

Effects of Mixing Conditions on the Reaction of 3-Octanoylthio-1-propyltriethoxysilane During Mixing with Silica Filler and Natural Rubber

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ABSTRACT: The effects of mixing temperature and mixing time on the reaction of 3-octanoylthio-1-propyltriethoxysilane (NXT silane) during mixing with precipitated silica and natural rubber (NR) were investigated. Results showed that the reaction between NXT silane and precipitated silica can proceed at temperatures above 130°C. Because of the blocking group of NXT silane, the silane–NR coupling reactivity is low, so that the reaction of NXT silane with NR occurs only during the curing period. There is no reaction between NXT silane and NR during mixing, which showed that the mixing time of silica-filled NR compound contain-

ing NXT silane must be longer than 10 min at 150°C to obtain the desired silane coupling efficiency. With increasing mill temperature, the coupling efficiency increases. A high mixing temperature promotes improvement of silane–silica coupling efficiency, although the tensile strength, 100% modulus, 300% modulus, and hardness of NR vulcanizates decrease. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2295–2301, 2004

Key words: rubber; silicas; mechanical properties; mixing; NXT silane

INTRODUCTION

It is well known that the performance of rubber compounds, with respect to such properties as tensile strength, tear resistance, and abrasion resistance, can be improved by incorporating carbon black and silica into rubbers. Precipitated silica is an especially useful addition to tire treads, not only to reduce rolling resistance, but also to reduce heat build-up.^{1–11} In the 1990s the European tire manufacturer Michelin made tires with tread formulations by incorporating silica, which has some important performance advantages over those based on conventional carbon black filler. Improvements are claimed for this “Green Tire” with respect to lower rolling resistance, better traction on water and snow, and lower heat build-up compared with such properties of conventional tires filled with carbon black.¹²

Because particle surfaces of precipitated silica have hydrophilic silanol groups, but nonpolar, olefinic hydrocarbon rubbers are hydrophobic, precipitated silica is not compatible with rubbers and their combination results in poor tensile strength and poor interface. Silane is used to improve their compatibilities. Silane coupling agents used in the rubber industry are usually bifunctional organosilanes, such as bis[(3-triethox-

ysilylpropyl) tetra sulfide] (TESPT), bis[(3-triethoxysilylpropyl) disulfide] (TESPD), and 3-octanoylthio-1-propyltriethoxysilane (NXT silane). The properties of silica-filled rubber compounds, such as tensile strength, shear strength, hardness, low loss, and heat build-up in the tire tread, can be improved by loading silanes, especially TESPT and TESPD.^{13–16}

Generally, silica, a coupling agent, and a rubber were simultaneously charged to a mixer. During mixing, two chemical reactions occurred.¹⁴ (1) Ethoxy groups of TESPT can react with the silanol groups of silica in the presence of water. First a single bond with the silica surface is formed with one ethoxysilyl group of the silane and a silanol group of the silica (primary reactions) as shown in Figure 1. Then there are further condensation reactions between pairs of neighboring silane molecules, which are already bound to the silica surface (secondary reaction) as shown in Figure 2. (2) A reaction occurs between organosilane and the rubber polymer at elevated temperatures, called prescorch.

Thus silane in a silica-reinforced rubber has two functions: dispersion and cocure effect. Reuvekamp et al.^{14,17} concluded that a minimum dump temperature of 130°C is required to ensure that the silica and TEPST react to the desired extent. However, at temperatures over 160°C the coupling agent (TESPT) either starts to react with rubber or donates sulfur.¹⁴ There is an increase of viscosity of the compound, which becomes scorched.

