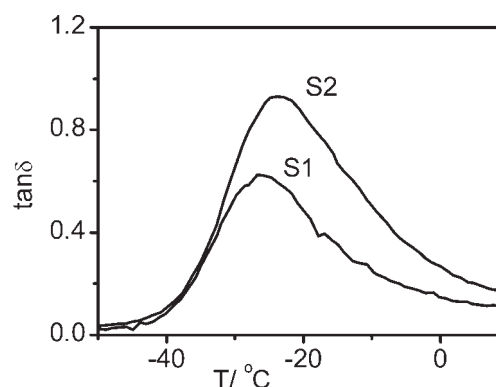


Figure 7 Curves of $\tan \delta$ versus temperature of S1 and S2 vulcanizates tested by DMTA.

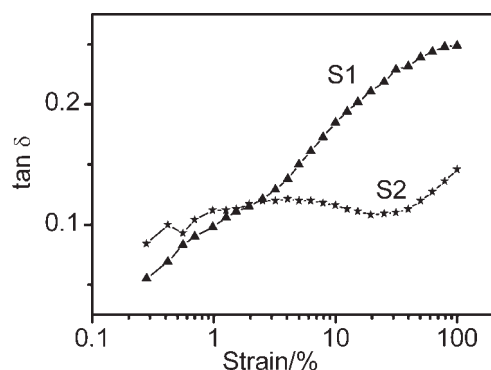


Figure 8 Curves of $\tan \delta$ versus strain of S1 and S2 vulcanizates tested by RPA at 60°C and 1Hz.

tion participating in the glass transition in S2 relative to S1 due to the better dispersion of silica. When compared with S1, the glass transition region of S2 became broader and the glass transition peak shifted to the higher temperature due to the strong chemical interfacial interactions in S2.

The curves of $\tan \delta$ versus strain of S1 and S2 vulcanizates are presented in Figure 8. From Figure 8, $\tan \delta$ of S1 increased rapidly with the increase in strain, and $\tan \delta$ of S1 was higher than that of S2 when the strain was higher than 3%, which is consistent with the results of S1 and S2 compounds (see Fig. 3). Because of the stronger stress during the deformation process of the vulcanizates, the filler network was destructed at lower strain than that for the corresponding compounds.

CONCLUSION

In situ modification with TESPT improved the content of bound rubber, the dispersion of silica, and, in the meantime, the chemical bonds were formed between silica and rubber, which enhanced the stability of silica dispersion. Compared to the compound without *in situ* modification, the compound with *in situ* modification silica exhibited higher $\tan \delta$

at low strains and lower $\tan \delta$ at high strains, which can be explained in terms of the filler network. After *in situ* modification, silica-filled SSBR vulcanizate exhibited higher $\tan \delta$ in the temperature range of -30 to 10°C, and lower $\tan \delta$ at 60°C. So, silica-filled SSBR vulcanizates should show low rolling resistance and high wet grip.

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