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Preparation of Nano-Zinc Oxide/EPDM Composites with Both Good Thermal Conductivity and Mechanical Properties

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ABSTRACT: In this article, nano-zinc oxide (ZnO) filled ethylene propylene diene monomer (EPDM) composites are prepared, and the mechanical (static and dynamic) properties and thermal conductivity are investigated respectively, which are further compared with the traditional reinforcing fillers, such as carbon black and nano-silica. Furthermore, influence of in-situ modification (mixing operation assisted by silane at high temperature for a certain time) with the silane-coupling agent Bis-(3-thiethoxy silylpropyl)-tetrasufide (Si69) on the nano-ZnO filled composites is as well investigated. The results indicate that this novel reinforcing filler nano-ZnO can not only perform well in reinforcing EPDM but can also improve the thermal conductivity significantly. In-situ modification with Si69 can enhance the interfacial interaction between nano-ZnO particles and rubber matrix remarkably, and therefore contribute to the better dispersion of filler. As a result, the mechanical properties and the dynamic heat build-up of the nano-ZnO filled composites are improved obviously by in-situ modification, without influencing the thermal conductivity. In comparison with traditioanl reinforcing fillers, in-situ modified nano-ZnO filled composites exhibit the excellent performance in both mechanical (static and dynamic) properties and better thermal conductivity. In general, our work indicates that nano-ZnO, as the novel thermal conductive reinforcing filler, is suitable to prepare elastomer products serving in dynamic conditions, with the longer expected service life. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1144–1155, 2011

Key words: nanocomposites; nano-zinc oxide; reinforcement; thermal conductivity

INTRODUCTION

As a kind of extremely significant and strategic material, rubber, with its excellent elasticity, usually works in the dynamic serving conditions, such as tire, rubber roller, rubber transmission belt, etc. To satisfy the practical applications, rubber reinforcement is very essential and necessary.[1–8] Among all kinds of methods, compounding nanofillers is the most effective.[5] For instance, in most cases carbon black and nano-sized silica are used to reinforce rubber products. In the case of the dynamic condition, a great heat build-up generally comes from two aspects: (1) the hysteresis loss of rubbery matrix; and (2) the internal frictions of various networks at the molecular level between, such as filler-filler, filler-rubber and rubber-rubber networks. Usually the latter dominates the heat build-up in most cases.[9] As most rubber materials have a low-thermal conductivity, the generated heat is accumulated, leading to the local high temperature. As a result, the high temperature aggravates the utilized properties and accelerates the aging of composites greatly. In actual, the damage of numerous rubber products, serving in the dynamic condition, results from the local high temperature. Currently, much work has been done for solving this problem mainly through one strategy that is to decrease the heat build-up of the rubber composite, mostly by enhancing filler-rubber

interaction and improving the filler dispersion. For example, the novel tin-coupled solution polymerized butadiene styrene rubber (SSBR) can be used in the lower heat build-up tread rubber by improving the interaction between carbon black and rubber matrix through the breakage and regeneration of Tin-carbon bond;[10–14] the filler-rubber interaction in the silica filled rubber system is improved effectively through the silane-coupling agent,[14–19] etc. In author's opinion, another effective way is to transport the generated heat from inner to outside. Short stainless steel fiber filled rubber composites have been studied by authors.[20] Although short stainless steel fiber can enhance the thermal conductivity effectively, it is harmful to the reinforcement of rubber composites remarkably. According to the nano-reinforcement theory of rubber,[1,2,5,6,21] here we brought out a new method: employing a kind of nano-sized thermal conductive filler, improving its dispersion by suitable methods, and then achieving the lower heat build-up, higher thermal conductivity and better mechanical properties.

Nano-sized zinc oxide (ZnO) is a kind of inorganic multifunctional filler with excellent bacteria restraint, ultraviolent resistance, and thermal conductivity, which has been developed in large scale recently. In the field of rubber science and technology, most of relevant researches about nano-ZnO focused on using them as a substitute of micro-ZnO for the action component of sulfur vulcanization system of rubber compounds.[22–26] In addition, Mu and Sim et al.[27–29] only investigated the thermal conductivity of nano-ZnO filled silicon rubber for heat dissipation purposes, without studying the dynamic mechanical properties of silicon rubber composites. To the best of our knowledge, systematically investigating the mechanical properties, the dynamic mechanical properties and the thermal conductivity of nano-ZnO highly filled rubber composites has not been reported in the literature.

