

Some Interesting Phenomena in Silica-Filled HNBR with the Addition of Silane Coupling Agent

Xin Ye, Miao Tian, Li-Qun Zhang

Key Laboratory for Nanomaterials of Ministry of Education, Key Laboratory of Beijing City for Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China

Received 16 March 2010; accepted 1 June 2011

DOI 10.1002/app.35024

Published online 11 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Hydrogenated nitrile rubber (HNBR)/silica nanocomposites were prepared by *in-situ* modification dispersion technology, and the silane coupling agent γ -methacryloxypropyl trimethoxy silane (KH570) was chosen to promote the interfacial strength between silica particles and HNBR matrix and further improve the dispersion of silica particles. Rubber Process Analyzer (RPA2000) was used to test the Payne effect of HNBR/silica compounds, from which some interesting phenomena were found: the Payne effect became stronger after KH570 was added to HNBR/silica compound at room temperature, which was a contrary result compared to SBR/silica system. However, after stored for a month at room temperature, the Payne effect weakened, which was contrary to the traditional phenomenon of storage hardening of filled rubber. All these results

are related to filler–filler interaction and filler–rubber interaction. The modulus at small strain amplitude of HNBR/silica compound with KH570 gradually decreased with the increase of times of circulatory strain sweep but that of compound without KH570 had almost no change, which was explained by Fourier Transform Infrared (FTIR) results that the reaction between silica and KH570 almost completed at the test condition: 80°C and about 1 h. The effects of silane amount, heat-treated temperature and time on the Payne effect of compounds and the mechanical properties of vulcanizates were also investigated. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 927–934, 2012

Key words: hydrogenated nitrile rubber (HNBR); silicas; dispersions; interfaces

INTRODUCTION

Prepared by controlled, selective catalytic hydrogenation of the butadiene units in NBR,^{1–3} Hydrogenated nitrile rubber (HNBR) is such a special elastomer because of possessing highly saturated structure and many polar groups. It also can be defined as an elastomer combining the oil and fuel resistance of NBR with the heat and oxidation resistance of EPDM.⁴ However, to achieve better properties to satisfy the increasing requirements of the automotive, aerospace, and other industries for extremely high operating temperature and extended material service lifetime, HNBR has to be modified. And in most cases, HNBR was used by blending with other elastomers such as FKM,^{5,6} IR,⁷ NR,⁸ Nylon6,^{9,10} and so on. At the same time some fillers like ZDMA,¹¹ OMMT,^{12,13} MWCNT,^{6,14} were also incorporated to improve the properties, And yet HNBR filled with silica is few researched.

Nanoparticles have been demonstrated to reinforce rubber better than microparticles. Many researches^{15–18} have pointed out that the particle size

of reinforcing agents is the first factor for their reinforcing capability, and nano-reinforcement is very necessary and essential for high reinforcement. Accordingly, nano-dispersion of nanofillers in rubber matrix is of utmost importance to realize their nano-reinforcement effect, although it is a challenge to achieve excellent nano-dispersion because of the high surface energy of the fillers with nano-size.

Silica, a kind of important nanofillers for rubber, has been used to obtain highly reinforced rubber composites for many years. Nowadays, the use of nanosilica has the trend to gradually replace carbon black for the following reasons: first, the production of silica is independent of fossil-fuel like coal and petroleum; second, silica has been used widely in the formulas of tire treads as a reinforced filler^{19,20} to balance the “magic-triangle” properties (good wet-skid resistance, excellent wear resistance, and low rolling loss) of tire treads to get “green tire”; third, unlike carbon black, the surface of silica is modifiable because of a great number of silanol groups on its surface, which not only have helped to improve the filler dispersion but also can form chemical interface between filler and rubber just meeting the performance requirement of HNBR products applied to high temperature field. However, the great number of silanol groups make silica surface very polar, which leads to its incompatibility with nonpolar elastomers such as SBR, NR, and BR and poor

Correspondence to: L.-Q. Zhang (Zhanglq@mail.buct.edu.cn).

dispersibility in them. Interestingly, the existence of hydrogen bonding between nitrile groups in NBR and silanol groups on silica surface was found.²¹ And by introducing NBR to silica filled SBR compounds, Choi²² observed an improved dispersion of silica fillers. On the basis of these results, we can conclude that hydrogen bonding interactions between nitrile groups in HNBR and silanol groups on silica surface might be beneficial to promote the dispersion of silica in HNBR. But unfortunately, although the existence of hydrogen bond makes the interaction between silica and polar rubber HNBR improve, it is still weaker than the interaction between carbon black and hydrocarbon rubber,²³ so nanosilica still needs to be organically modified to enhance its interaction with HNBR and further improve its dispersion.

