

Effect of Surface Modifier on the Properties of SSBR/BR Nanocomposites

Filled With Modified Silica

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Abstract: Three types of nano-SiO₂ modified with organic modifiers hexamethyldisilazane (denoted as HMDS; molecular formula: C₆H₁₉NSi₂); KH570 (molecular formula: C₁₀H₂₀O₅Si) containing C=C double bond and Si69 (Bis [3-(triethoxysilyl) propyl] tetrasulfide) were prepared by in situ surface-modification method. As-obtained nano-SiO₂ particles were characterized by Fourier transform infrared spectrometry and transmission electron microscopy, and they were also used to reinforce the blend of butadiene rubber and solution polymerized styrene-butadiene rubber (denoted as SSBR/BR) in order to improve the comprehensive properties to meet the performance requirements for green tire tread compound. The mechanical properties, heat aging property, abrasion resistance, dynamic mechanics properties and vulcanization property of composites were performed and compared to commercially obtained Rhodia Z-1165MP. Hopefully, the mechanical property and dynamic mechanics property of obtained nano-SiO₂/SSBR/BR nanocomposites especially tear strength weigh against even better than Z-1165MP/SSBR/BR composites. Moreover, in situ surface modification method to modified silica by KH570 or other modifier containing organic functional groups is a good way to increase reaction activity of silica and improve the miscibility and compatibility of silica with rubber matrix, which could be of special significance to developing high performance nano-SiO₂/SSBR/BR compounds.

Keywords: nano-SiO₂/SSBR/BR nanocomposites, situ surface-modification method, mechanical property, dynamic mechanics properties

1. INTRODUCTION

In recent years, the increasing demand for low-energy consumption and environmental friendly products has led to the development of the green tire tread [1], which has good performances with low rolling resistance and high wet skid resistance [2]. At present, one of the good choices for tire tread rubber is the blend of the butadiene rubber (denoted as BR) and solution polymerized styrene-butadiene rubber (denoted as SSBR) [3]. Butadiene rubber (BR) has outstanding elasticity and good abrasion resistance as well as good dynamic performance [4]. While solution Polymerized styrene-butadiene rubber (SSBR) is well balanced between rolling resistance and wet skid resistance, and excellent in abrasion resistance and stability [5]. That is why styrene-butadiene rubber (SSBR) becoming the main raw material of the green tire tread and being extensively used. SSBR/BR blending helps to improve the comprehensive properties and processing performance [6]. But mechanical properties need to improve by adding Fillers to rubber to achieve desired properties suitable for specific applications [7]. Silica is well known as one of the most common fillers in the rubber industry [8], especially applied to green tire tread [9]. Nevertheless, the adhesion between the surfaces of silica and rubber is rather poor, since the silica surface is hydrophilic, while the rubber surface is hydrophobic [10]. Moreover nanoparticles usually possess high surface activity and tend to agglomerate. The weak adhesion and agglomeration can result in a poor compatibility with the polymer and weak heterogeneous dispersity in the rubber matrix, which can greatly impact the performances of the composite materials [11]. To overcome this drawback, a number of researchers have tried to modify the silica surface by various ways. Liu Li and co-workers had modified silica with bis(3-triethoxysilylpropyl)tetrasulfide (TESPT) at different temperature to fill solution styrene butadiene rubber (SSBR) composites, and proved that TESPT was ideally bonded on the surface of silica via chemical bonds[9]. Zhixin Jia et al. [12] synthesized an original type of rubber antioxidant, silica-supported 2-mercaptobenzimidazole (SiO₂-s-MB) by utilizing 2-mercaptobenzimidazole (MB) and chlorosilane-modified silica (m-SiO₂), and showed that SiO₂-s-MB presented homogeneously dispersity in the styrene butadiene rubber (SBR). Chakrit Sirisinha et al [13] made use of a xanthate reaction to modify precipitated silica environmental friendly and enhanced silica dispersion when added into natural rubber matrix. Thirawudh Pongprayoon [14] and co-workers modified silica by admicellar polymerization and found that the mechanical properties of rubber reinforced with silica were improved. As is well known, the most effective modification of silica is involving the chemical bonding between the silica and modifying agent [15-17].