In this article, the nano-ZnO filled EPDM composites are prepared, and we design the method to improve the nano-particle dispersion and the filler-rubber interaction. The mechanical (static and dynamic) properties and the thermal conductivity have been investigated comprehensively. Some interesting and valuable experimental results are found.

EXPERIMENTAL PART

Materials

Ethylene propylene diene monomer (EPDM, Grade 4045) is purchased from Jilin Chemical Industry (China), nano-sized ZnO is provided by Shanxi Four High NanoTechnology (China), Carbon black (Grade N330) is bought from Tianjin Dolphin Carbon Black (China), Precipitated silica (Grade Tokusil 225) is supplied by Nanji Chemical Industry (China), Bis-(3-thiethoxy silylpropyl)-tetrasufide (Si69) is purchased from Nanjing Shuguang Chemical Group (China), and Other reagents such as Naphthenoid oil, Antioxidant 4010NA, Accelerator Tetramethyl thiuram disulfide (TMTD), Accelerator 2-Mercaptobenzothiazole, Stearic acid, Activated ZnO, and Insoluble sulfur S are all commercially available products.

Compound recipes

Untreated nano-ZnO filled composites: EPDM 100 phr (Parts per hundred part rubber), naphthene oil 20 phr, ZnO 5 phr, Stearic acid 1 phr, TMTD 1.5 phr, 2-Mercaptobenzothiazole (M) 0.5 phr, Insoluble Sulfur 1.5 phr, Antioxidant 4010NA 0.5 phr, nano-ZnO* (*The content of nano-ZnO is 10, 20, 40, 60, 80, 110, 140, 180, and 210 phr, respectively).

In-situ modified nano-ZnO filled composites have the same composition as the recipe of untreated nano-ZnO filled system, but additionally with the silane-coupling agent Si69 8 phr.

Traditional reinforcing fillers filled composites: (i) the composition is same as the recipe of untreated nano-ZnO filled system, but carbon black N330 80 phr is filled respectively instead of nano-ZnO; (ii) the composition is same as the recipe of in-situ modified nano-ZnO filled system, but silica 80 phr is filled instead of nano-ZnO.

Preparation and vulcanization of the composites

The rubber and all the additives are mixed using a 6-inch two-roll mill. Then the compounds are cured in the XLB-D 350 × 350 hot press (Huzhou Eastmachinery, China) with 15 MP pressure at 160°C for their optimum cure time T_{90}, which is tested by using the Disk Oscillating Rheometer (P3555B2, Beijing Huanfeng Chemical Machinery Experimental Factory, China).

Mixing operation with the silane-coupling agent at the high temperature for a certain time is often called in-situ modification[16] For in-situ modified nano-ZnO filled composites, EPDM, nano-ZnO, and Si69 are mixed uniformly on a 6 inches two-roll mill. Then, the semi-finished compound is sheared for 5 min in the electrically heated two-roll mill at 150°C (in-situ modification). All the other additives are mixed into the compound gradually at room temperature.

Volume fraction

Volume fraction is calculated through the following equation, according to the filler amount, density of filler, and density of rubber composites.

$$\phi = \frac{m_F / \rho_F}{m_C / \rho_C} \times 100\%$$

where ϕ is the volume fraction, m_F is filler amount, m_C is total amount of the composite, ρ_F and ρ_C are density of filler and rubber composites, respectively.

Tensile and tear tests

Specimens were die-cut from the vulcanized sheet and tested after at least 16 h storage at room temperature. The mechanical properties of the composites were tested by the Type CMT4104 universal materials tester (SANS, Shenzhen, China) at 23°C, as described by ASTM D 412 and ASTM D 624 test methods.

Dispersion morphology tests

For SEM characterization, micrographs of tensile-section of specimens are obtained by using S4700 scanning electron microscope (Hitachi Corporation, Tokyo, Japan), with an accelerating voltage of 20.0 KV.

