Measurement of the Condensation Temperature of Nanosilica Powder Organically Modified by a Silane Coupling Agent and Its Effect Evaluation

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ABSTRACT: The proper condensation temperatures of nanosilica powder modified by silane coupling agents such as 3-methacryloxypropyl trimethoxy silane (MEMO), [3-(2-aminoethyl)aminopropyl] trimethoxy silane (AMMO), and bis[3-(triethoxysilyl)propyl] disulfide (TESPD) were measured with Fourier transform infrared. Moreover, the structure and properties of solution-polymerized styrene–butadiene rubber (SSBR) filled with nanosilica powder that was organically modified by the three silane coupling agents at different temperatures were investigated. The results showed that the proper condensation temperatures of nanosilica powder modified by MEMO, AMMO, and TESPD were about 80, 80, and 100°C, respectively. Compared with SSBR filled with silica powder, SSBR filled with silica powder modified by a silane coupling agent exhibited not only better filler-dispersion and mechanical properties but also lower internal friction loss in a selected range of strains. Furthermore, when the organic modification was carried out at the proper condensation temperature, the improvement of the modification effect became more obvious. Among these silane coupling agents, AMMO presented the most remarkable modification effect for nanosilica. The mechanism of modification for silica powder and its enhancement of the properties of SSBR were examined. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3038–3045, 2008

Key words: dispersions; FT-IR; modification; silicas

INTRODUCTION

With the development of modern cars with high speed, security, energy savings, and comfort, the demands for high-performance tires have increased year after year. Therefore, the tire tread should have the characteristics of good wet-skid resistance, excellent wear resistance, and low rolling loss, which are called the "magic-triangle" properties.[1] Since the 1990s, silica has been used widely in the formulas of tire treads as a reinforced filler[2–5] to balance the magic-triangle properties of tire treads.

Unlike carbon black, silica with a great number of Si—OH groups exhibits a hydrophilic nature.[6–12] Furthermore, these hydroxyl groups can form hydrogen bonds, resulting in easy aggregation of silica particles. Silane coupling agents usually are used to modify nanosilica to hinder the (re)formation of agglomerates[13] and increase the chemical adsorption or linkage between the macromolecular chains of rubber and free functional groups on the surface of organically modified silica powder.[14] The mechanical properties of composites filled with silica modified by a silane coupling agent will be enhanced.

There are two main modification methods for nanosilica using a silane coupling agent. The first is an *in situ* modification method in which a silane coupling agent is added to rubber compounds in the mixing process, and a coupling reaction between the macromolecular chains and nanosilica particles is achieved in a mixing process at a high temperature.[15–18] This is a timesaving and convenient modification method. However, its shortcoming is the nonhomogeneous distribution of the silane coupling agent in the compound, so some of the free molecules do not come into contact with nanosilica particles, and the efficiency of the coupling reaction decreases. In the other method, a diluted silane coupling agent solution is sprayed onto the surface of silica powder; after drying at room temperature, the silica powder, coated with the silane coupling agent, is put into the oven, and a condensation reaction between the alkoxy groups of the silane coupling agent and hydroxyl groups of silica takes place at a high temperature.[19–22] Then, an organically modified

silica powder can be obtained. For excellent affinity between the organically modified silica powder and rubber, the nanosilica powder can be mixed with a rubber matrix or rubber solution quickly to prepare nanosilica-reinforced composites.

Anyway, the key piece of information needed for preparing an organically modified silica powder is the condensation temperature between the functional groups of the silane coupling agent and the hydroxyl groups of silica. However, there have been few studies on this.

In this study, the reaction of silica with three kinds of silane coupling agents at different temperatures was traced with IR spectrometry. The proper condensation temperature was acquired by the determination of the abundance of the groups. Subsequently, an organically modified silica powder was prepared at the proper condensation temperature by the second method previously mentioned. The results of an extraction experiment for the organically modified silica powder demonstrated that silane coupling agents had been grafted onto the surface of the silica powder. By investigating the mechanical properties, dynamic mechanical properties, and microstructure morphology of solution-polymerized styrene–butadiene rubber (SSBR) filled with organically modified silica powder, we proved that the chosen condensation temperature was suitable.