In this study, we applied in situ surface modification method [18] to prepare dispersible nano-SiO₂ particles (abridged as DNS); reactive nano-SiO₂ (coded as RNS) and functional nano-SiO₂ (coded as DNS-SX). They were surface-capped by silane coupling agents

hexamethyldisilazane (denoted as HMDS; molecular formula: $C_6H_{19}NSi_2$); KH570 (molecular formula: $CH_2=C(CH_3)COOC_3H_6Si(OCH_3)_3$ containing C=C double bond and silane coupling agent Si69 (bis-(γ -triethoxysilylpropyl)-tetrasulfide; molecular formula: $C_{18}H_{42}O_6Si_2S_4$) respectively. We applied the modified nano-SiO₂ to SSBR/BR blended rubber matrix and researched the mechanical properties, heat aging property, abrasion resistance, dynamic performance and vulcanization property of composites. We also had a comparison with SiO₂ manufactured from Qingdao Rhodia (named Z-1165MP), which refers to commercially obtained SiO₂. Hopefully, the mechanical property and dynamic mechanical viscoelasticity of nano-SiO₂/SSBR/BR nanocomposites especially tear strength weigh against even better than Z-1165MP/SSBR/BR composites. More importantly, it is feasible to adjust and control the mechanical properties of the composites by properly adjusting the kinds of surface-modifiers during the preparation of in situ surface-capped nanosilica, which could make it possible for silica to possess functionalized groups; improve their dispersion in the rubber matrix and enhance rubber–filler interaction and develop high performance composites.

2. EXPERIMENTAL

2.1 Materials

Commercial solution Polymerized styrene-butadiene rubber (SSBR) and Butadiene rubber (BR) are provided by Beijing University of Chemical Technology. Precipitated silica of RhodiaZ-1165MP was produced from Rhodia silica (Qingdao) co., LTD. The dispersible nano-SiO₂ (DNS) and reactive nano-SiO₂ (RNS) and functional nano-SiO₂ (DNS-SX) are synthesized by Engineering Technology Research Center for Nanometer Material of Henan province. All other materials were commercially available.

2.2 Preparation of surface modified nano-SiO₂

The dispersible nano-SiO₂ (DNS); reactive nano-SiO₂ (RNS) and functional nano-SiO₂ (DNS-SX) are prepared in situ surface modification method. That is to say modification occurs at the beginning of the formation of particles. DNS is surface-modified by silane coupling agents hexamethyldisilazane (denoted as HMDS; molecular formula: $C_6H_{19}NSi_2$); RNS is surface-capped by KH570 (molecular formula: $CH_2=C(CH_3)COOC_3H_6Si(OCH_3)_3$) containing C=C double bond in order to improve the interaction with the rubber matrix. DNS-SX is surface-modified by silane coupling agent Si69 (bis-(γ -triethoxysilylpropyl)-tetrasulfide; molecular formula: $C_{18}H_{42}O_6Si_2S_4$).

