Effect of Coupling Agent on Properties of Silica/Natural Rubber Nanocomposites (Postprint)

Authors: Zhang Pengyu, Wang Na, Yang Feng, Kang Hailan, Fang Qinghong

Date: 2023-03-18T00:00:00+00:00

Abstract

The effects of coupling agent on the vulcanization characteristics, mechanical properties, stress-softening effect, Payne effect, loss factor, compression heat build-up, and dynamic thermomechanical properties of silica (15 nm, 30 nm, 80 nm)/natural rubber nanocomposites with different particle sizes were investigated, and compared with those of composites without coupling agent. The results show that: the addition of coupling agent Si69 improves the dispersion of silica in rubber, enhances the bonding between silica and rubber matrix, improves the mechanical properties of silica/NR composites, and reduces the optimum cure time of the compounds; the smaller the silica particle size, the more pronounced the effect of Si69, which is more beneficial for improving the vulcanization characteristics and mechanical properties of the composites; the addition of Si69 reduces the Payne effect, loss factor, and temperature rise under constant load compression heat build-up of 15 nm and 30 nm silica composites, but has little effect on 80 nm silica composites.

Full Text

Preamble

Vol. 29 No. 8
CHINESE JOURNAL OF MATERIALS RESEARCH
August 2015

Influence of Coupling Agent Si69 on Properties of Silica/Natural Rubber Nanocomposites

ZHANG Pengyu, WANG Na, YANG Feng, KANG Hailan, FANG Qinghong**
(School of Material Science and Engineering, Shenyang University of Chemical Technology, Shenyang 110142, China)

ABSTRACT: The effect of coupling agent silane Si69 on properties of natural rubber nanocomposites filled with different sized nano-silica (15, 30, and 80 nm) was investigated in terms of curing performance, mechanical properties, Mullins effect, Payne effect, loss factor, dynamic heat build-up, and dynamic mechanical properties, using the same composites without coupling agent as a comparison. Results show that with the addition of Si69, the dispersity of nano-silica in the rubber matrix and the interfacial binding between silica and rubber were improved, effectively enhancing the mechanical properties of the composites while shortening the positive vulcanization time (t90). Notably, the smaller the silica particle size, the more pronounced the effect of Si69, leading to greater improvements in curing characteristics and mechanical properties. The addition of Si69 reduced the Payne effect, loss factor, and temperature rise under constant load compression for 15 nm and 30 nm silica composites, but had minimal influence on the 80 nm silica composite.

KEY WORDS: composites, nano-silica, silane coupling agent, static mechanical properties, dynamic mechanical properties, Payne effect

Introduction

Silica is an inorganic nanomaterial with a unique three-dimensional network structure that is produced and used on a large scale. Comprising 95%-99% amorphous SiO_2, silica is non-toxic, tasteless, odorless, heat-resistant, and water-insoluble [1]. Its surface is rich in siloxane and hydroxyl groups, exhibiting high specific surface area and surface activity. The ultrafine effect of silica can effectively enhance the comprehensive performance of rubber composites [2-4], making it an important reinforcing agent in the rubber industry. The reinforcing effect of silica on various rubbers is superior to other white fillers and second only to carbon black. Compared with carbon black-filled vulcanizates, silica/rubber composites offer advantages such as good electrical insulation, low heat generation, high tear strength, low rolling resistance, and improved wet skid resistance [5-7].

Particle size, surface activity, and structure are three critical factors for reinforcing materials. Zhang Liqun [8] and Hamed et al. [9] from the University of Akron have identified particle size as the primary factor for nanomaterial reinforcement. In silica-reinforced composites, silica particles often exist as loosely aggregated "nebula-like" secondary structures. However, SiO_2 is a polar particle with poor compatibility with non-polar polymers and exhibits strong adsorption and aggregation tendencies. Consequently, silica particles tend to undergo secondary agglomeration through hydrogen bonding, making them difficult to disperse uniformly in rubber during mixing and preventing the achievement of ideal composite properties [10-13]. Therefore, surface modification of SiO_2 is necessary to improve its compatibility and bonding with polymers, enabling the preparation of nanocomposites with good dispersion and strong interfacial interactions. Silane coupling agents are commonly added to modify silica surfaces, compensating for these deficiencies [14] and enhancing compatibility with the rubber matrix while weakening filler-filler interactions. Through chemical modification, silane coupling agents can improve interactions between the silica surface and polymer while reducing filler-filler interactions [15].