In this article, we are interested in the affinity between silica particles and HNBR matrix as well as the influence of surface modification of silica on the filler dispersion and some interesting phenomena were found. *In-situ* modification dispersion technology,²⁴ which is a convenient and economical method for filler dispersion: namely the coupling agents are added during the process of blending filler with rubber at a high temperature, was adopted to modify the surface of silica and improve filler dispersion. The principle is that the filler surface modification and the dispersion can be achieved at the same time because of the high process temperature and the high shear stress. Thus, the technological parameters such as process temperature, mixing time, and the modifier content are the important influence factors on the reaction between filler and modifier, as well as the efficiency of filler surface organically modification and the filler dispersion. In this work, we have mainly focused on the influences of the silane coupling agent amount, the temperature, and the time of heat treatment on the micro-dispersion of silica particles in HNBR by characterizing their "Payne effect" using Rubber Process Analyzer (RPA2000) and the mechanical properties of the composites.

EXPERIMENTAL

Raw materials

The samples in this work were made of silica particles (HI-sil 255N, Jiangxi Nanji Chemical Technology Plant, China)-filled Hydrogenated nitrile rubber (HNBR) matrix with 36% acrylonitrile content (Zetpol 2010L, Zeon, Japan). The silane coupling agents used to modify the silica surface are γ -aminopropyl triethoxy silane (KH550), γ -glycidoxypropyl trimethoxy silane (KH560), and γ -methacryloxypropyl trimethoxy silane (KH570), which have the molecular

TABLE I
Formulation (phr^a)

Ingredients	Content (phr)
HNBR 2010L	100
Silica	60
Silane coupling agent (KH550, KH560, KH570)	Variable ^b
Antioxidant 1010 ^c	1
Zinc carbonate	1
Stearic acid	0.5
2,2,4-trimethyl-1,2-dihydroquinoline	1
<i>N</i> -isopropyl <i>N'</i> -phenyl 1,4-phenylenediamine	1
Plasticizer (santicizer261: santicizer438 = 1 : 1)	5
Curing agent [brominated phenolic resin (Resin-201)]	15

^a phr is the abbreviation of weight parts per 100 weight parts rubber.

^b 6 phr was chosen when other condition changed.

^c Tetra-[methylene- β -(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate] methane.

formulas $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$, $\text{OCH}_2\text{CHCH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{CH}_2\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, respectively, purchased from Nanjing Shuguang Chemical Group. To improve the heat resistance performance of the vulcanizates, brominated phenolic resin (Resin-201) produced by Shanxi provincial institute of chemical industry was used as curing agent to replace traditional sulfur and peroxide. The other rubber additives, such as zinc oxide, stearic acid, were commercial grades. The formulation is given in Table I.

Preparation of samples

Mixing was carried out on a two-roll mill. First, HNBR, silica, silane, and antioxidant1010 were mixed uniformly on a two-roll mill at room temperature to get the compounds. Then, the compounds were compounded on a two-roll mill at 150°C for different time (ranging from 1 to 10 min) or at different temperature from room temperature to 150°C for 5 min, which is defined as *in-situ* modification dispersion process called heat treatment in following discussion. For comparison, silica-filled HNBR without KH570 was also prepared. Other additives were blended into the compounds on two-roll mill at room temperature after the heat-treated compounds cooled down. Prior to measuring the mechanical properties of the composites, the filled rubbers were vulcanized at 160°C \times t90.

Characterization

Cure characteristics were determined at 150°C with a P3555B2 oscillating disk rheometer (Beijing Huangfeng Chemical Machinery Trial Plant, Beijing,

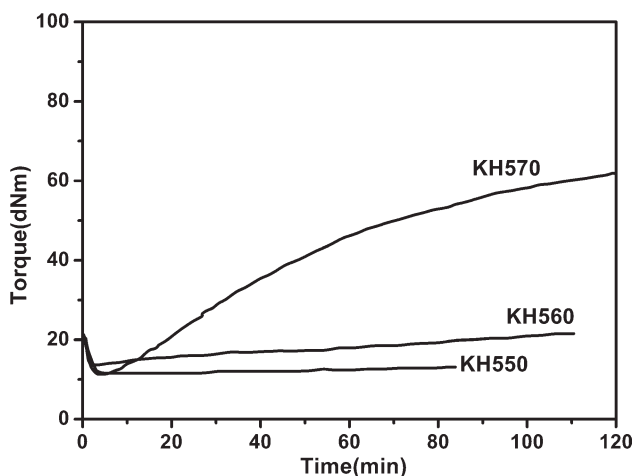


Figure 1 The influence of different kinds of silane coupling agents on the cure characteristics of HNBR/silica compound.