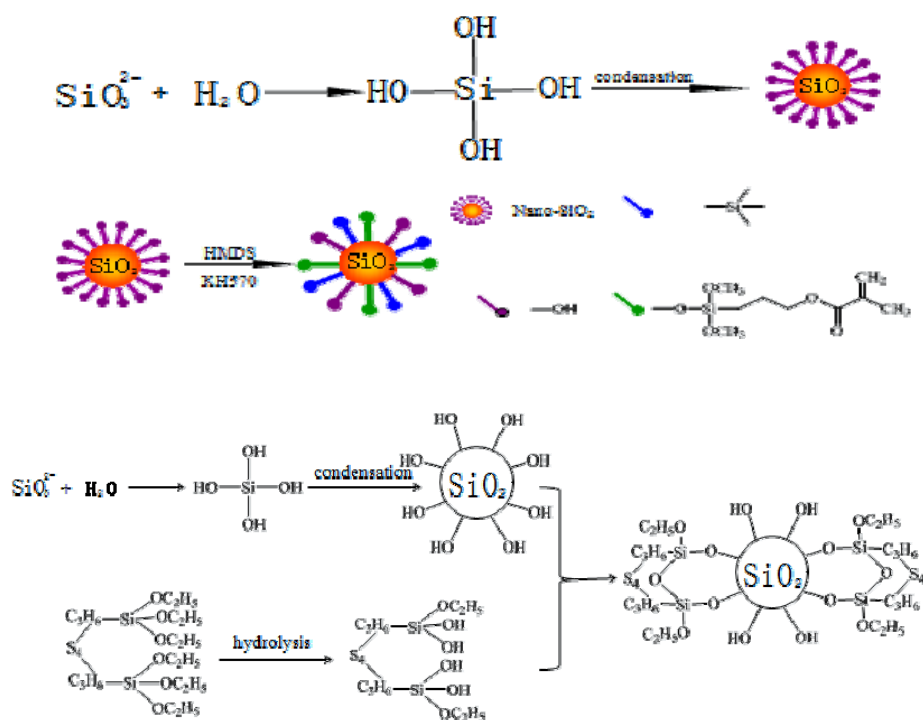


Fig.1. Formation mechanism of surface modified nanosilica.

2.3 Preparation of nano-SiO₂/SSBR/BR composites

Table1 Formulation of nano-SiO₂/SSBR/NR compounds.

Materials	Amount/phr
SSBR	96.25
BR	30
nano-SiO ₂	70
Si69	7
Zinc oxide	3
Stearic acid	1
N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine	1.5
Paraffin wax	1
N-Cyclohexyl-2-benzothiazolesulfenamide	1.5
DPG	2
Sulfur	1.4

The formulation for the preparation of nano-SiO₂/SSBR/BR compounds is shown in Table 1. Firstly, the nano-SiO₂, Si69, zinc oxide, stearic acid, antiager and paraffin wax were mixed with SSBR/BR on a two-roll mill (SK-160; Shanghai light industry machinery co., LTD; China) at 60°C, and placing it for two hours, then all of the other ingredients were uniformly

blended sequentially on a two-roll mill, and placing it for twelve hours, lastly, the mixture was vulcanized at 150 °C and the optimum cure time (t_{90}) with a Rubber Flat Vulcanizing Machine(XLB-D; Ningbo Qianpu machinery manufacture co., LTD; china). The t_{90} was obtained by a rubber vulcanization tester(MZ-4010B; Jiangdu Mingzhu Testing Machinery Co., Ltd; china).

2.4 Characterization

The dispersible nano-SiO₂ (DNS), reactive nano-SiO₂ (RNS), functional nano-SiO₂ (DNS-SX) and Rhodia-SiO₂ (Z-1165MP) were characterized by Fourier transform infrared spectrometry (FTIR; Nicolet 170sx, USA) and transmission electron microscopy (TEM; JEM-2010, Japan). The section morphology of nano-SiO₂/SSBR/BR composites was observed with a scan electron microscope (SEM; JSM-5600LV, JEOL, Japan). The tensile strength, tear strength and elongation at break of nano-SiO₂/SSBR/BR composites were determined according to ASTM D412 and ASTM D624 with electronic tensile testing equipment (WDW-10D; Jinan Shijin Testing Machine Group Co., Ltd; China) at a tensile rate of 500 mm/min. The rebound resilience and hardness of the composites were measured according to ASTM D7121 and ASTM D2240-2005 with an MZ-4065 rubber resilience testing machine and an LX-A Shore hardness tester. Akron abrasion test was brought on a MZ-4061 Akron abrasion tester according to GB/T1689-1998. The vulcanization behavior of nano-SiO₂/SSBR/BR composites was examined with an MZ-4010B non-rotor rheometer (all of them were purchased from Jiangdu Mingzhu Testing Machinery Co., Ltd, China). The dynamic viscoelastic properties of the composites were measured on a861e DMA (METTLER TOLEDO) in the shear mode. The temperature was from -90°C to 80 °C, the heating rate was 3°C/min, the frequency was 10 Hz, and the strain amplitude was 0.1%.