TEM observations are performed on an H-800-1 transmission electron microscope (Hitachi, Tokyo, Japan) with an acceleration voltage of 200 KV to acquire a direct visualization of the distribution state of nano particles in the composites. The ultrathin sections of cured nano-ZnO filled composites for TEM experiments are microtomed at about −100°C and collected on a copper grid.

FT-IR tests

Fourier transform infrared (FTIR) analysis is performed on a TENSOR 27 FTIR spectrometry (Bruker Optik GmbH, Germany). The operating conditions are 4 cm^{-1} resolution with 64 scans being averaged.

Modified nano-ZnO sample is prepared as following steps: (1) nano-ZnO particles are wet-pretreated by Si69/Ethanol solution (V_{Si69}:$V_{Ethanol}$ = 1:10) and dried in the vacuum oven at 80°C for 4 h to remove the ethanol; (2) wet-pretreated nano-ZnO particles are heated in the vacuum oven at 150°C for 30min; (3) the Soxhlet exaction with ethanol is carried out to remove the unreacted Si69 molecules for 72h; (4) modified nano-ZnO particles are dried at 100°C for 4 h finally.

Thermal conductivity tests

Thermal conductivity measurements are carried out under steady state condition by using HC-110 thermal conductivity tester (Laser Comp, MA). Disc
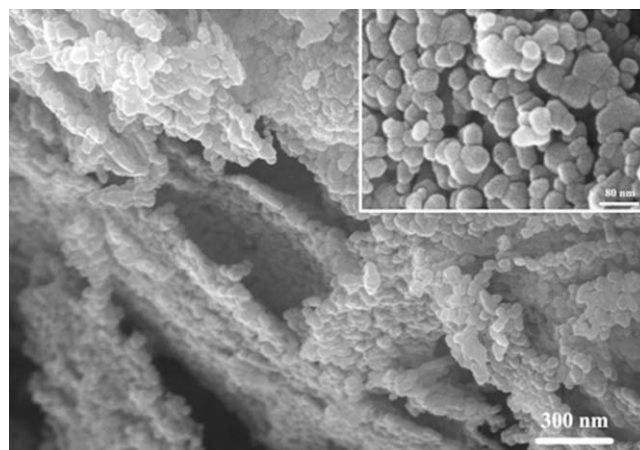
Figure 1 SEM micrograph of nano-ZnO particles.

shaped specimens are 60 mm in diameter and 6.0 mm in thickness. Measurements are carried out with the specimens clamped between the cooling calorimeter and heating calorimeter. The temperature of cooling calorimeter and heating calorimeter are set at 20°C and 40°C separately and the contact pressure was 414 KPa.

Strain sweep measurements

Dynamic properties tests are performed in the RPA2000 rubber process analyzer (Alpha Technologies Co., Akron, OH). The specimens are first vulcanized in the die cavity at 160°C for T_{90}, followed by an air-cooling step to 60°C. The tangents of the loss angle (tanδ) of vulcanized compounds are tested at 60°C and 1 Hz as a function of strain amplitude from 0.28 to 100%. The dynamic storage modulus G' of gross rubber is measured at 60°C and 1 Hz as a function of strain amplitude from 0.28 to 450%.

Compression fatigue tests

Compression dynamic deformation rate and heat build-up of the vulcanized compounds are obtained using YS-III (Beijing Wanhuiyifang Science, China). Cylinder shaped specimens are 29 mm in diameter and 25.0 mm in height. The testing conditions are 4.45 mm of compression stroke, 1 MPa of compression load, 55°C of environmental temperature and 25 min of testing time.