EXPERIMENTAL

Materials and compounding

SSBR 2305 (styrene content = 25.64%, vinyl content = 34%) was produced by the Synthetic Rubber Plant of Yanshan Petrochemical Co. (Beijing, China). The precipitated silica (Tixosil 383) with an average particle diameter of 20–40 nm and specific surface area of 100–200 m^2/g came from Rhodia (Qingdao, China). 3-Methacryloxypropyl trimethoxy silane (MEMO) and [3-(2-aminoethyl)aminopropyl] trimethoxy silane (AMMO), which have the molecular formulas $CH_2C(CH_3)$ $COO(CH_2)_3Si(OCH_3)_3$ and $H_2N(CH_2)_2NH(CH_2)_3$ $Si(OCH_3)_3$, respectively, were produced by Beijing Shenda Fine Chemical Co., Ltd. (Beijing, China). Bis[3-(triethoxysilyl)propyl] disulfide (TESPD), which has the molecular formula $(C_2H_5O)_3Si(CH_2)_3S_2(CH_2)_3$ $Si(C_2H_5O)_3$, was produced by Jingzhou Jianghan Fine Chemical Co., Ltd. (Jingzhou, China). The other rubber additives, such as zinc oxide, stearic acid, and sulfur, were commercial grades.

Formulation

The formulation of the SSBR/SiO_2 nanocomposites was as follows: 100 parts SSBR 2305, 20 parts pre-cipitated silica, 4 parts zinc oxide, 1 part stearic acid, 1.5 parts polymerized 2,2,4-trimethyl-1,2-dihydroquinoline, 1.2 parts benzothiazyl disulfide, 0.6 parts diphenyl guanidine, and 1.8 parts sulfur.

The overall content of the filler was 20 phr in each composite, and the mass fractions of MEMO, AMMO, and TESPD were 7.5, 7, and 7% of the mass of the nanosilica powder, respectively.

The samples are identified as follows: 0#: SSBR filled with unmodified silica powder.

A1, A2, and A3: SSBR filled with silica powder modified by MEMO at 60, 80, and 100°C, respectively.
B1, B2, and B3: SSBR filled with silica powder modified by AMMO at 60, 80, and 100°C, respectively.
C1, C2, and C3: SSBR filled with silica powder modified by TESPD at 60, 80, and 100°C, respectively.

Measurement of the condensation temperature

The silane coupling agent was diluted with the solvent ethanol and was sprayed onto the surface of silica powder, and then homogeneous stirring was performed for an hour. When all the ethanol had evaporated at room temperature, the samples were put into an air oven to dry again at 40°C for 2 h. Afterward, the Si—OH group abundance in the silica powder was detected by the IR spectrometer with the temperature gradually elevated in steps of 10°C. The proper temperature of the condensation reaction between hydroxyl groups on the silica surface and Si—OH groups that were formed by hydrolysis of the silane coupling agent could be defined.