3. RESULTS AND DISCUSSION

3.1 Structure characterization of nano-SiO₂

Fig. 2 shows the FTIR spectra of the RhodiaZ-1165MP, DNS-SX, DNS and RNS, respectively. The absorption band around 3430 cm⁻¹ is attributed to Si-OH group and 1633 cm⁻¹ is adsorbed water. As we can see, all of them have obvious absorption peak of Si-OH group around 3430 cm⁻¹, that is to say, there are a mass of exposed Si-OH group on the surface of nano-silica, and modified silica partially far from 100% condensation reaction, but the intensity of the absorption peak gets weaker. Besides, after the modification by HMDS, KH570 and Si69, the FTIR spectrum of silica nanoparticles appears methene(-CH₂) characteristic peak around 2925 cm⁻¹. We assume that -CH₂ group is introduced by chemical modifiers. In addition the strong peaks near 1100 cm⁻¹, 810 cm⁻¹ and 470 cm⁻¹ are assigned to asymmetric stretching vibration, symmetric stretching vibration, and bending vibration of Si-O-Si.

However, the stretching vibration of C=C in RNS overlaps with the bending vibration of adsorbed water around 1633 cm^{-1} . From the following analysis of mechanical properties, it indicates that C=C has been bonded to the surface of RNS. At the same time, HMDS and Si69 have been modified on the surface of nano-SiO₂ to increase reinforcing ability in the rubber matrix.

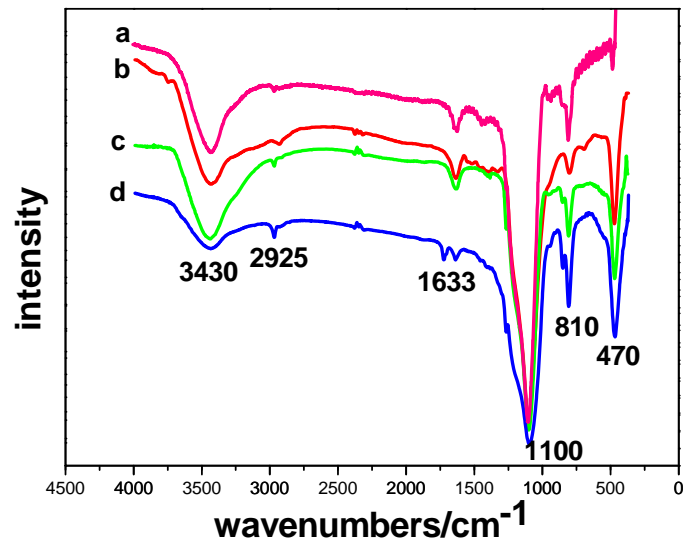


Fig.2.FTIR spectrum of silica nanoparticles: (a) RhodiaZ-1165MP, (b) DNS-SX, (c) DNS and (d) RNS