China). The strain dependence of dynamic storage modulus G' of the compounds (Payne effect) were measured by a Rubber Process Analyzer (RPA2000, Alpha Technological). Strain sweep from 0.28 to 400% were tested at 80°C, 1 Hz. Fourier transform infrared spectroscopic (FTIR) measurement in transmission mode was used to investigate the possible chemical reaction between KH570 and silica at 80°C. The sample for FT-IR test is the mixture of KH570 and silica (1 : 10 by weight) pressed with KBr powder. Six times sweeps were carried out, after every sweep, the sample was taken out and heated at 80°C for some time for next sweep, which could avoid the influence of sample amount on the transmittance. They were performed at a resolution of 4 cm^{-1} by using a Nicolet ul3101-1 spectrometer (Nicolet, America). Field Emission-Scanning electron microscopy (SEM, JSM-6301F FEG) was used to observe the cryo-fracture surface of silica filled HNBR compounds (unvulcanized and without other ingredients). SEM photomicrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 10 kV. The mechanical behavior of the nanocomposites were characterized at 23°C by means of tensile tests according to ASTM D638 using a CMT4104 electrical tensile tester (SANS, ShenZhen, China). The Shore A hardness of the vulcanizates was measured with a rubber hardness apparatus made by the 4th Chemical Industry Machine Factory (Shanghai, China).

RESULTS AND DISCUSSION

The selection of silane coupling agent

Silane coupling agents are always used to decrease the strong filler–filler interactions and increase the filler–rubber interactions. Alkoxy groups at one end

of silane molecules always react with silanol on the surface of silica to form siloxane bonds and the other end of silane molecules bonded to the silica surface always adsorb on or react with rubber molecules, then crosslinks between silica particles and polymer chains through the silane molecules are formed. In addition, silane coupling agents always prevent the adsorption of curatives on the silica surface and affect the vulcanization characteristic of silica filled rubber.

In this work, three different kinds of silane coupling agents were used. The vulcanization characteristic curves are showed in Figure 1. It can be seen that only the torque of the compound with KH570 increased and the other two compounds with KH560 and KH550 have nearly zero delta torque, which means that silanes KH560 and KH550 prevent the compounds from crosslinking but only KH570 is harmless to compounds crosslink. With further considering about the existence of polarity interactions between ester groups in KH570 and nitrile groups in HNBR and the possibility of the reaction between the double bonds in KH570 and rubber when the compounds were cured, both of which can promote the interaction between silica and rubber, KH570 was chosen for the following study.

Introduction of KH570 at room temperature

Silica and KH570 (10 : 1 by weight) were divided into three parts respectively and were introduced into HNBR alternately on a two-roll mill at room temperature. The strain dependence of storage modulus (G') of the compounds with and without KH570 is lined in Figure 2 with solid dots. It is found that the value of G' of the compound with KH570 is higher than that without KH570, which means that HNBR/silica compound with the

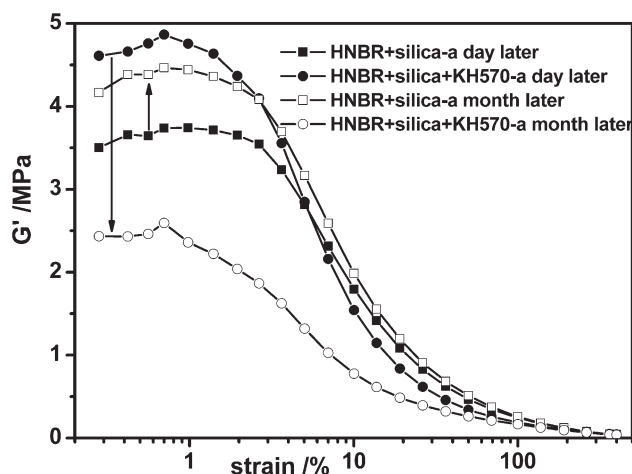


Figure 2 Strain dependence of G' at 80°C and 1 Hz for HNBR/Silica compounds with or without KH570 after a month storage and compare with before.

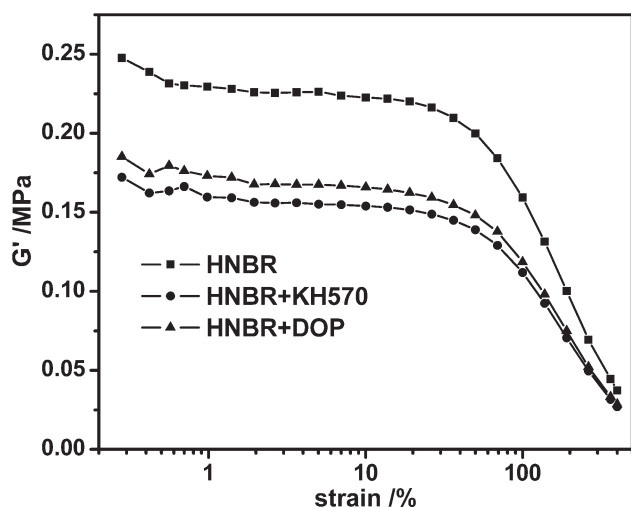


Figure 3 Strain dependence of G' at 80°C and 1 Hz for HNBR, HNBR with KH570 and with DOP for comparison.