The condensation reaction scheme between a silane coupling agent and silica is displayed in Figure 1.
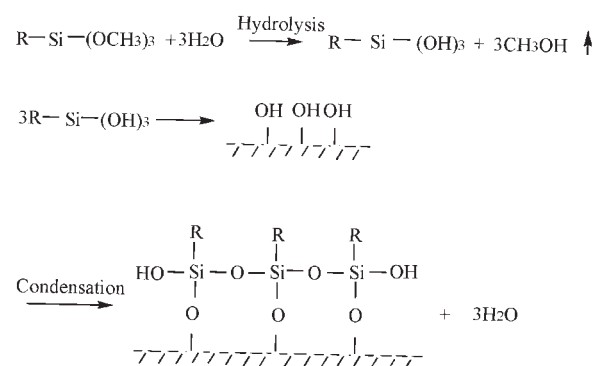
Figure 1 Condensation reaction between a silane coupling agent and silica.
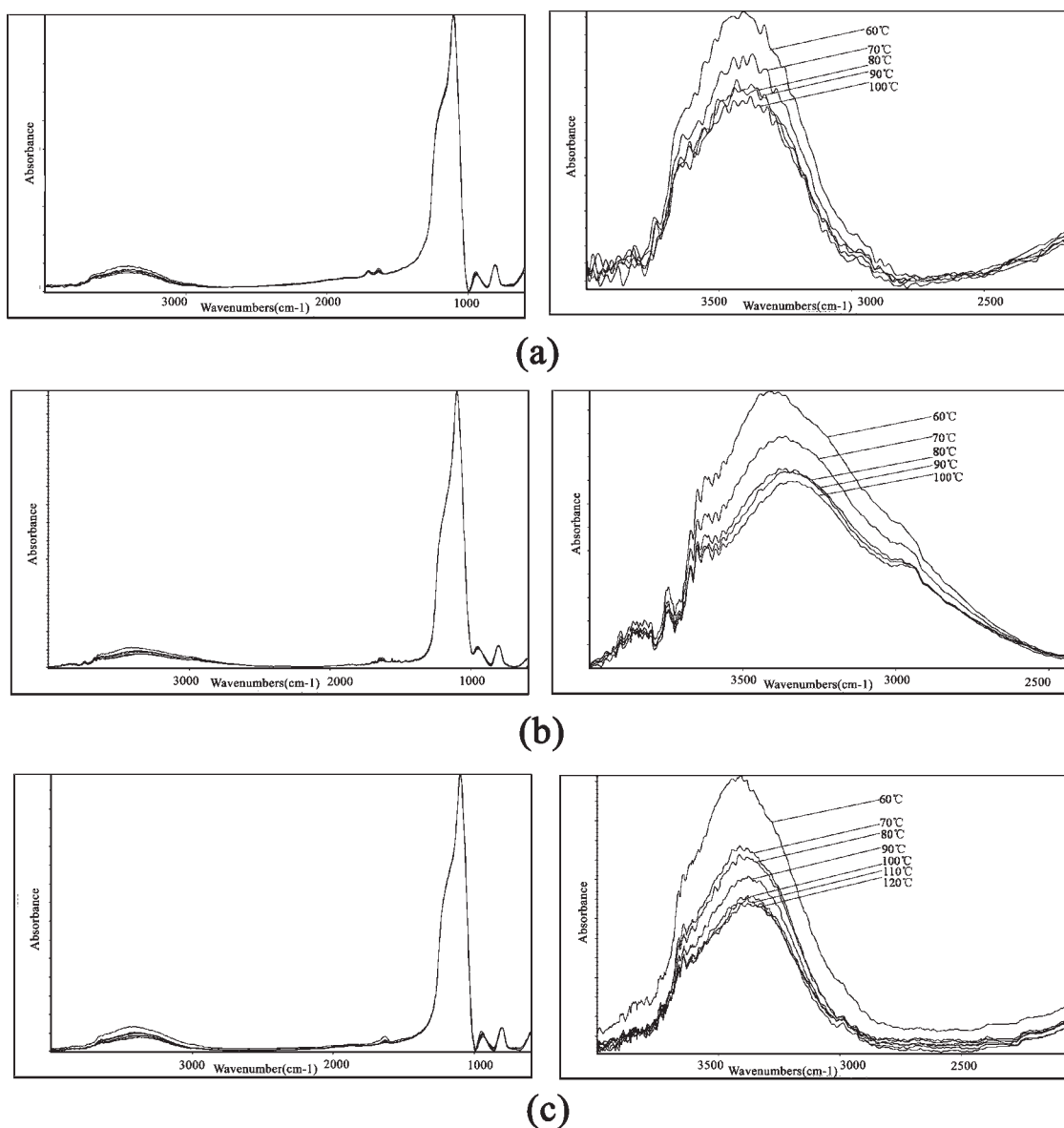
Figure 2 IR spectra of real-time detection of the reaction between silica and silane coupling agents at different temperatures: (a) MEMO, (b) AMMO, and (c) TESPD.

Preparation of the vulcanizates

The rubber compounds were prepared with a 6-in. mill (Guangdong Zhanjiang Machinery Plant, Zhangjiang, China) with the conventional mixing technique. A plate vulcanization machine (Shanghai Rubber Machinery Works, Shanghai, China) was used to prepare the vulcanizates, and the curing condition was $150°C \times$ (curing time) t_{90}.

Instruments and techniques

Samples were extracted in a Soxhlet continuous extractor (Beijing Huake Bomex Glass Co., Ltd, Beijing, China) at 80°C for 48 h, and the solvent was ethanol.