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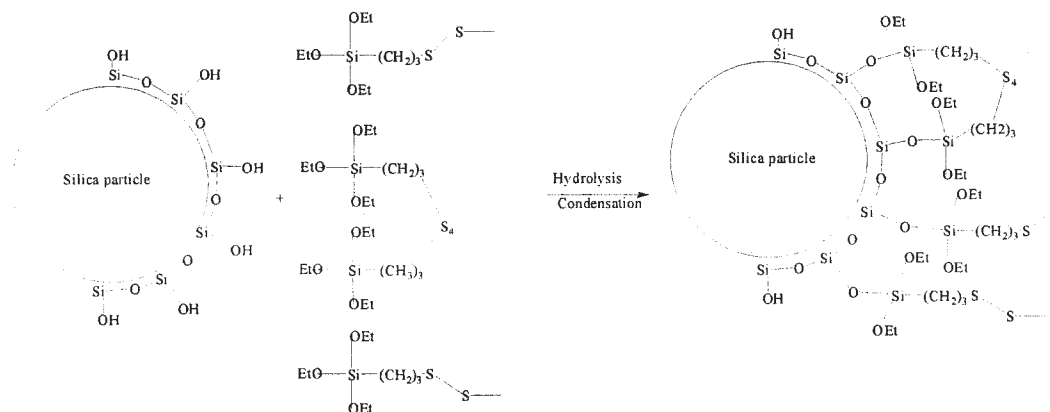
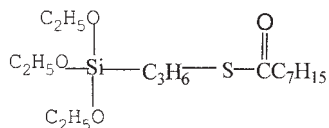


Figure 1 Primary reaction of TESPT and silica.

The molecular structure of NXT silane is as follows:



The octanoyl group as blocking group of NXT silane leads to lower reactivity of the silane during mixing process.¹⁸ However, for the reaction of NXT silane with silica-filled natural rubber during mixing process, no experimental investigation has been reported. This article reports the investigation of the effects of mixing time and temperature on the dynamic mechanical properties of uncured silica-filled NR compound. At the same time mechanical properties and dynamic mechanical properties of cured NR vulcanizates were also investigated.

EXPERIMENTAL

Materials

Materials used in this experiment are listed in Table I. All materials were used as received.

Experiments were performed according to the recipe shown in Table I.

Sample preparation

The compounds were mixed in three steps on a two-roll mill unless otherwise indicated. The first step was to mix compounds containing natural rubber (NR), silica, diphenyl guanidine (DPG), antioxidant, ZnO, and stearic acid (SA), at temperatures about 50°C. After uniform mixing, the compounds were mixed on a mill at a certain temperature for 10 min or at 150°C for different times. Then, the accelerator and sulfur were added to the compounds on a two-roll mill.

Curing

The curing behavior of NR compounds was determined with an oscillating disk rheometer in accordance with ASTM D2084-92. Cured sheets of 2 mm were compression molded for optimum cure time (T_{90}) at a temperature of 160°C.

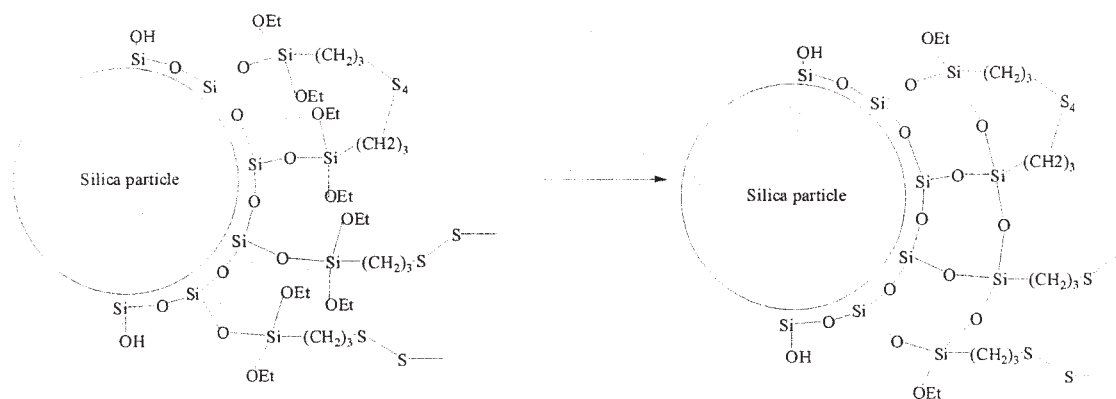


Figure 2 Secondary reaction of TESPT and silica.