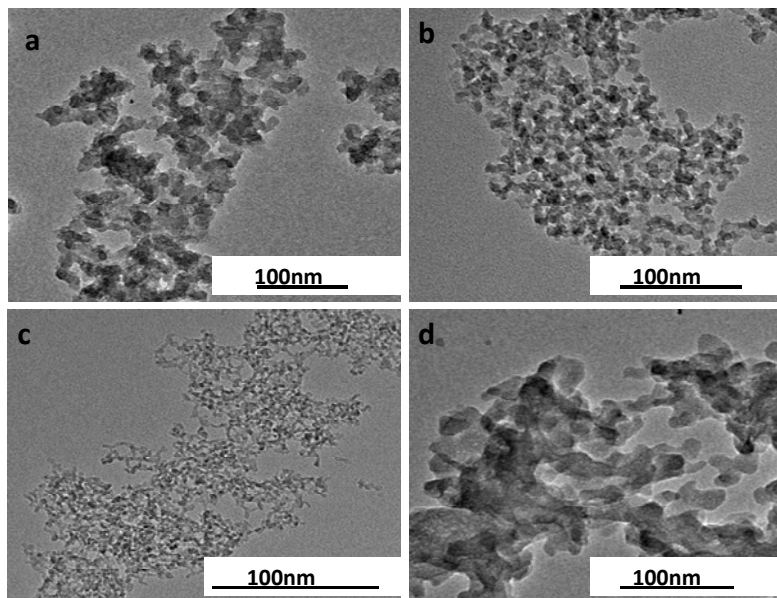


Fig. 3.TEM images of silica nanoparticles: (a) RhodiaZ-1165MP, (b) DNS-SX, (c) DNS and (d) RNS

Fig. 3 displays the TEM images of the four types of nano-SiO₂ dispersed in absolute alcohol. As we can see, the four types of nano-SiO₂ show relatively good dispersibility in the solvent, especially the DNS, which is due to surface capping by HMDS and smaller diameter of particle (about 5nm) while others approximately 10nm. that is to say, the obtained nano-silica is achieved similar even better compatibility to RhodiaZ-1165MP. At the same time, nano-SiO₂ is functionalized with TESPT and KH570.

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3.2 The dispersivity of the nano-SiO₂ in organic matrix

Fig.4 shows the SEM micrographs of the brittle fractured surfaces of various nano-SiO₂/SSBR/BR nanocomposites (the samples for SEM observations were obtained by treatment in liquid nitrogen and brittle fracture). It can be seen that, as-obtained nano-SiO₂ is uniformly distributed in rubber matrix and little aggregation of the silica nanoparticles, it's because the change of the surface structure of nano-SiO₂ that the surface hydroxyl are partially replaced by organic groups, which should be beneficial to improving the dispersibility and increasing the interaction of rubber - filler.

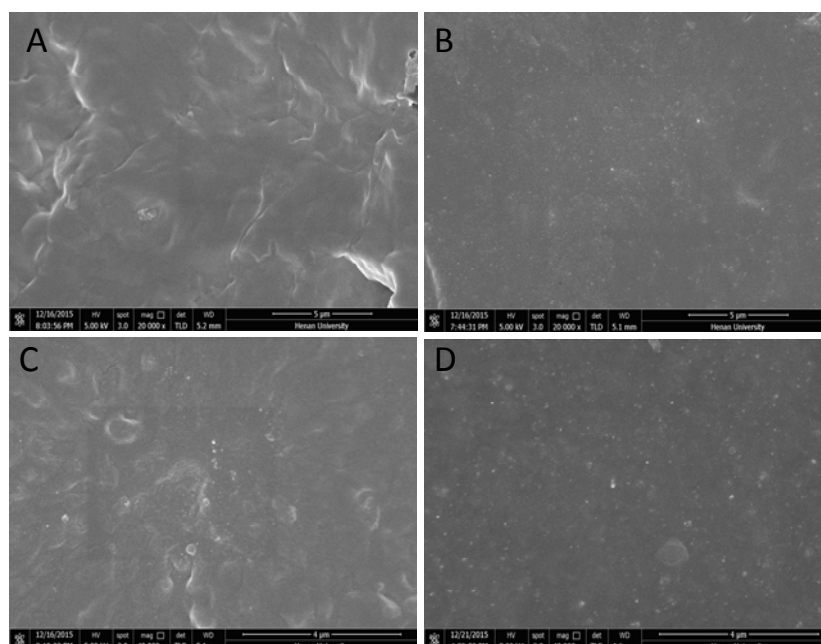


Fig. 4. SEM micrographs of the brittle fractured surfaces of various nanocomposites: (a) RhodiaZ-1165MP, (b) DNS-SX, (c) DNS and (d) RNS