Transmission electron microscopy (TEM) observations were performed on an H-800-1 transmission electron microscope (Hitachi Corporation, Tokyo, Japan) with an acceleration voltage of 200 kV.

The mechanical properties of all vulcanizates were measured at $25 \pm 2°C$ according to ASTM D 638 with a CMT4104 electrical tensile tester (SANS, Shenzhen, China) at a tensile rate of 500 mm/min. The Shore A hardness of the vulcanizates was measured with a rubber hardness apparatus made by the 4th Chemical Industry Machine Factory (Shanghai, China).

Strain-sweep experiments were performed with an RPA 2000 rubber process analyzer (Alpha Technologies Co.) at the frequency of 1 Hz and at 60°C for the vulcanizates. The strain was varied from 0.28 to 100%.

TABLE I
Relative Peak Area Values of the Si—OH Group of Silica Coated with Silane Coupling Agents at Different Temperatures from FTIR

Compound	Temperature						
	60	70	80	90	100	110	120
A	1	0.865	0.719	0.711	0.686	—	—
B	1	0.815	0.698	0.685	0.654	—	—
C	1	0.866	0.851	0.736	0.668	0.656	0.640

A = relative peak area of the Si—OH group of MEMO-modified silica; B = relative peak area of the Si—OH group of AMMO-modified silica; C = relative peak area of the Si—OH group of TESPD-modified silica.

IR spectra were taken with an Avatar 360 IR spectrometer (Thermo Nicolet Corporation, Madison, WI). The samples were pressed into pellets with KBr. This instrument had ZnSe windows, a spectral range of 7400–375 cm^{-1}, and a resolution better than 0.9 cm^{-1}.

RESULTS AND DISCUSSION

### Fourier transform infrared (FTIR) analysis

FTIR spectra for the reaction progress of silica with MEMO, AMMO, and TESPD at different temperatures are shown in Figure 2.

As shown clearly in Figure 2, there is a great similarity of peak positions in all the samples. The vibration peak of the Si—OH group is around 3600–3000 cm^{-1}. The peak area of the samples in this zone decreases with the reaction temperature increasing. According to the reaction equation depicted in the Experimental section, the reduction of this peak area corresponding to the Si—OH group is able to well detect the degree of the condensation reaction between the alkoxy groups of the silane coupling agent and hydroxyl groups of the silica particles.[23–28]

From the FTIR spectra, the relative peak area values of the Si—OH group of silica organically modified by silane coupling agents at different temperatures are listed in Table I. The relative peak area value is defined as the ratio of the peak area of the Si—OH group at each temperature to the peak area of the group at 60°C.

Table I shows that the peak area of the Si—OH group of silica powder coated by MEMO or AMMO remains nearly constant above 80°C, and the peak area of the Si—OH group of silica powder coated by TESPD remains almost unchangeable above 100°C. These results show that the graft reaction between the silane coupling agent and silica is sufficient above those temperatures. Therefore, the suitable graft temperatures of silica powder organically modified by MEMO, AMMO, and TESPD are about 80, 80, and 100°C, respectively.