RESULTS AND DISCUSSION

Morphology observations

As shown in Figure 1, nano-ZnO particles are mainly spherical particles in shape, constituting the comb-like layer structure through strong attractive
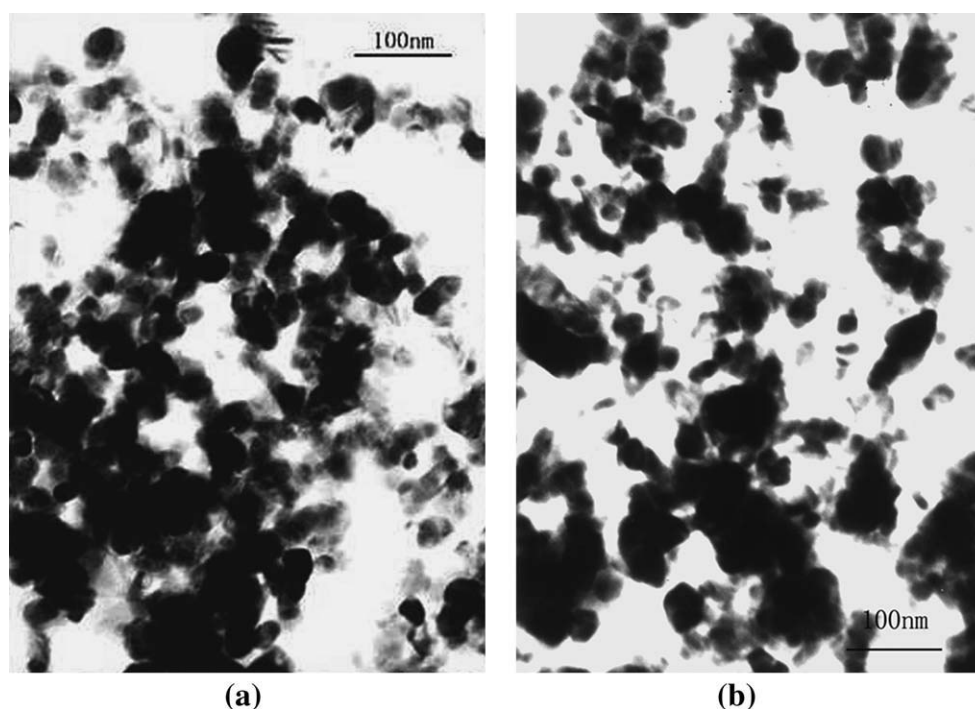
Figure 2 TEM micrographs of nano-ZnO filled EPDM composites at the loading of 180 phr: (a) untreated nano-ZnO filled composites; (b) in-situ modified nano-ZnO filled composites.

forces. Because of the wide distribution of particle diameters and self-aggregation of nano-ZnO particles, the diameter of particles is roughly estimated from 30 to 80 nm. The diameter of most of primary nano-ZnO particles is $\sim$ 50nm.

The dispersion state of filler is important to not only the reinforcement of elastomer but also the thermal conductivity, as under reinforcement science and the percolation theory.[5] Figure 2 displays the dispersion state of nano-ZnO particles in EPDM composites at the loading of 180 phr. As shown in Figure 2(a), many clusters can be observed in the untreated nano-ZnO filled composites, which suggests that the dispersion state is bad because of strong self-aggregation of nano-ZnO particles. However, after in-situ modification procedure, the dispersion state of nano-ZnO particles in the composite is improved obviously, with fewer agglomerates in the TEM micrograph as shown in Figure 2(b). Additionally, more nano-ZnO particles are dispersed on the scale of less than 100 nm, which will lead to the better mechanical properties and dynamic properties.

Figure 3 shows the tensile fracture surface morphology of untreated and in-situ modified nano-ZnO filled composites at the loading of 180 phr by SEM. Effect of in-situ modification with Si69 on the interfacial interaction and the dispersion state of filler can be observed clearly. Bulk clusters can be clearly seen in untreated nano-ZnO filled system, as well as large gaps between clusters and rubber matrix, as shown in Figure 3(a). Whereas, the large

gaps disappear completely after in-situ modification as expected, which indirectly suggests that the chemical bonding between the particle surface and rubber matrix might form. Some regions, which look like clusters, seem to be combination of nano-ZnO particles enrichment region penetrated and encapsulated by the rubber chains. In summary, in-situ modification can improve the dispersion state of nano-ZnO particles remarkably by enhancing the interfacial interaction through chemical bonding.