3.3 The processing performance of rubber compounds

Table 2 lists the processing performances of rubber compounds

	Z-1165MP /SSBR/BR	DNS-SX /SSBR/BR	DNS /SSBR/BR	RNS /SSBR/BR
Mooney viscosity (ML(1+4)100°C)	89.8	75.8	83.7	82.9
ML/(N·m)	0.232	0.332	0.379	0.440
MH/(N·m)	1.303	1.434	2.669	2.559
MH-ML/(N·m)	1.071	1.102	2.29	2.119
T ₁₀	3:47	0:25	2:29	3:36
T ₉₀	35:40	17:02	33:57	32:08

As the table2 shown, compared to Z-1165MP /SSBR/NR, the Mooney viscosity of mix filled by various nano-silica with different modification is relatively lower. It indicated that silica capped by HMDS, KH570 and Si69 can efficiently decrease the alcoholic hydroxyl groups on the surface of silica particles, reduce the agglomeration phenomenon of the fillers and lowered the network interaction of filler-filler. The decrease of the Mooney viscosity signifies better processing performance of mixing rubber, what is meaning for improving production efficiency and energy saving. The optimum cure time (t_{90}) and scorch time (t_{10}) of obtained-silica/SSBR/BR is shorter than Z-1165MP /SSBR/BR, Especially DNS-SX /SSBR/BR. This illustrates that the curing rate of system filled by modified silica is faster than it filled by Z-1165MP. The reason may lie in that with the adding of surface-modifier KH570, HMDS and Si69, the reaction happen between modifier and Si-OH on the surface of nano-SiO₂, polar functional groups on the surface of SiO₂ particles are eliminated or restricted, the activity of SiO₂ is decreased, thus the interaction and compatibility of nano-SiO₂ with rubber matrix can be effectively improved. However, the main cause of obvious low t_{10} of DNS-SX /SSBR/BR is the facilitation of polysulfur bonds to the rubber vulcanization. The difference between MH and ML increases with modification for silica, showing the improvement of filler-rubber coactions in SSBR/BR/nano-SiO₂ nanocomposites.

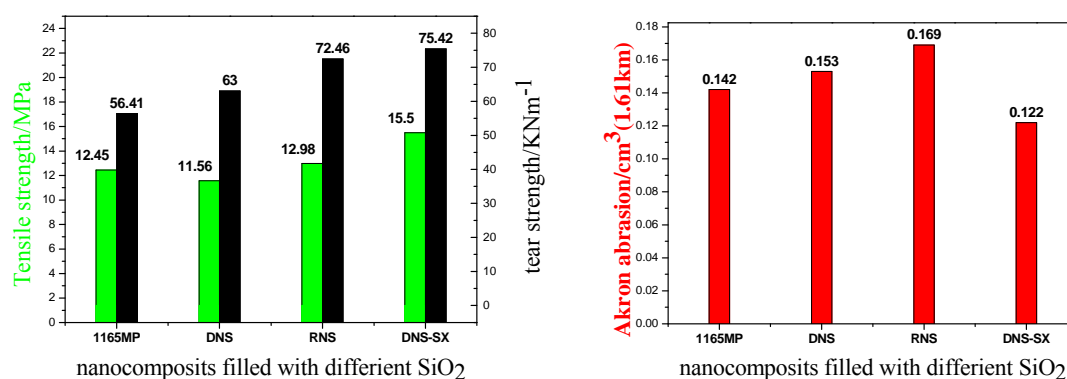
3.4 Analysis of the mechanical properties of nano-SiO₂/SSBR/BR nanocomposites

Table3 lists the mechanical properties of RhodiaZ-1165MP/SSBR/BR and prepared nano-SiO₂/SSBR/BR nanocomposites, and Fig. 5 shows the tensile strength, tear strength and Akron abrasion volume of various nanoSiO₂/SSBR/BR nanocomposites. It can be seen that tensile strength, tear strength and elongation at break of composites filled by RNS and DNS-SX are higher than 1165MP/SSBR/BR, Especially higher tear strength. Compared to the