TABLE I
Compound Recipe

Component	Source	phr
Step I		
Natural rubber	RSS1, Thailand	100
Silica	High-dispersion silica 7000 GR, Degussa, supplied by Red Avenue Chemical Co., Ltd.	50
NXT silane	OSI Specialties, Crompton Corp.	6
TESPT silane	Guangdong Tianhe Science and Technology Co.	Variable
Antidegradants 4020 ^a	Tongling Chemical Industry Group Corp., China	2
Rhenogran DPG-80 ^b	Bayer Company RheinChemie Ltd.	2
Rhenogran ZnO-80	Bayer Company RheinChemie Ltd.	4
Stearic acid	Industry grade	2
Step II		
Heat exposure on two-roll mill		
Step III		
Rhenogran CZ-80 ^c	Bayer Company RheinChemie Ltd.	2
Rhenogran S-80	Bayer Company RheinChemie Ltd.	2

^a Antidegradants 4020 is *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine.

^b Diphenyl guanidine.

^c *N*-Cyclohexyl-2-benzothiole sulfenamide.

Characterization

Dumbbell-shape specimens were cut and tested in an Instron 4465 univertal testing machine at a crosshead speed of 500 mm/min according to ASTM D412. Hardness was measured using an indentation hardness tester according to ASTM D2240-75.

The dynamic mechanical properties of compounds were measured under a multiwave dynamic tension mode at a frequency of 10 Hz with a dynamic stress of 1.26×10^5 Pa for silica-filled NR vulcanizates on a Rheometric Scientific (Piscataway, NJ) DMTA IV apparatus. Dimensions of the specimen were $20 \times 4 \times 0.9$ mm (length \times width \times thickness). The storage modulus G' , loss modulus G'' , and $\tan \delta$ were reported at the same time.

Dynamic measurements of the uncured compounds without sulfur and accelerators were performed with the aid of an advanced rheology expanded system (ARES) at 100°C and 0.5 Hz with different strains. Temperature sweep measurement (110–180°C) were performed on the uncured compound without sulfur and accelerators in the ARES at 0.5 Hz and 50% strain.

The compound of step I was mixed on a two-roll mill. Then the compound was charged to a Haake (Bersdorff, Germany) mixer at 150°C for 20 min at a rotor speed of 30 rpm. The torque required to operate the rotors during mixing was recorded every 6 s.

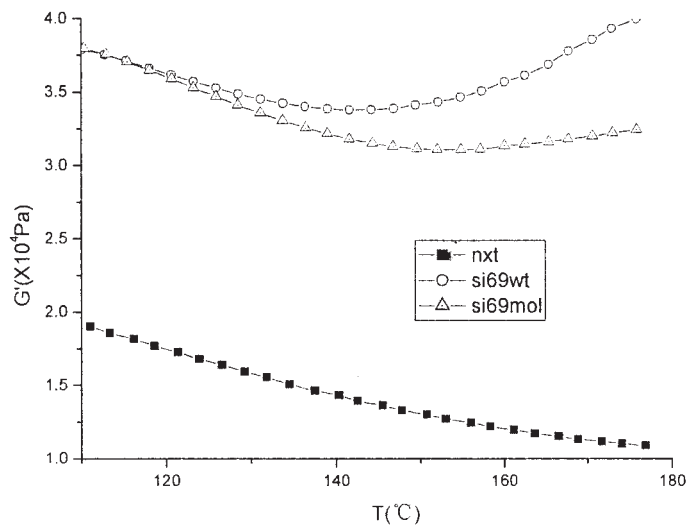


Figure 3 G' modulus versus temperature.