bifunctional silane coupling agent KH570 has stronger Payne effect, stronger filler network and worse filler micro-dispersion. This phenomenon is opposite to the usual result that the filler network always gets weak after the introduction of coupling agent in silica filled SBR system.²⁵ It is well known that silane coupling agents are always used to decrease silica surface energy and increase its dispersion to get lower Payne effect. Then, why this abnormal phenomenon happened? The first reason is supposed to the plastication effect of KH570 on HNBR. To prove it, DOP, extensively used as the plasticizer of polar rubber, was chosen and added into HNBR with the same content as KH570 for comparison (Fig. 3). It can be seen that the addition of KH570 leads to the decrease of the modulus of HNBR the same as DOP does, which prove the existence of the plasticization effect of KH570 on HNBR. In other words, the polar interactions between the ester groups in KH570 molecules and the nitrile groups the only polar groups in HNBR chains expand the space among the rubber chains and make the viscosity lower, which lower the positive effect of the shear stress on the dispersion of silica particles during mixing process. Another reason we can conclude is described as follows: the polar interaction between the ester groups in KH570 molecules and nitrile groups in HNBR might be easier to form than the hydrogen bonds between silanol groups in silica and nitrile groups in HNBR, because KH570 is a kind of molecules with low molecular weight and might be easier to move than silica particles, for this reason, the amount of nitrile groups acting with silanol groups on silica surface decreases and the total interactions between filler and rubber decreases because the siloxane groups in KH570 have not reacted with

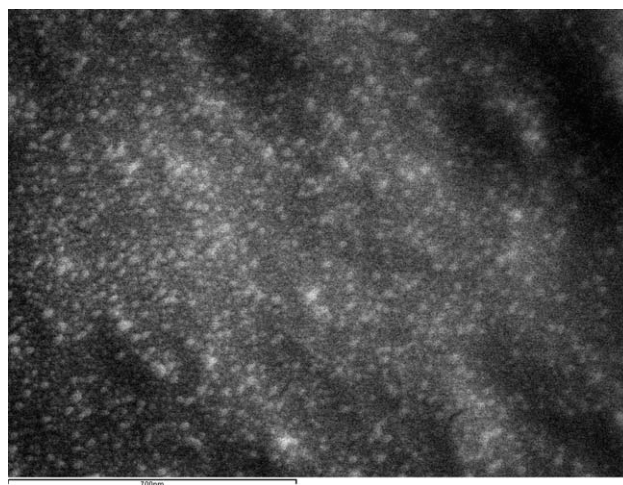


Figure 4 SEM photograph of the surface of HNBR/silica compound.

silanol groups in silica at this time, so the silica network gets stronger and the G' value increases.

After storage at room temperature for a month, the G' values of the compounds with and without KH570 at small strain amplitude shown in Figure 2 with hollow dots change differently. The G' value of the compound without KH570 increases, which can be explained by the traditional storage hardening phenomenon²⁶ that filler will agglomerate to form filler network in storage period resulting in stronger Payne effect. During the storage time, as the interaction between silanol groups in silica surface is stronger than that between nitrile groups and silanol groups concluded from electronegativity order of oxygen atom and nitrogen atom, silica particles reagglomerated and Payne effect of the compound became stronger. However, the G' value of HNBR/silica compound with KH570 did not increase but decrease more than 2 MPa, that is to say, silica

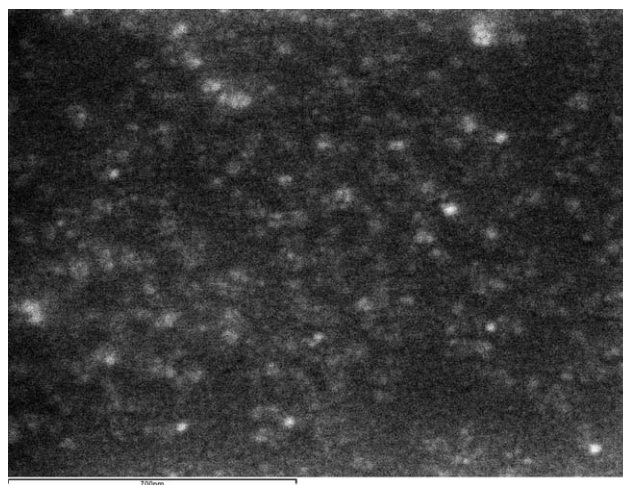


Figure 5 SEM photograph of the surface of HNBR/silica compound with KH570.