RhodiaZ-1165MP/SSBR/BR, the Akron abrasion volume of DNS-SX/SSBR/BR is lower, which is meaningful for tire to improve wearing capacity and lengthen the service life of the tire tread. It's also worth mentioning that the comprehensive mechanical performance of DNS-SX/SSBR/BR is outstanding, and RNS/SSBR/BR is second. This indicates that, with the assistance of surface-modification by silane coupling agents TESPT and KH570, the miscibility and compatibility of nano-SiO₂ and interaction with rubber matrix can be effectively improved thereby contributing to mechanically strengthening rubber and leading to increased mechanical strength of the rubber-matrix composites. Hopefully, by introducing Si69 and KH570, the performance has been raised substantially. That is to say, it is feasible to increase some performance of nanocomposites via introducing some functional groups on the surface of nanosilica to meet different product's needs.

Table 3 The mechanical properties of RhodiaZ-1165MP/SSBR/BR and prepared nano-SiO₂/SSBR/BR nanocomposites

nano-SiO ₂ types	Mechanical properties			
	Modulus at 100% elongation/MPa	Shore A hardness	Rebound resilience/%	Elongation at break/%
Z-1165MP	5.04	68	44	245.36
DNS	6.49	83	53	227.56
RNS	6.84	82	51	282.96
DNS-SX	4.14	73	29	371.20



3.5 Analysis of the aging resistant performance of nano-SiO₂/SSBR/BR nanocomposites

Vulcanized rubber was cut into slices and put in an ageing oven with a rotating stents, and placed 72 hours at 100°C. The results after aging are shown in Table 4. From Table 4, we can observe that after aging tests, the mechanical properties of prepared nano-SiO₂/SSBR/BR nanocomposites are superior to RhodiaZ-1165MP/SSBR/BR. It is noteworthy that the change

rates of various performance of RNS/SSBR/BR is smaller than RhodiaZ-1165MP/SSBR/BR, which indicates that its superior aging resistant performance than RhodiaZ-1165MP/SSBR/BR. The reason may due to introduce of C=C of KH570, it made the interaction between filler-rubber more closely, Wrapped more tightly, it is difficult to be destroyed by the heated oxygen air.

Table 4 The aging resistant performance of nano-SiO₂/SSBR/BR nanocomposites

Different types of silica	Z-1165MP	DNS	RNS	DNS-SX
Tensile strength/MPa	10.50	11.19	12.66	11.44
Change of tensile strength/%	-15.66	-3.20	-2.47	-26.19
Elongation at break/%	134.84	128.44	185.92	201.68
The rate of elongation/%	-45.04	-43.56	-34.29	-45.67
Modulus at 100%/MPa	6.63	9.10	10.12	5.30
Rate of modulus at 100%/%	31.55	40.22	47.95	28.02
Tear strength/MPa	45.57	56.675	61.60	65.78
The change of tear strength/%	-19.22	-10.04	-14.99	-12.78