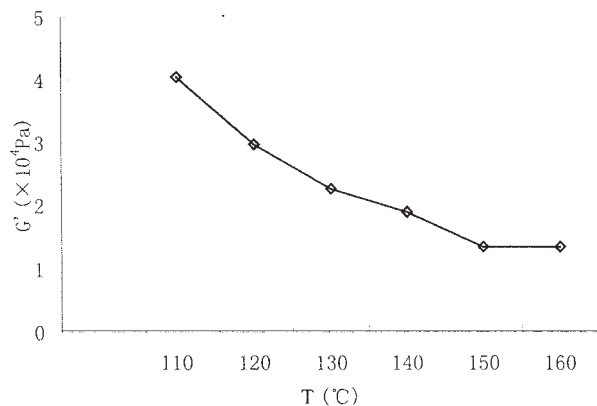


Figure 4 G' at 0.1% strain versus temperature.

RESULTS AND DISCUSSION

The primary and secondary reactions and rubber-silane reaction may take place when the mixing temperature increases. Assuming that the mill temperature is a main parameter influencing the degree of reactions, we investigated the effects of mixing temperature and time on the dynamic mechanical properties of the NR compounds.

Temperature sweep measurements as an indicator of scorch sensitivity of silane nxt

To investigate the reaction between NXT silane and rubber, the temperature sweep of the NR compounds without accelerators and sulfur, at the temperature range from 110 to 180°C, were performed by ARES. At the same time TESPT, which can react with NR at temperatures above 160°C, was used as a reference. The compound was milled at 150°C for 10 min. Figure 3 shows the relationship between G' and temperature. NXT silane and TESPT are of the same molarity and weight, respectively. The compounds containing TESPT showed a substantial increase in G' at temperatures above 150°C. Reuvekamp et al.² studied this

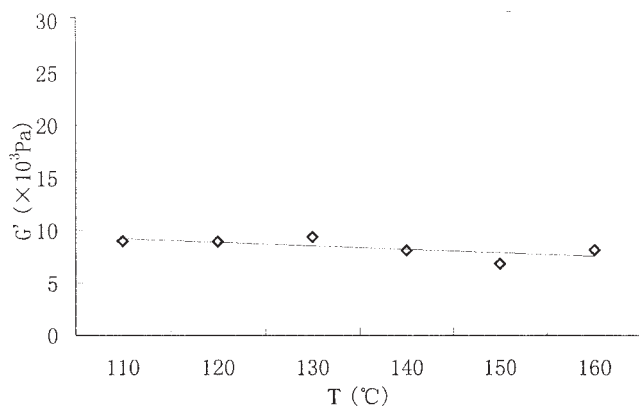


Figure 5 G' at 100% strain versus temperature.

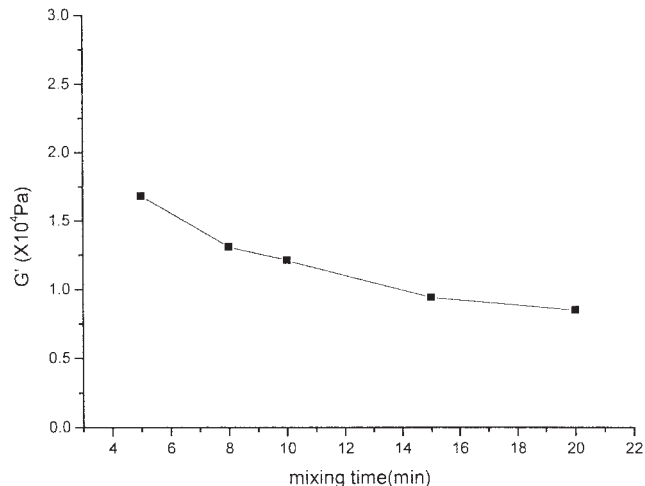


Figure 6 G' at 0.1% strain versus mixing time.

topic in detail and indicated that the crosslinking results from the sulfur donated by TESPT in combination with the accelerator functionality of TESPT. However, in the range of measurement temperatures, the compound containing NXT silane does not increase in G' . Thus the reaction between silane NXT and rubber will not occur at temperatures below 180°C.