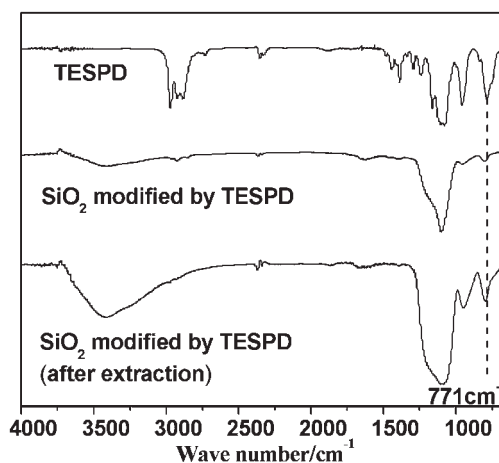Silica powder modified by a silane coupling agent at the proper graft temperature (MSiO$_2$) was extracted by ethanol for 48 h. Then, the FTIR spectra
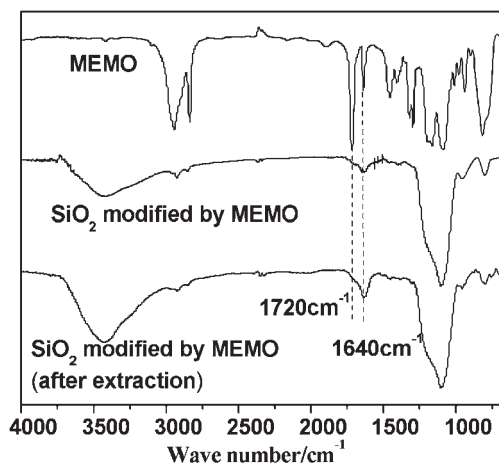
(a)
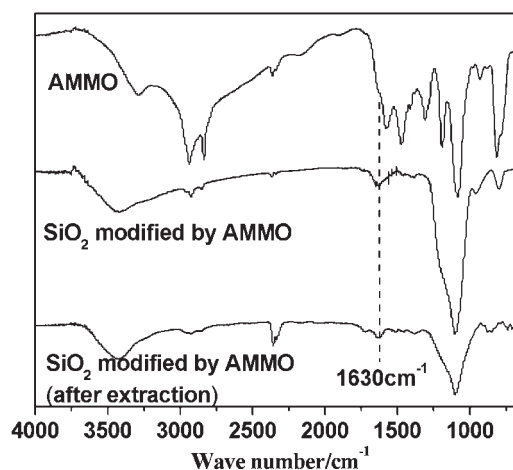
(b)

(c)

Figure 3 IR spectra of silica modified by silane coupling agents: (a) MEMO, (b) AMMO, and (c) TESPD.

TABLE II
Mechanical Properties of SSBR Filled with Silica Modified by Silane Coupling Agents at Different Temperatures

No.	t_{10} (min)	t_{90} (min)	Hardness	Modulus at 300% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Permanent set (%)	Tear strength (kN m^{-1})
0#	7 : 54	47 : 53	61	3.0	7.1	629	14	22.9
A1	10 : 40	18 : 29	59	3.3	8.7	489	8	27.9
A2	10 : 35	21 : 25	59	3.6	10.3	542	8	30.9
A3	11 : 41	21 : 23	59	3.4	9.6	580	12	29.0
B1	1 : 54	14 : 50	58	4.3	14.2	515	12	30.5
B2	2 : 04	19 : 38	58	4.6	15.8	551	12	32.8
B3	2 : 20	15 : 41	59	3.9	14.8	530	12	31.6
C1	8 : 58	19 : 32	61	3.7	9.5	476	10	25.3
C2	11 : 05	23 : 43	61	4.9	10.9	505	10	28.8
C3	11 : 17	21 : 46	61	4.6	9.8	415	10	26.5

t_{10}, scorch time; t_{90}, curing time.

of MSiO$_2$ and its FTIR spectra after extraction, together with the FTIR spectra of the corresponding silane coupling agents, are shown in Figure 3.