3.6 Dynamic mechanics properties of various nano-SiO₂/SSBR/BR vulcanizates by DMA

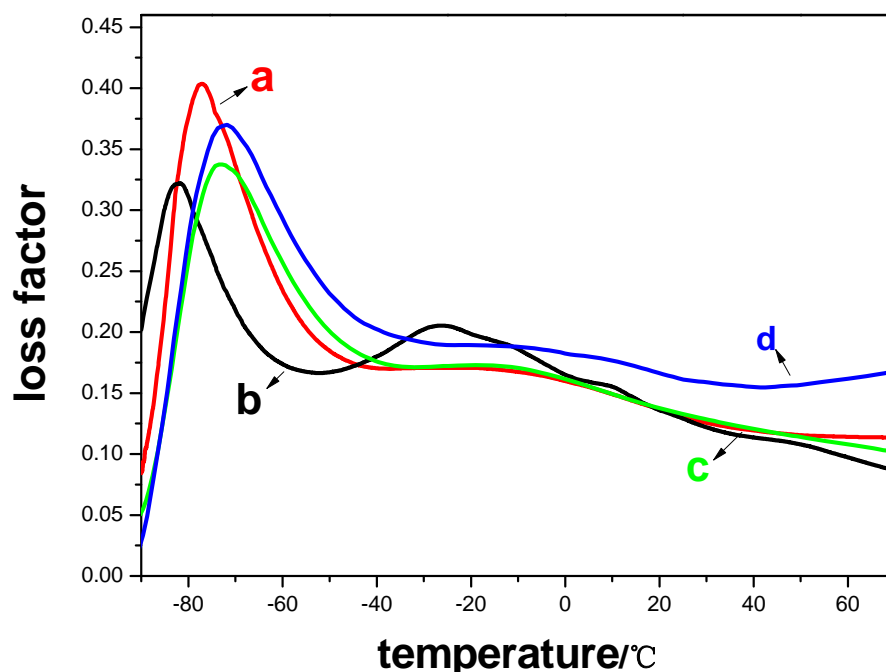


Fig. 5. loss factor of the various nano-SiO₂/SSBR/BR nanocomposite: (a) RhodiaZ-1165MP /SSBR/BR, (b) DNS /SSBR/BR, (c) RNS /SSBR/BR and (d) DNS-SX /SSBR/BR

The dynamic mechanical viscoelasticity of nano-SiO₂/SSBR/BR vulcanizate is shown in Fig. 5. As we have known, the wet skid resistance of vulcanized rubber can be characterized by the loss factor tested at 0°C, On the other hand, the hysteresis of tread composites, characterized by tanδ at 60°C, is a key parameter that shows a good correlation with the rolling resistance of tires. High performance rubber materials should have a combination of a high tanδ at 0°C and a low tanδ at 60 °C, thus rubber tyre can possess good running safety and reduce fuel consumption. As shown in Fig. 5, the value of tan δ at 0°C of the prepared nanosilica/SSBR /BR is higher than Z-1165MP, meanwhile, the tanδ values at 60°C of RNS/SSBR/BR and DNS/SSBR/BR are lower than Z-1165MP filled vulcanizate, indicating the high wet skid resistance and low rolling resistance of the vulcanizate. It suggests that rubber filled by the nano-silica surface-modified by silane coupling agents HMDS and KH570, vulcanizate has the strongest rubber–filler interaction and reduces the filler network structure, which resulted from the uniform dispersion of silica in the rubber matrix and the strong interfacial interaction between the silica and the rubber. Thus, the silica modified by HMDS and KH570 has a high ability to reduce the rolling resistance with the maintenance of a good wet skid resistance of rubber composites. Moreover, in situ surface modification method to modified silica by HMDS and KH570 or other modifier containing organic functional groups is a good way to improve reaction activity of silica and increase the miscibility and compatibility of silica with rubber matrix, which is beneficial to enhance the overall performance of tread compound.

4. CONCLUSION

Dispersible nano-SiO₂ particles (abridged as DNS), reactive nano-SiO₂ (coded as RNS) surface-modified with silane coupling agents HMDS and KH570 and functional nano-SiO₂ (coded as DNS-SX) capped by Si69 (bis-(γ-triethoxysilylpropyl)-tetrasulfide; molecular formula: C₁₈H₄₂O₆Si₂S₄) were prepared in situ surface modification method. It has been found that these modifiers were combined to the surface of nano-SiO₂ by covalent bonds and changed the surface properties of nano-SiO₂. As-obtained nano-SiO₂ was applied to SSBR/BR in order to improve the mechanical properties wear-resisting properties and dynamic mechanics properties. Results showed that as-obtained nano-SiO₂ particles are homogenously distributed in SSBR/BR matrix. In the meantime, the comprehensive mechanical performance of SiO₂/SSBR/BR is superior to Z-1165MP /SSBR/BR. The silica modified by HMDS and KH570 has a high ability to reduce the rolling resistance with the maintenance of a good wet skid resistance of rubber composites. In our later work, we can have a try to prepare surface-modified SiO₂ with various modifiers with different organic functional groups in situ surface modification method to enlarge the application scope of silica.

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