Effects of mill temperature and time on the storage modulus at different strain amplitudes

To study the reaction of the ethoxyl group of NXT with the surface silanol group of precipitated silica, uncured compounds were measured using ARES at different strains. When a rubber is filled with a reinforcing filler, filler-filler interactions occur above a critical filler concentration, which is a result of the decrease in the distances between the filler aggregates in the rubber compounds. These interactions are particularly perceptible when deformations are small. At low strain amplitudes, such as a strain of 0.1%, such filler-filler interactions can be particularly well measured.¹⁷ Far fewer filler-filler interactions occur at higher strains. High strains of 100% consequently represent mainly the effect of the rubber network. This effect is commonly known as the Payne effect, which is calculated from the difference in dynamic elastic modulus, G' , at low strain and high strain amplitude. It should be noted that when using silica, the high level of the elastic modulus and the decrease of the elastic modulus at higher strain amplitudes are commonly cited to prove the existence of a filler network formed by the silica.¹⁷

Figure 4 shows the storage modulus G' at 0.1% strain versus mill temperature. As shown in Figure 4, G' decreases steadily with increasing mill temperature to 150°C, and then remains at a low level. At 100%

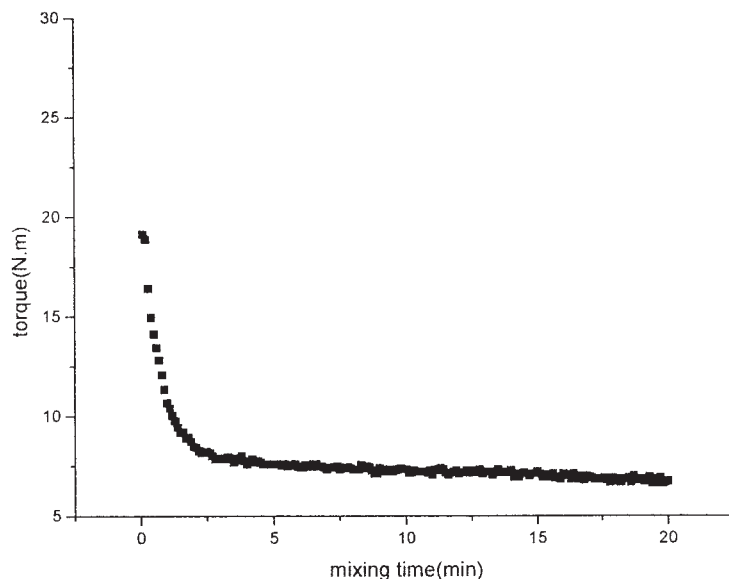


Figure 7 Mixing torque as a function of mixing time of NXT compound.

strain, the mill temperature has little effect on the G' (Fig. 5).

The primary and secondary reactions of NXT silane with the silica surface result in decreases in G' at a low strain and have little effect on G' at high strain. A higher coupling effect leads to fewer filler–filler interactions, and therefore leads to a decrease in G' at a low strain with increasing mill temperature. Because of the blocking of the octyl group, NXT neither donated sulfur nor reacted with rubber molecules at the mixing temperature range, so the G' at a high strain remains constant.

To investigate the effect of mixing time on the rubber compound, the first-step compound was mixed at 150°C for a given time. Figure 6 shows the G' at 0.1% strain versus mixing time. As shown in Figure 6, the trend was almost the same as that obtained at different mill temperatures: the G' at 0.1% strain decreases with increasing mixing time. At the same time, the torque curve of the compound was also investigated (Fig. 7). The torque of the compound obviously decreases be-

fore 2.5 min, and decreases slightly thereafter. Because the silanol group of silica could react with the ethoxyl group of NXT, the filler–filler interaction was decreased before 2.5 min; and then the torque decreases slightly, which might be ascribed to the secondary reaction or degradation of NR.

Effect of mill temperature on the mechanical properties of NR vulcanizate

The hardness of cured compounds decreases with increasing mill temperature (Fig. 8). Because hardness reflects low-strain properties, it is sensitive to filler–filler interaction between silica particles. With increasing mill temperature, the primary and secondary reactions should have occurred, leading to decreased filler–filler interaction.