Payne effect

The Payne effect is the particular characteristics of rubber, especially rubber composites containing nano-sized fillers. It is manifested as a dependence of the viscoelastic storage modulus on the amplitude of the applied strain. For a certain applied strain amplitude, the storage modulus decreases rapidly with the increase of the strain amplitude. At sufficiently large strain amplitude, the storage modulus approaches to a low plateau. From a fundamental point of view, the Payne effect is associated with the change of the material's microstructure induced by deformation, that is, the breakage and recovery of filler network formed through physical interactions between adjacent filler clusters. The Payne effect is directly related to the filler network structure and thus mainly depends on the filler content, the filler-filler interaction, the filler-rubber interaction, and the dispersion state of filler.[30,31]
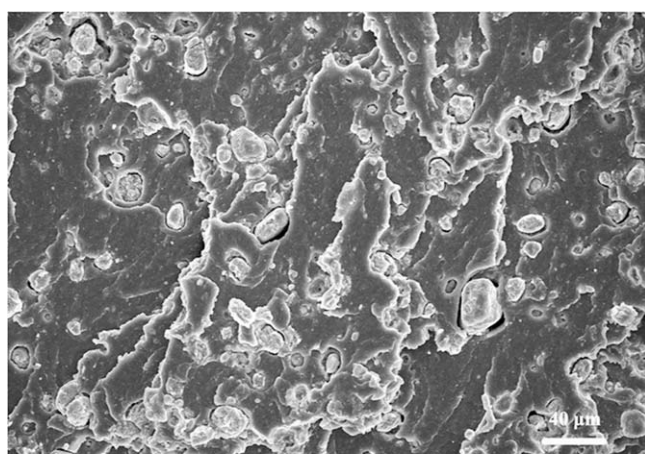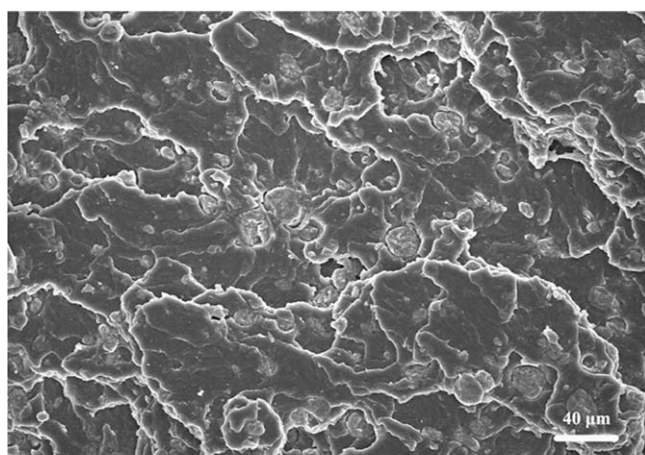
Figure 3 SEM micrographs of tensile fracture morphology of nano-ZnO filled EPDM composites at the loading of 180 phr: (a) untreated nano-ZnO filled composites; (b) in-situ modified nano-ZnO filled composites.

We study the Payne effect to indirectly characterize the filler network structure and the spatial dispersion state of nano-ZnO particles in EPDM matrix. The influence of in-situ modification on the Payne effect of nano-ZnO filled systems with respect to the applied strain at different nano-ZnO loadings is presented in Figure 4, respectively. As shown in Figure 4(a,b), there occurs a plateau region in the storage modulus versus strain curve at a certain content, and the shear storage modulus G' of gross rubber quickly decreases over the critical strain. The higher the filler content the stronger the network structure, and consequently the greater is the initial value of shear storage modulus G'. Filler networks exist in both untreated and treated nano-ZnO filled composites, but the structure and stability of filler networks are different. Figure 4 shows that the initial value of storage modulus of untreated nanocomposites is higher than that of treated nanocomposites at the same filler loading.