The most commonly used surface-modifying silane coupling agent is bis-[3-(triethoxysilyl)-propyl] tetrasulfide (Si69) [16, 17]. Gao Yi et al. [18] reacted silane coupling agent KH550 with hydroxyl groups on the nano-SiO_2 surface, reducing the number of surface hydroxyl groups and altering the physical and chemical properties of SiO_2 from hydrophilic to hydrophobic, thereby improving its compatibility and bonding with rubber. This study investigates the influence of silane coupling agent Si69 on the curing characteristics, mechanical properties, Mullins effect, Payne effect, loss factor, compression heat build-up, and dynamic thermomechanical properties of natural rubber composites reinforced with different particle sizes of silica.

Experimental

Materials and Formulation

Raw materials: Natural rubber (NR) with relative molecular weight of 300,000; precipitated nano-silica with particle sizes of 15 nm, 30 nm, and 80 nm; coupling agent Si69; stearic acid (SA); zinc oxide (ZnO); antioxidant 4010; accelerator NOBS; and sulfur (S).

Basic formulation (phr, parts per hundred rubber): NR 100, stearic acid 2, ZnO 5, accelerator NOBS 0.75, antioxidant (4010) 2, sulfur 2.5, coupling agent (Si69) 1, nano-silica (15 nm, 30 nm, or 80 nm) 15.

Sample Preparation

The natural rubber was passed 13 times through an XK-160 two-roll mill, after which stearic acid, ZnO, antioxidant, silica (with Si69), vulcanization accelerator NOBS, and sulfur were added sequentially. The mixing temperature was controlled between 30-50°C to ensure uniform mixing. The compounded rubber was stored for 8 hours before testing. The vulcanization characteristics were measured using a GT-M2000-A rubber vulcameter at 150°C. Based on the measured t90 (optimum cure time), samples were vulcanized in an XLB plate vulcanizing press at 150°C and 10 MPa pressure.

Characterization

Mechanical properties and Mullins effect were tested using an Instron universal testing machine at a tensile rate of 500 mm/min. Dynamic mechanical properties were evaluated with an RPA8000 rubber process analyzer at 60°C, 1 Hz frequency, and strain amplitude of 1%-100%. Compression heat build-up was measured using a GT-RH-2000 dynamic compression heat tester on cylindrical specimens (25 mm height, 17.5 mm diameter) under 1.0 MPa pre-stress, 5.70 mm stroke, and 55°C temperature. DMA tests were conducted on a DHR-2 rotational rheometer at 1 Hz frequency, 0.01% strain, and temperature range of -100°C to 100°C. Morphology was examined using an SU8010 field emission scanning electron microscope (SEM). All physical properties were tested according to corresponding national standards.

Results and Discussion

2.1 Curing Characteristics and Mechanical Properties

As shown in Table 1 , for composites without Si69, both scorch time (t10) and optimum cure time (t90) gradually decreased with increasing silica particle size, indicating accelerated vulcanization rates, while MH-ML values showed little variation. This is primarily because silica particles strongly adsorb vulcanization accelerators in the compound, delaying cure. Smaller particles have larger specific surface areas, adsorb more accelerator, and thus require longer cure times.

After adding Si69, both t10 and t90 decreased for composites with the same silica particle size, indicating that Si69 effectively reduces the number of hydroxyl groups on the silica surface, decreasing its adsorption of accelerators and improving dispersion, which lowers torque and MH-ML values. With the addition of coupling agent, tensile strength and elongation at break both improved to some extent, with the most significant improvements observed for the 15 nm silica composite, while the 80 nm silica composite showed only modest increases. This demonstrates that the coupling agent creates strong bonding between silica and rubber macromolecules, preventing interfacial failure during tensile fracture. However, the 100% and 300% modulus values for composites without coupling agent were higher than those with Si69. This suggests that at low to moderate deformations, silica particles without coupling agent easily form filler networks that provide good reinforcement, but under large deformation, the silica-rubber interface in the non-coupled system readily breaks, resulting in lower tensile strength and elongation. Thus, the effect of coupling agent is more pronounced with smaller silica particles, benefiting both curing characteristics and mechanical properties.

2.2 Effect of Coupling Agent Si69 on Mullins Effect

Similar to the Payne effect at small deformations, the stress-softening phenomenon observed during static cyclic loading at large deformations is known as the Mullins effect. Both phenomena originate from the destruction of the filled network microstructure, where the Mullins effect specifically refers to the inability of the microstructure to return to its initial state after being damaged during the first stretching cycle.