Figure 3(a) shows that peaks of the characteristic functional groups of MEMO, such as the carbonyl group and C=C bond, appear at 1700–1730 and 1620–1650 cm^{-1} (with partial overlapping between them), respectively. These two characteristic peaks still exist in the FTIR spectra of MSiO$_2$ extracted by ethanol. In Figure 3(b), the peak of the functional group of AMMO, namely, the amino group, appears at 1600–1650 cm^{-1}, and it becomes obvious in the FTIR spectra of MSiO$_2$ extracted by ethanol. Similarly, in Figure 3(c), the peak of the characteristic functional group of TESPD, namely, the —CH$_2$—S— group, appears at 740–780 cm^{-1}, and in the FTIR spectra of MSiO$_2$ extracted by ethanol, the peak width decreases and the peak position remains fixed. All these results indicate that the silane coupling agent has been grafted onto the surface of the silica particles.
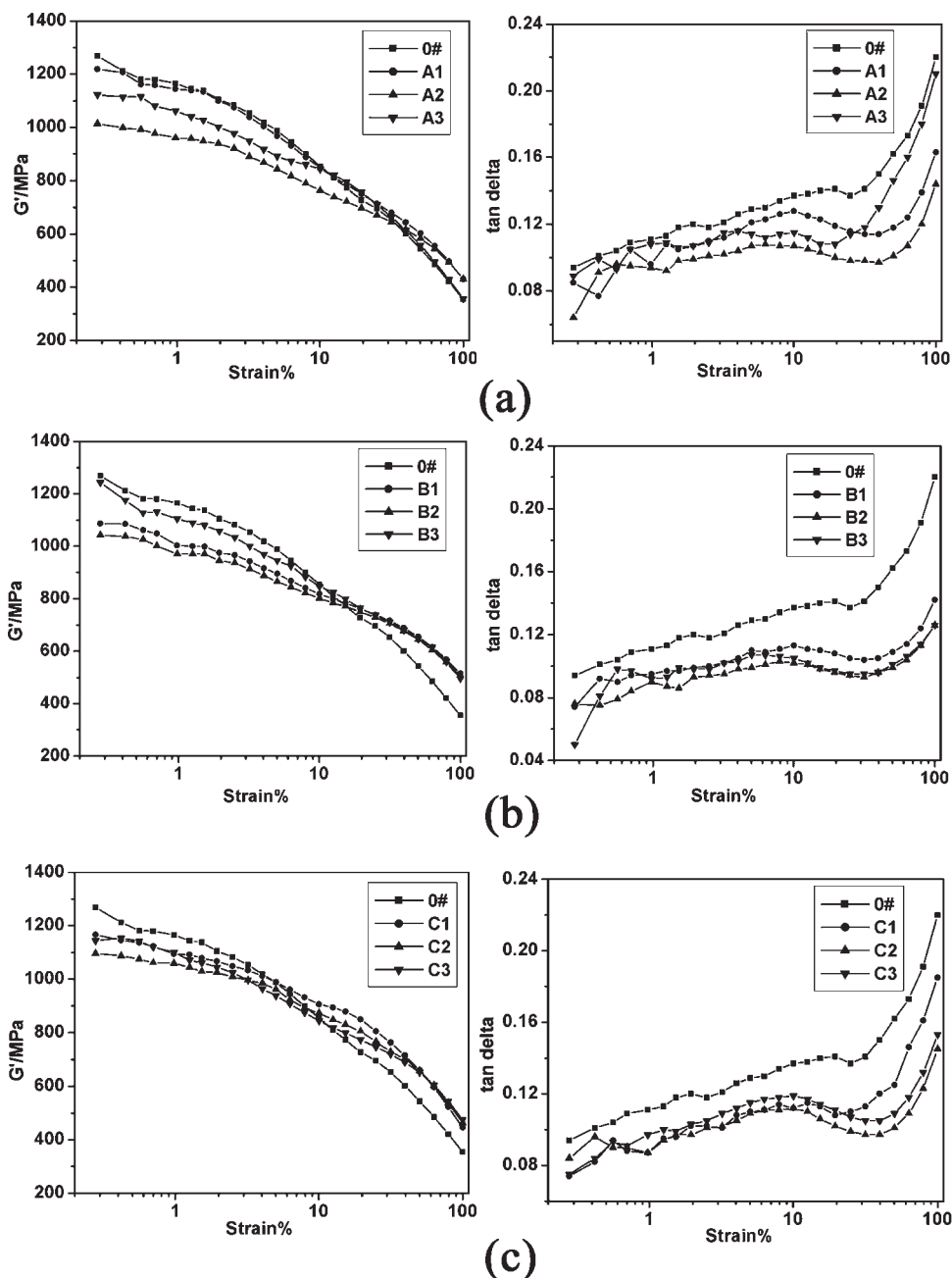
Mechanical properties

The mechanical properties of SSBR filled with nanosilica powder modified by the three silane coupling agents at different temperatures are shown in Table II.

As shown in Table II, compared with that of SSBR filled with unmodified silica powder, the scorch times of SSBR filled with silica powder modified by MEMO or TESPD are both longer, and that of SSBR filled with silica powder modified by AMMO is shorter. This indicates that the amino group in the silane coupling agent can accelerate the vulcanization. SSBR filled with organically modified silica powder exhibits a shorter curing time. This result shows that the silane coupling agent can increase the curing rate of the rubber compound. As also shown in this table, the hardness, tensile strength, tear strength, modulus at 300%, and permanent set of SSBR filled with organically modified silica powder are all improved.