Additionally, for untreated nano-ZnO filled EPDM system, the critical strain corresponding to the abrupt decrease of the storage modulus decreases with the filler loading, and the initial modulus increases. In contrast, for the in-situ modified nano-ZnO filled system, the plateau region maintains within a large range of applied strain and the critical strain is increased greatly, especially at high filler loadings, which indicates that the filler network structure is more stable. The main reason is that, it is easier for untreated nano-ZnO particles to form the stronger filler network, which should be attributed to the high surface tension and self-aggregation of nano-ZnO particles. The in-situ modification with Si69 would weaken the interactions between filler particles by grafting the organic molecules, and enhance the interfacial interaction between filler particles and rubber
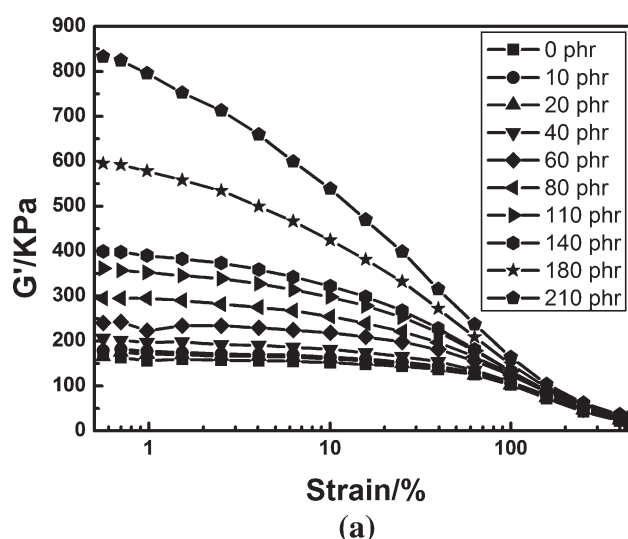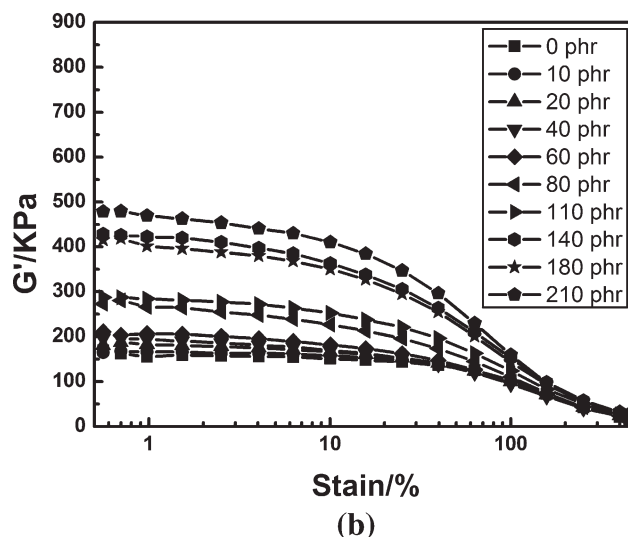
Figure 4 Payne effect of nano-ZnO filled gross rubber: (a) untreated nano-ZnO filled composites; (b) in-situ modified nano-ZnO filled composites.
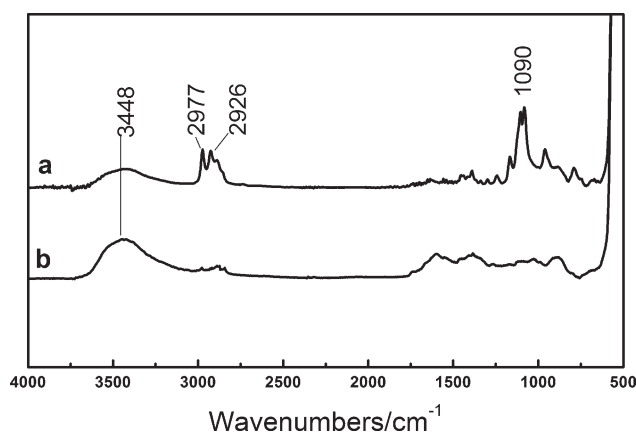
Figure 5 Comparison of normalized FT-IR spectra among: (a) Si69 treated nano-ZnO particles; (b) untreated nano-ZnO particles.

chains through chemical bonding, and therefore decrease the filler agglomeration effectively, leading to the formation of the more stable filler network structure and the lower shear storage modulus.

Mechanism of in-situ modification with Si69

The silane-coupling agent Si69 is a kind of bifunctional coupling agent, which is widely used to modify the polar inorganic nanofillers to enhance the interfacial interaction and improve the dispersion state in the rubber matrix.[19,32,33] Here we characterize nano-ZnO particles by FT-IR to examine whether the chemical reactions occur during the in-situ modification, just as we expected. As it is difficult to extract the Si69 in-situ modified nano-ZnO particles from the