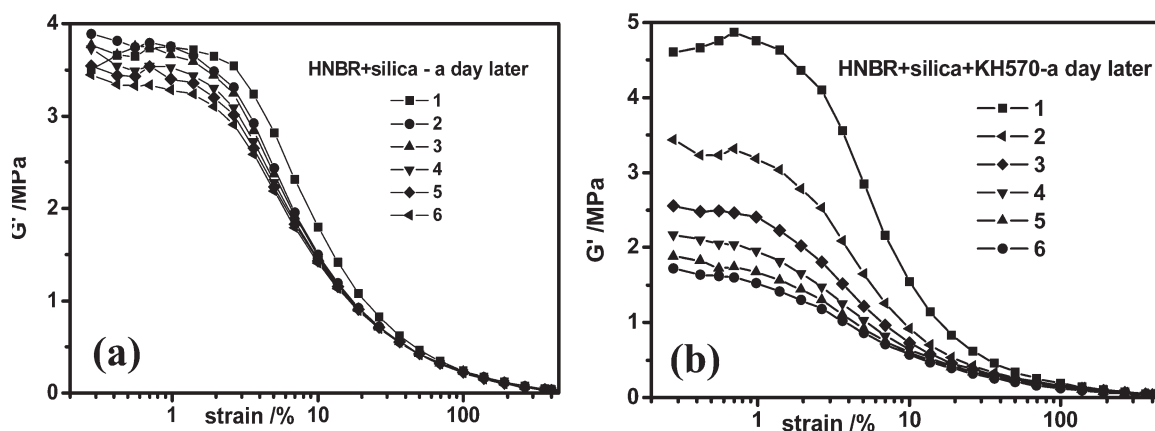


Figure 6 Circularly strain sweeps of HNBR/Silica compounds without (a) or with (b) KH570 for six times at 80°C and 1 Hz.

particles in HNBR with KH570 did not reaggregate but dispersed better. This strange phenomenon could be explained by two imaginable reasons. First, the higher modulus of compound with KH570 means higher viscosity which is good for keeping silica particles from reaggregating. Second, as literature²⁷ said, KH570 can be grafted onto silica nanoparticles for a long time (48 h) at room temperature, which lead to organically modified silica surface, thus the difference of surface energy between silica and HNBR decreases and the micro-dispersion of silica gets better.

In view of these results, it is presumed that the HNBR/silica compound without KH570 having lower modulus possesses more filler-polymer interaction because of the existence of the interaction between silanol groups and nitrile groups. But during the storage time, silica particles reaggregate under the derive force of the stronger hydrogen bond interaction between silanol groups resulting in more filler-filler interaction and the increase of modulus. On the contrary, for the compound with

KH570, the interaction between ester groups in KH570 and nitrile groups competes against that between silanol groups in silica and nitrile groups when silica and KH570 are added alternately at room temperature on a two-roll mill and obviously the former is the dominating one. As a result, the KH570 molecules are prior to be adsorbed on rubber chains leading to lower matrix viscosity and lower total interactions between nitrile groups and silanol groups, then more filler-filler interactions exist in the compound with KH570 at the end of the first mixing stage. During storage at the room temperature for a month, KH570 molecules react with silica and polymer chains adsorb on the surface of organically modified silica particles, thus more filler-polymer interactions generate which is responsible for the decrease of modulus.

The SEM micrographs of the HNBR/silica compounds without and with KH570 are shown in Figures 4 and 5, respectively. The light-colored areas represent for the silica particles and the dark bases for the rubber matrices. From Figure 4, it can be

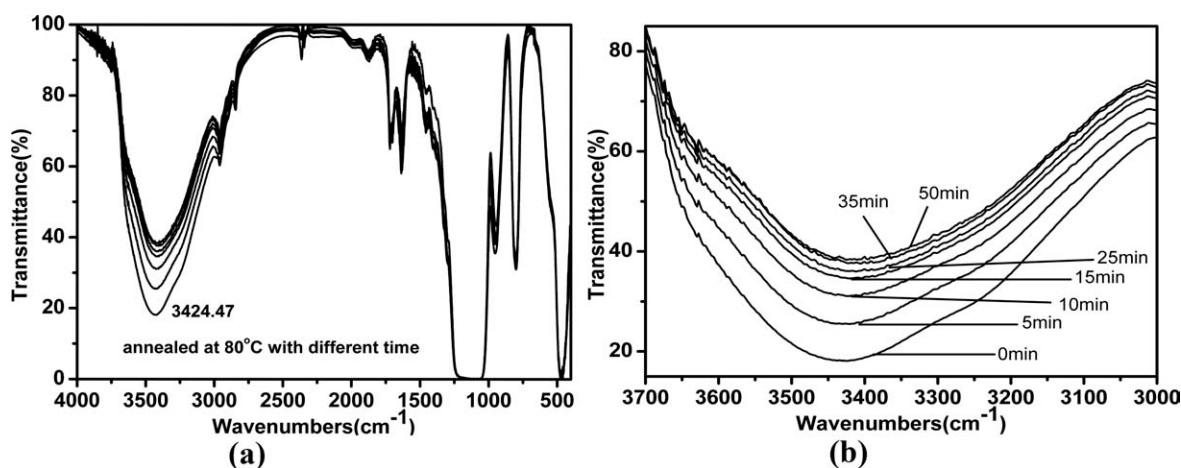


Figure 7 The FTIR result of Silica/KH570 mixture heat at 80°C with different time.