As can be seen in Figure 9, tensile strength of the

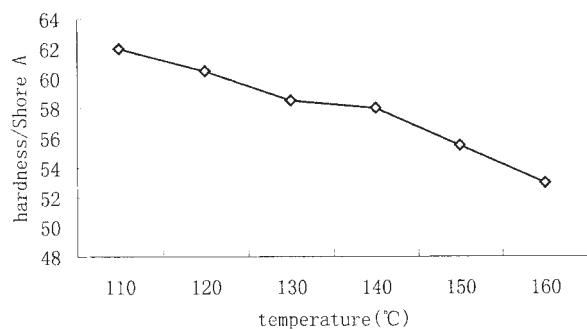


Figure 8 Hardness versus mill temperature.

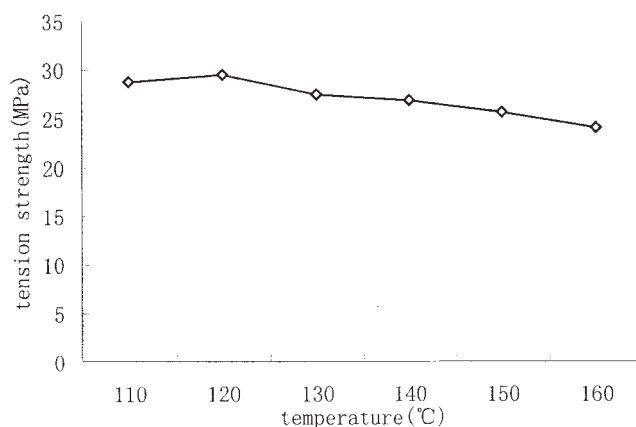


Figure 9 Tensile strength versus mill temperature.

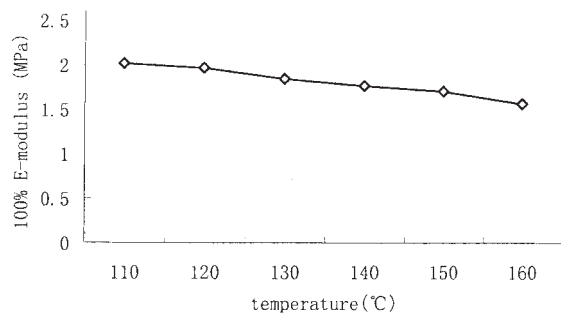


Figure 10 100% modulus versus mill temperature.

compound remains constant at mill temperatures below 130°C, and then the tensile strength decreases with increasing mill temperature. The decrease in the hardness is attributed to a reaction between NXT silane and silica, either the primary or secondary reaction or both. The primary and the secondary reactions will react to the desired extent at mill temperatures above 130°C. Below 130°C the reactions were slow, so the tensile strength remained constant.

The 100% modulus decreases slightly with increasing mill temperature, as seen in Figure 10. A similar tendency can be seen for 300% modulus (Fig. 11). According to Rauline¹⁹ the M_{300}/M_{100} ratio is reported as an alternative measure for coupling efficiency (Fig. 12). The ratio increases with increasing mill temperature: results show that the coupling efficiency increases with increasing mill temperature. The extent of coupling reaction between the ethoxyl group of NXT silane and the silanol group of silicas increases with increasing mill temperature.

Effects of mill temperature on dynamic mechanical properties of NR vulcanizate

Table II shows G' , G'' , and $\tan \delta$ values for NR vulcanizate obtained at different mill temperatures. The storage modulus increases with increasing mill temperature below the glass-transition temperature (T_g);

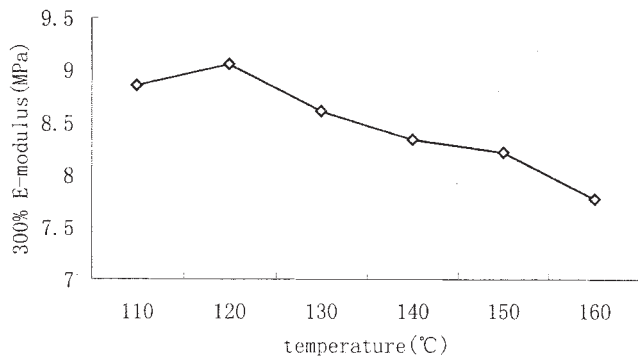


Figure 11 300% modulus versus mill temperature.