The addition of modified silica to SSBR can improve its properties. This can be ascribed to two factors. First, its alkoxy group reacts with the hydroxyl group on the surface of silica to improve hydrophobicity and decrease aggregation. Second, the filler–rubber interaction is able to be further improved only if the characteristic functional group on the filler surface adsorbs or links with macromolecular chains. It should be pointed out that these three silane coupling agents all can react with silica particles. Among these silane coupling agents, the modification effect of AMMO is the best. This is because the two nitrogen atoms of AMMO grafted onto the surface of silica[29] have two lone pairs of electrons and they show large delocalization; thus, the hydrogen bond is formed between the lone pair of electrons and SSBR. Macromolecular chains are adsorbed onto the surface of silica particles modified by AMMO and can slide on it. Moreover, their full orientation is generated in the tensile process, so the tensile strength of SSBR filled with silica modified by AMMO is higher. However, for the chemical bond formed between macromolecular chains and the silica particles modified by MEMO or TESPD, macromolecular chains cannot generate complete orientation in the tensile process. SSBR filled with silica modified by TESPD presents lower tensile strength but higher modulus at 300%, which is the contribution of the sulfur atom of TESPD. Because the C=C bond located in an isolated position of MEMO has low reactive activity, the modulus at 300% of SSBR filled with silica modified by MEMO is lower than that of SSBR filled with silica modified by TESPD. Furthermore, because sulfur is used for the curing system, it is hard for this C=C bond to form a sufficiently crosslinked network with macromolecular chains.

Among SSBR samples filled with silica powder modified by MEMO and AMMO, A2 and B2 have excellent mechanical properties. This indicates that it is feasible that these two kinds of silane coupling

Figure 4 G'(storage modulus)/strain and tan δ/strain curves of SSBR filled with silica modified by (a) MEMO, (b) AMMO, and (c) TESPD at different temperatures.

agents graft onto silica powder when the heat treatment is at about 80°C, which contributes to good mechanical properties of the composites. Similarly, in Table II, C2 (SSBR filled with silica powder modified by TESPD at 100°C) also displays good mechanical properties. These facts indicate that the silane coupling agent has high reactivity with silica powder at the proper temperature, and this improves the organization degree of the inorganic filler and results in good reinforcement of the composites. These results are in accordance with the previous conclusion.

Dynamic mechanical properties

The dynamic mechanical properties of SSBR filled with nanosilica powder modified by the three silane coupling agents at different temperatures are shown in Figure 4.

As can be seen in Figure 4, SSBR filled with organically modified silica powder has a lower $\Delta G'$ value (i.e., a lower Payne effect) which is defined as the drop in storage modulus, than SSBR filled with unmodified silica powder. The Payne effect can be a measurement of the three-dimensional network
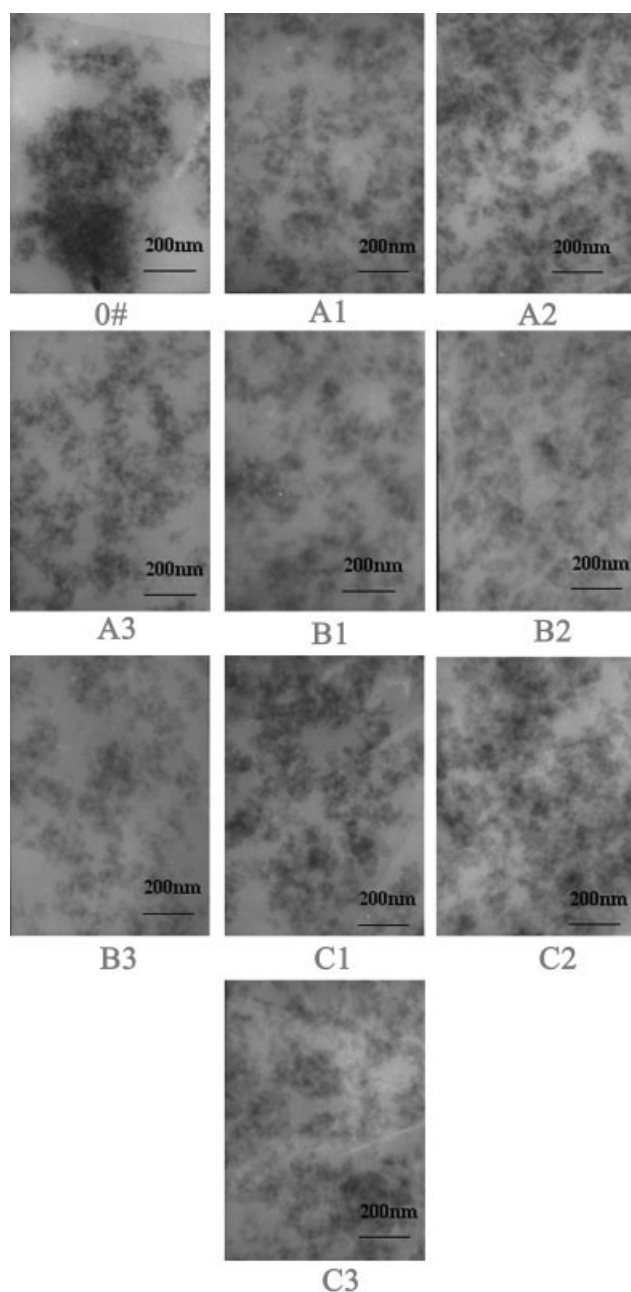
Figure 5 TEM observations of vulcanizates.