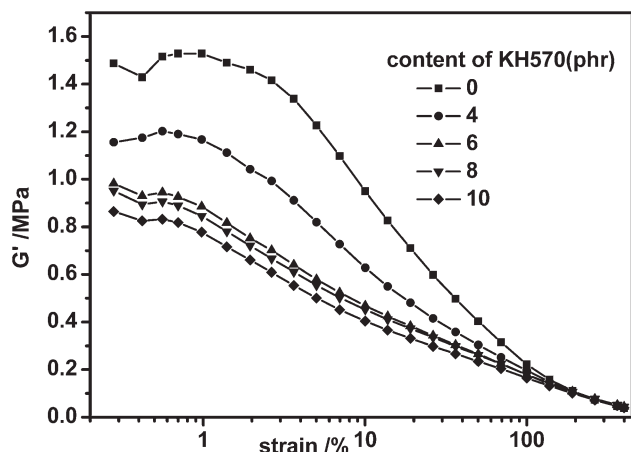


Figure 8 Strain dependence of G' at 80°C and 1 Hz for HNBR/Silica compounds with different KH570 content and heat-treated at 150°C for 5 min.

seen that the silica particles in HNBR without KH570 disperse finely and homogeneously, i.e., the silica particles almost dispersed as single particles and separated by matrix rubber, as said before, more filler-polymer interaction existed. Silica aggregates contained three or more silica particles are found in Figure 5, which demonstrate the worse filler dispersion in HNBR/silica compound with KH570 and more filler-filler interaction existed.

The reaction between KH570 and silica at RPA test temperature

According to the previous section results, It looks like that the introduction of KH570 is useless for the better dispersion of silica particles in HNBR matrix within a short time, but another strange phenomenon was found when HNBR/silica compounds with or without KH570 mixed at room temperature were tested in strain sweep mode at 80°C repeatedly for six times with 2-min intervals and the samples remain in the test cavity under pressure. The strain amplitude dependence of modulus of the compounds without and with KH570 are illustrated in Figure 6(a,b), respectively. The results appear that the storage modulus of compound with KH570 at low deformation decrease drastically but the ones without KH570 don't change so clearly. Considering

the testing temperature, time and the reaction kinetics of KH570 with silica, Silica/KH570 mixtures heated at 80°C with different time were made for FTIR test and the results are shown in Figure 7. It can be seen from the picture that the peaks intensity at the wave number 3424.47 cm^{-1} represented for silanol groups on the silica surface decrease with increase of heating time. As said in Characterization section, the samples for six sweeps were the same ones which mean the constituents and content of samples did not change, so the strength of the peak directly reflects the content of silanol groups on silica surface. The strength of peaks at 3424.47 cm^{-1} reduces gradually with increasing heating time, after 35 min, the decrease is not obvious, which means the reaction between KH570 and silica at 80°C almost completed within 35 min. A single sweep illustrated in Figure 6 needs about 8 min, with the sweep times increasing, the reaction between KH570 and silica is furthered, thus KH570 with one end adsorbed on HNBR chains are chemically connected with silica via another end. In the sweep interval, silica modified by KH570 no longer reaggregate together so that the filler network is weakened and the G' value can't be recovered any more (Fig. 6).

In-situ modification dispersion technique

As stated above, silane coupling agent KH570 can react almost completely with the silanol group on silica surface at 80°C within 35 min or at room temperature for a longer time (a month), and it can be seen that only if the reaction occurs the micro-dispersion of silica will get better. So, the process parameters in *in-situ* modification dispersion technique: the amount of coupling agent, the heat treatment temperature and the treating time, are the important factors which could affect the micro-dispersion of silica and will be discussed in the following.

The influence of the amount of silane coupling agent

As can be seen in Figure 8, the modules of the uncured compounds at small strain amplitude

TABLE II
The Mechanical Properties of Composites with Different Content of KH570

KH570 content (phr)	Modulus at 100% (MPa)	Modulus at 300% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Permanent set (%)	Tear strength (KN m^{-1})	Hardness (Shore A)
0	4.7	17.6	24.5	355	26	58.6	91
4	6	26.2	29.8	330	24	59.2	90
6	6.1		27.5	310	18	61.4	91
8	7.2		26	276	20	56.9	92
10	6.3		24.6	303	20	62.4	92