TABLE II
Dynamic Mechanical Properties of Cured Compounds

Property	Mill temperature (°C)					
	110	120	130	140	150	160
$\tan \delta$, 60°C	0.12	0.11	0.11	0.11	0.09	0.11
$\tan \delta_{\max}$	0.65	0.65	0.82	0.80	1.16	1.25
$\tan \delta$, -70°C	0.03	0.06	0.06	0.11	0.02	0.02
G' (MPa), 60°C	6.93	6.88	6.15	5.94	4.87	4.23
G' (100 MPa), -70°C	6.73	8.94	10.3	7.78	45	52.6
G'' (Pa), 60°C	8.08	7.54	6.58	6.34	4.4	4.55
G'' (10 MPa), -70°C	2.23	5.3	6.16	9.15	10.7	12.5

however, the trend is opposite above T_g . The same trend is shown in loss modulus of the cured compound. As shown in Table I, the T_g of NR vulcanizate decreases with increasing mill temperature. However, the $\tan \delta$ increases with increasing mill temperature. Because of the occurrence of primary and secondary reactions (i.e., the ethoxyl group of NXT reacts with silanol on the surface of silica with increasing mill temperature), the silica becomes less hydrophilic and more hydrophobic, and thus silica has better compatibility with NR. Silica can disperse well in NR and is therefore less aggregated.

NXT and TESPT

Reuvekamp et al.¹⁷ concluded that compounds containing TESPT will react with the rubber matrix at mixing temperatures over 160°C. As shown in Figure 3, however, the compound with NXT would not react with NR rubber at mixing temperatures below 180°C (i.e., NXT has better scorch properties than those of TESPT). Blocking of the octanoyl group in NXT leads to lower reactivity of the silane with NR during processing. The deblocking energy of the octanoyl group

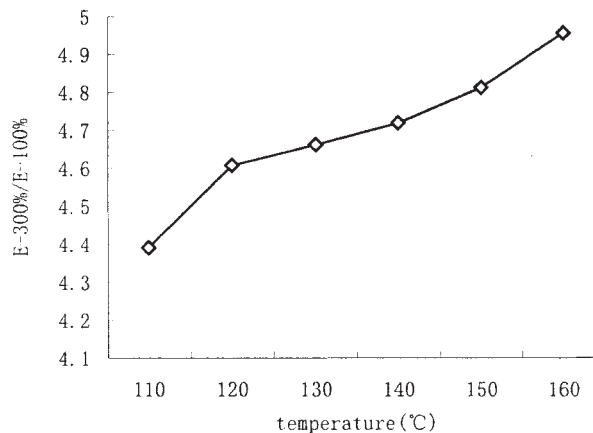


Figure 12 M_{300}/M_{100} versus mill temperature.

in NXT is higher than that of TESPT; thus the reaction between silane NXT and NR is more difficult than that between NR and TESPT.

CONCLUSION

Silane coupling agents can improve the compatibilities between precipitated silica and nonpolar rubbers. It is important to investigate the coupling effectiveness between silica and silane. Mixing temperature is a parameter of paramount importance in mixing silica and rubber with 3-octanoylthio-1-propyltriethoxysilane (NXT silane). A minimum temperature of 130°C is required. A mixing time of 10 min at 150°C is necessary to ensure a complete coupling reaction of silica and silane NXT. Silane NXT offers good scorch safety, and will not react with NR during mixing.

With increasing mill temperature, the tensile strength, 100% modulus, 300% modulus, and hardness of NR vulcanizate decrease, as shown in Figure 12, but the coupling efficiency increases. A high mixing temperature promotes improved silane-silica coupling efficiency.

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