As shown in Figure 1 [Figure 1: see original paper], although the degree of stress-softening varies, the general trend is consistent. The addition of Si69 enhances the composite’ s ability to resist deformation and increases the stress it can withstand, while correspondingly intensifying the Mullins effect and increasing static strain energy loss. This occurs because Si69 significantly improves bonding between silica particles and rubber macromolecular chains, reducing relative slippage between chains and between chains and filler. However, in composites without coupling agent, the particle network experiences less damage, resulting in stronger reinforcement and lower stress-softening. The figure also reveals that Si69 has a greater influence on 15 nm and 30 nm silica composites but minimal effect on the 80 nm silica composite. This is because smaller silica particles tend to agglomerate more readily, while larger particles already have relatively good dispersion, making the coupling agent’ s effect on stress-softening negligible for the 80 nm system.

2.3 Effect of Coupling Agent Si69 on Payne Effect

The Payne effect primarily arises from the disruption of filler networks formed by interactions between fillers or filler aggregates. A smaller decrease in storage modulus indicates a weaker Payne effect and better dispersion of the reinforcing system. As shown in Figure 2 [Figure 2: see original paper], the storage modulus G’ of composites with Si69 is lower than that without Si69. The G’ of the 15 nm silica composite without coupling agent shows the greatest change upon adding Si69, while the 80 nm silica composite shows minimal variation. This indicates that adding Si69 improves the dispersion of smaller silica particles more effectively. The coupling agent reduces the probability of particle network formation. When silica particle size reaches 30 nm, the influence of Si69 on dispersion decreases, and the negligible change in G’ for 80 nm silica suggests that Si69 has limited effect on the dispersibility of larger particles.

2.4 Effect of Coupling Agent Si69 on Loss Factor and Compression Heat Build-up

Figure 3 [Figure 3: see original paper] shows the effect of different silica particle sizes and Si69 addition on the loss factor (tanδ) of composites. Before adding Si69, poor filler dispersion leads to destruction of the network structure at large deformations, causing a sharp modulus drop and consequently higher tanδ values. After Si69 addition, the loss factor decreases, indicating reduced destruction of the filler network at high strains (or that the coupling agent inhibits particle network formation), resulting in lower hysteresis. Additionally, the effect of Si69 on tanδ is more pronounced for smaller silica particle sizes.

As shown in Figure 4 [Figure 4: see original paper], compression temperature rise gradually decreases with increasing silica particle size. This is because smaller silica particles have higher surface energy and tend to aggregate, resulting in poorer dispersion, increased internal friction, and higher temperature rise, consistent with the tanδ trend. After adding Si69, the compression temperature rise decreased for 15 nm and 30 nm silica composites, but showed no obvious change for the 80 nm silica composite. This demonstrates that Si69 improves the dispersion of smaller silica particles, forming a more uniform crosslinked network that reduces internal friction and compression heat build-up.

2.5 Effect of Coupling Agent Si69 on Dynamic Thermomechanical Properties

Figure 5 [Figure 5: see original paper] presents the temperature dependence of mechanical loss tanδ for the two compound systems. The glass transition temperature of the composites is approximately -40°C. Compared with composites without Si69, the addition of Si69 increased the Tg (mechanical hysteresis peak) for 15 nm and 30 nm silica-filled composites but decreased it for the 80 nm silica-filled composite. Since the tanδ value at 0°C for elastomeric composites characterizes wet skid resistance, Figure 5a shows that without Si69, smaller silica particle size yields better wet skid resistance. Figure 5b reveals that adding Si69 increased the tanδ value at 0°C for the 30 nm silica composite, indicating that Si69 can effectively improve the wet skid resistance of 30 nm silica-filled composites.

2.6 Morphology of Silica/NR Composites

Figure 6 [Figure 6: see original paper] shows SEM images of cryogenic fracture surfaces for six vulcanized composite samples. In Figures 6a-c (without Si69), silica exists as flocculates in the rubber matrix with non-uniform dispersion, creating silica-rich regions and silica-free matrix domains. Both 15 nm and 30 nm silica show poor dispersion with numerous aggregates, while the 80 nm silica composite exhibits relatively uniform silica distribution on the fracture surface.