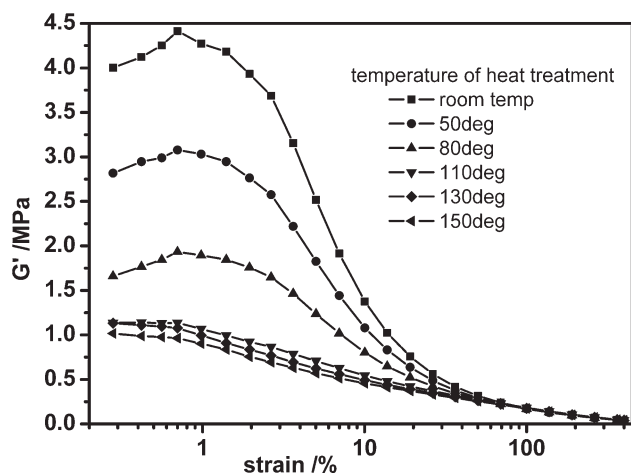


Figure 9 Strain dependence of G' at 80°C and 1 Hz for HNBR/Silica compounds with 6 phr KH570 and heat-treated at different temperature for 5 min.

reduce with the increase of the amount of KH570, which implies the better filler micro-dispersion, but the decrease rate diminished after the amount of KH570 up to 6 phr.

The mechanical properties of silica-filled HNBR with different content of KH570 heat-treated at 150°C for 5 min are shown in Table II. As shown in Table II, compared with the composite without KH570, the tensile strength, tear strength, modulus at 100%, modulus at 300% and permanent set of silica filled HNBR with KH570 are all improved. This indicates that the coupling agent KH570 is very useful to improve the interaction between filler and rubber. As also shown in this table, the modulus of HNBR/silica compound with KH570 increases as the content of KH570 increases while the tensile strength decreases with the content of KH570 increases. These results also related to the filler-rubber interaction affected by KH570.

The influence of the temperature of heat treatment

In Figure 9, as the temperature of heat treatment rising, the modules of the compounds gradually decrease, which indicates that the Payne effects and the filler networks generally weaken, accordingly

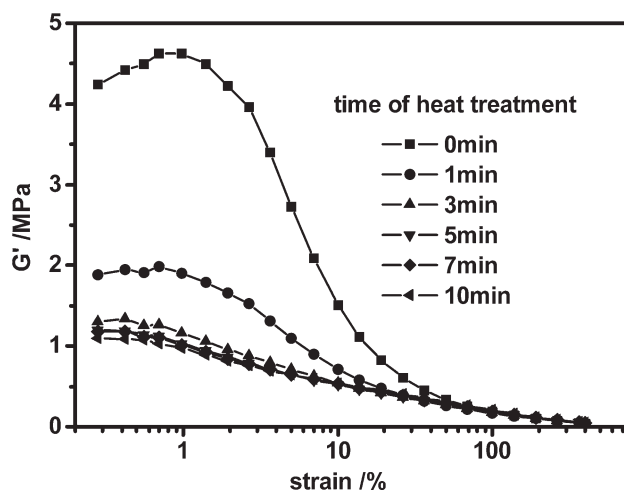


Figure 10 Strain dependence of G' at 80°C and 1 Hz for HNBR/silica compounds with 6 phr KH570 and heat-treated at 150°C for different time.

the silica micro-dispersion gets better. However, the micro-dispersion of silica improves slowly after 110°C.

The mechanical properties of silica filled HNBR with 6phr KH570 heat-treated at different temperature for 5 min are shown in Table III. As shown in Table III, the modulus at 100% and at 300% of the composites increase while the elongation at break and tear strength decrease with the increase of the temperature of heat treatment. This indicates that the increase of heat-treated temperature is helpful to the reaction between filler and KH570 and makes the interfacial strength stronger. What's more, it was also showed in Table III that the tensile strength increases as the treatment temperature increases when temperature is below 110°C, and then decrease, while the hardness changes little as the temperature increases.

The influence of time of heat treatment

The heat treatment obviously reduces the modulus of compounds in Figure 10, even treated with 1min, the modulus of the compound decreases from more than 4 to 2 MPa. With the treating time continued to

TABLE III
The Mechanical Properties of Composites with Different Heat-Treated Temperature

Heat treatment temperature (°C)	Modulus at 100% (MPa)	Modulus at 300% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Permanent set (%)	Tear strength (KN m ⁻¹)	Hardness (Shore A)
30	4.6	16.1	27.1	401	32	59.2	92
50	5.1	20.1	30.1	377	20	58	92
80	5.3	21.3	30.6	368	20		92
110	5.4	21.1	30.1	366	28	58.6	92
130	7.3		28.8	291	24	57.6	93
150	6.6	26.2	27.6	303	24	56.3	92

TABLE IV
The Mechanical Properties of Composites with Different Heat-Treated Time

Heat treatment time (min)	Modulus at 100% (MPa)	Modulus at 300% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Permanent set (%)	Tear strength (KN m ⁻¹)	Hardness (Shore A)
1	5.9	22.1	30	378	24	65	94
3	5.5	20.7	31.2	394	24	66.4	94
5	6	23.2	31.6	371	22	65.7	94
7	5.6	21.5	31.5	391	26	65.7	94
10	5.8	22.9	30.4	363	20	67.6	94

extend, the modulus decreases further but slowly and 5 min is enough for filler dispersion.