structure construction for the filler–filler interaction and polymer–filler interaction. A lower Payne effect manifests a stronger polymer–filler interaction, better dispersion, and lower internal friction loss between the filler and polymer.

A2, B2, and C2 have the lowest $\Delta G'$ values of the corresponding composites. This shows that nanosilica powder organically modified at the proper temperature dispersed well in the SSBR matrix. A2, B2, and C2 show the lowest internal friction loss factor (tan δ), and this indicates that stronger polymer–filler interactions exist in these composites.

Microstructure of the composites

In Figure 5, the light part is the rubber matrix, and the dark part is silica particles that have formed in a continuous network structure. It can be seen that organically modified silica particles with a spherical shape dispersed in the SSBR matrix homogeneously. The particle size has a narrow distribution and ranges from 20 to 30 nm. From the photograph of 0#, SSBR filled with unmodified silica presents poor filler–polymer interactions, and many silica particles aggregate severely in the rubber matrix. The aforementioned results indicate that adding a silane coupling agent as a molecular bridge, which connects the interface between the inorganic particle and organic matrix, can decrease the aggregation of silica particles and improve their dispersion in the matrix. Compared with other composites, A2, B2, and C2 have more homogeneous filler dispersions, smaller particle sizes, and fewer aggregates. Furthermore, a strong interfacial interaction between the filler and matrix leads to excellent dispersion in these samples, which exhibit almost the same space intervals among particles. In these three composites, silica particles organically modified by a silane coupling agent firmly connect with and homogeneously dispersed around the macromolecular chains by their stronger interfacial interaction. This shows that silica organically modified by a silane coupling agent at the proper temperature can provide high reinforcement and low heat buildup for SSBR.

In summary, silica powder modified at the appropriate temperature can strengthen the interaction with the matrix to remarkably improve the dispersion and homogeneity of nanosilica particles in the SSBR matrix and enhance the mechanical properties and dynamic mechanical properties of composites. All the aforementioned results testify to the correctness of the previous conclusion from FTIR.

CONCLUSIONS

1. Tracking the change in the characteristic peak area of Si—OH at different temperatures in FTIR can detect the reaction process and organic modification degree of silica powder with a silane coupling agent. The proper temperatures of MEMO, AMMO, and TESPD grafted onto silica powder are about 80, 80, and 100°C, respectively.
2. The hardness, tensile strength, tear strength, modulus at 300%, and permanent set of SSBR filled with silica powder organically modified at the proper temperature are obviously superior to those of SSBR filled with unmodified silica powder and SSBR filled with silica powder organically modified at another temperature.

SSBR filled with silica powder organically modified by AMMO exhibits excellent mechanical properties.

3. SSBR filled with silica powder organically modified at the proper temperature exhibits lower values of tan δ and $\Delta G'$ in the strain range of 0.28–100%, and this shows that these composites display a lower internal friction loss and Payne effect.

4. Silica powder organically modified at the proper temperature can be well and homogeneously dispersed in the SSBR matrix. The particle size of silica ranges from 20 to 30 nm. This indicates that completely organic modification of silica powder can improve the compatibility and reactivity between the silica powder and rubber matrix.

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