After adding Si69 (Figures 6d-f), silica dispersion improves significantly, with the most dramatic improvement observed for 15 nm silica. This confirms that the reaction between Si69 and hydroxyl groups on the nano-silica surface eliminates or reduces surface silanol groups, transforming the surface from hydrophilic to hydrophobic, thereby enhancing affinity with the polymer and effectively improving silica dispersion in rubber while simultaneously improving interfacial adhesion through bonding with rubber macromolecules.

Conclusions

1. The addition of Si69 coupling agent improves silica dispersion in rubber, enhances interfacial bonding between silica and the rubber matrix, increases the mechanical properties of silica/NR composites, and reduces

optimum cure time. The effect is more pronounced with smaller silica particles, leading to greater improvements in curing characteristics and mechanical properties.

2. Adding Si69 reduces the Payne effect, loss factor, and constant-load compression heat build-up temperature rise for 15 nm and 30 nm silica composites, but has minimal influence on 80 nm silica composites. Si69 addition also improves the wet skid resistance of 30 nm silica-filled composites.

References

1. LI Xi, LIU Lianli, WANG Lili, "Status quo and progress in research on nano-SiO_2," *Journal of Bohai University (Natural Science Edition)*, 27(4), 304 (2006)
2. S. J. Ahmadi, Y. D. Huang, W. Li, "Synthetic Routes, Properties and future application of polymer-layered silicate nanocomposites," *Mater. Sci.*, 39(6), 1919 (2004)
3. ZHANG Yuefeng, ZHANG Yuqing, "Applications and research progress of composite nano-SiO_2," *Journal of Tarim University*, 22(1), 152 (2010)
4. LIU Jingchao, LI Xiaobing, ZHANG Hualin, YANG Yahui, FU Wanli, "Study of epoxy resin reinforced and toughened by nm SiO_2," *Chinese Journal of Colloid & Polymer*, 18(4), 15 (2000)
5. YANG Qingzhi, *Practical Rubber Process Engineering* (Beijing, Chemical Industry Press, 2005) p.93-96
6. S. S. Choi, "Improvement of properties of silica-filled natural rubber composites using polychloroprene," *J. Appl. Polym. Sci.*, 83, 2609 (2002)
7. S. S. Choi, "Improvement of properties of silica-filled styrene-butadiene rubber compounds using acrylonitrile butadiene rubber," *J. Appl. Polym. Sci.*, 79, 1127 (2001)
8. ZHANG Liqun, WU Youping, WANG Yiqing, "The nano-reinforcing and nano-compounding technique of rubber," *China Synthetic Rubber Industry*, 23(2), 71 (2000)
9. G. R. Hamed, "Reinforcement of rubber," *Rubber Chemistry and Technology*, 73(3), 524 (2000)
10. LI Guangliang, *Silicone Polymer Chemistry* (Beijing, Science Press, 1998) p.149
11. S. Wolff, U. Gorl, M. J. Wang, "How does silica differ from carbon black," *Eur. Rubb. J.*, 176(1), 17 (1994)

12. M. L. Hair, W. Hsrtl, "Acidity of surface hydroxyl groups," *The Journal of Physical Chemistry*, 74(1), 91 (1970)
13. J. A. Hockey, B. A. Pethica, "Surface hydration of silicas," *Transactions of the Faraday Society*, 57, 2247 (1961)
14. M. J. Wang, S. Wolff, J. B. Donnet, "Filler-elastomer interactions: Silica surface energies and interactions with model compounds," *Rubber Chem. Technol.*, 64(3), 559 (1990)
15. ZHANG Bijun, HE Lizhong, "Preliminary study of silica and natural rubber coupling agent Si69 interaction mechanism,"*Carbon Black Industry*, 12(5), 26 (1992)
16. A. Ansarifar, L. Wang, R. J. Ellis, "Enhancing the mechanical properties of styrene-butadiene rubber by optimizing the chemical bonding between silanized silica nanofiller and the rubber," *Journal of Applied Polymer Science*, 105(2), 322 (2007)
17. JIANG Qibin, JIA Demin, NING Kaijun, YAN Zhiyun, "Interaction between carbon black and silica with a coupling agent Si69," *China Synthetic Rubber Industry*, 26(6), 362 (2003)
18. GAO Yi, ZHAO Suhe, LIU Xiao, "Characterization and evaluation on organization degree of nano-silica," *Synthetic Rubber Industry*, 29(6), 424 (2006)

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.