The mechanical properties of silica filled HNBR with 6phr KH570 heat-treated at 150°C for different time are shown in Table IV. As shown in Table IV, the properties of the composites almost do not change with the increase of the treating time. According to the former discussion, silica modified by KH570 can be happened at low temperature. Additional, there is a long cure time at high temperature (160°C) after the compounds heat-treated, so if the temperature of heat-treated adopt 150°C, the time of heat-treated can be very short and almost have no influence on the interaction between silica and HNBR matrix and the mechanical properties.

CONCLUSIONS

The effect of the silane coupling agent γ -methacryloxypropyl trimethoxy silane (KH570) on silica dispersion is strongly dependent on temperature and time both of which affect the reaction between silica and KH570. The filler dispersion gets worse when KH570 is added to HNBR/silica compounds at room temperature, which is opposite to SBR/silica system. But the filler dispersion improves when the storage time at room temperature was prolonged or KH570 is added at high temperature even with a short time, because the reaction between KH570 and silica happens. The silica dispersion gets better and the interfacial strength between silica and HNBR enhances with the increase of amount of KH570, heat-treated temperature or heat-treated time.

References

- Shan, L. J.; Hua, H. H. *Chin J Synth Chem* 2004, 12, 112.
- Achary, P. S.; Ramaswamy, R. *J Appl Polym Sci* 1998, 69, 1187.
- Cooper, A. R. *Polym Eng Sci* 1991, 31, 727.
- Hashimoto, K.; Watanabe, N.; Oyama, M.; Todani, Y. In *Proceedings of the Rubber Division Meeting; American Chemical Society: Los Angeles, April 23–26, 1985.*
- Hirano, K.; Suzuki, K.; Nakano, K.; Tosaka, M. *J Appl Polym Sci* 2005, 95, 149.
- Xu, D.; Karger-Kocsis, J.; Majorand, Z.; Thomann, R. *J Appl Polym Sci* 2009, 112, 1461.
- Smitthipong, W.; Nardin, M.; Schultz, J.; Suchiva, K. *Int J Adhes Adhes* 2009, 29, 253.
- Elizabeth, K. I.; Alex, R.; Kuriakose, B.; Varghese, S.; Peethambaran, N. R. *J Appl Polym Sci* 2006, 101, 4401.
- Das, P.; Ambatkar, S.; Sarma, K.; Sabharwal, S.; Banerji, M. *Polym Int* 2006, 55, 118.
- Das, P.; Ambatkar, S.; Sarma, K.; Sabharwal, S.; Banerji, M. *Polym Int* 2006, 55, 688.
- Lu, Y.; Liu, L.; Tian, M.; Geng, H.; Zhang, L. *Eur Polym J* 2005, 41, 589.
- Gatos, K. G.; Sawanis, N. S.; Apostolov, A. A.; Thomann, R.; Karger-Kocsis, J. *Macromol Mater Eng* 2004, 289, 1079.
- Gatos, K. G.; Százdi, L.; Pukánszky, B.; Karger-Kocsis, J. *Macromol Rapid Commun* 2005, 26, 915.
- Bhattacharjee, S.; Bhowmick, A. K.; Avasthi, B. N. *Polym Degrad Stabil* 1991, 31, 71.
- Zhang, L. Q.; Wu, Y. P.; Wang, Y. Q. *China Synth Rubber Ind* 2000, 23, 71.
- Zhang, Q.; Tian, M.; Wu, Y.; Lin, G.; Zhang, L. *J Appl Polym Sci* 2004, 94, 2341.
- Hamed, G. R. *Rubber Chem Technol* 2007, 80, 533.
- Hamed, G. R. *Rubber Chem Technol* 2000, 73, 524.
- Mathew, G.; Huh, M.-Y.; Rhee, J. M.; Lee, M.-H.; Nan, C. *Polym Adv Technol* 2004, 15, 400.
- Suzuki, N.; Ito, M.; Yatsuyanagi, F. *Polymer* 2005, 46, 193.
- Suzuki, N.; Ito, M.; Ono, S. *J Appl Polym Sci* 2005, 95, 74.
- Choi, S.-S. *J Appl Polym Sci* 2001, 79, 1127.
- Tan, E.-H.; Wolff, S.; Haddeman, M.; Grewatta, H. P.; Wang, M.-J. *Rubber Chem Technol* 1993, 66, 594.
- Wang, M. J. *Rubber Chem Technol* 1998, 71, 520.
- Yang, J.; Wu, Y.; Xu, C.; Zhang, L. *China Rubber Ind* 2006, 53, 586.
- Leblanc, J. L.; Cartault, M. *J Appl Polym Sci* 2001, 80, 2093.
- Zhang, K.; Chen, H.; Chen, X.; Chen, Z.; Cui, Z.; Yang, B. *Macromol Mater Eng* 2003, 288, 380.