gross rubber compound, the modified nano-ZnO particles were prepared through pretreating with Si69 at the same temperature for FT-IR characterization, instead of in-situ modification process. As shown in Figure 5, compared with the infrared spectrum of untreated nano-ZnO, the band of hydroxide group ([—]OH) located at 3448 cm^{-1} declines obviously, which is possibly attributed to the reaction between the hydroxide group on the nano-ZnO particles surface and the silicon coupling agent Si69 during the in-situ modification. The peaks at 2977 cm^{-1} and 2926 cm^{-1}, which are methylene ([—]CH$_2$[—]) and methyl group ([—]CH$_3$) respectively, increase slightly. As the silicon-oxygen bond, as the part of the silane-coupling agent, surely comes from Si69, the appearance of the band of silicon-oxygen bond ([—]Si[—]O[—]) at 1090 cm^{-1} reconfirms that the reaction indeed takes place. Based on the results from FT-IR spectra, it can be concluded that there exists the reaction between the hydroxide group on the nano-ZnO particles surface and the silane-coupling agent Si69 during the pretreatment, and the same chemical reaction probably takes place during the in-situ modification process.

Figure 6 shows the schematic of the reactions. First, the coupling agent needs to be grafted on the surface of nano-ZnO particles through the condensation reaction between the hydroxide group and the ethoxyl. The second step is that the multi-sulfur bond will be broken and the new generated single sulfur bond or multi-sulfur bond will be connected to the rubber chains with the curing ingredient sulfer together to constitute the cross-linking network.
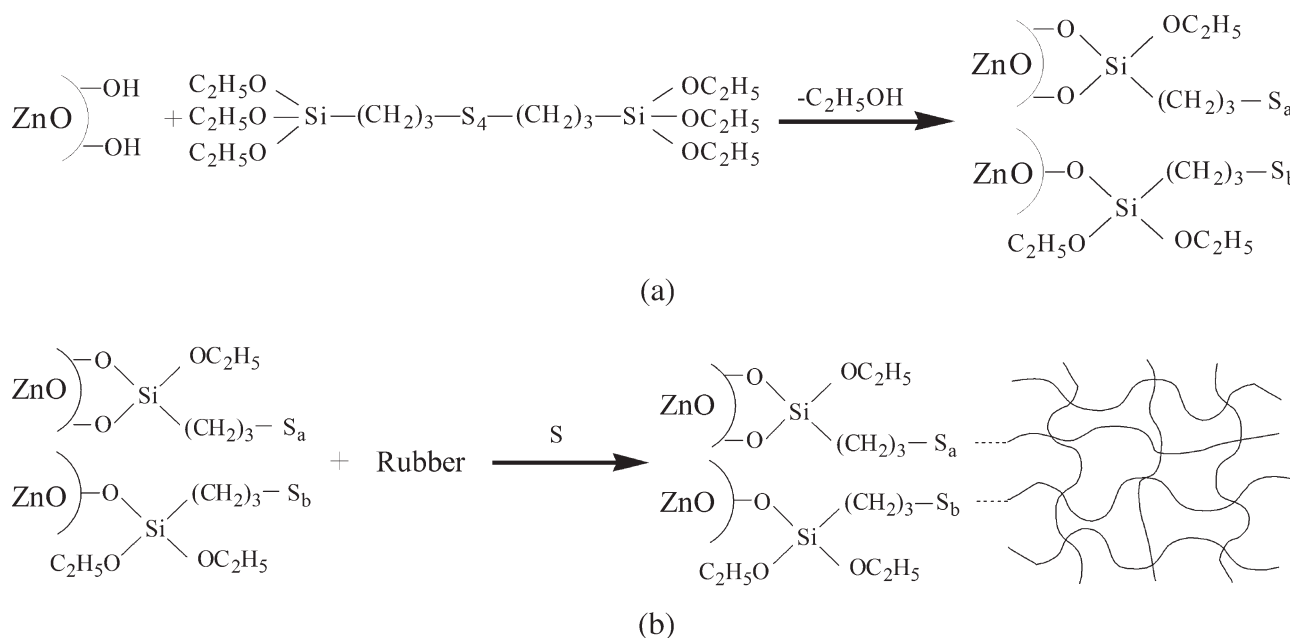

(a)

(b)

Figure 6 Schematic of the reactions during the in-situ modification procedure: (a) Reaction between nano-ZnO particles and silane-coupling agent Si69; (b) Reaction between modified nano-ZnO particles and rubber chains during vulcanization.
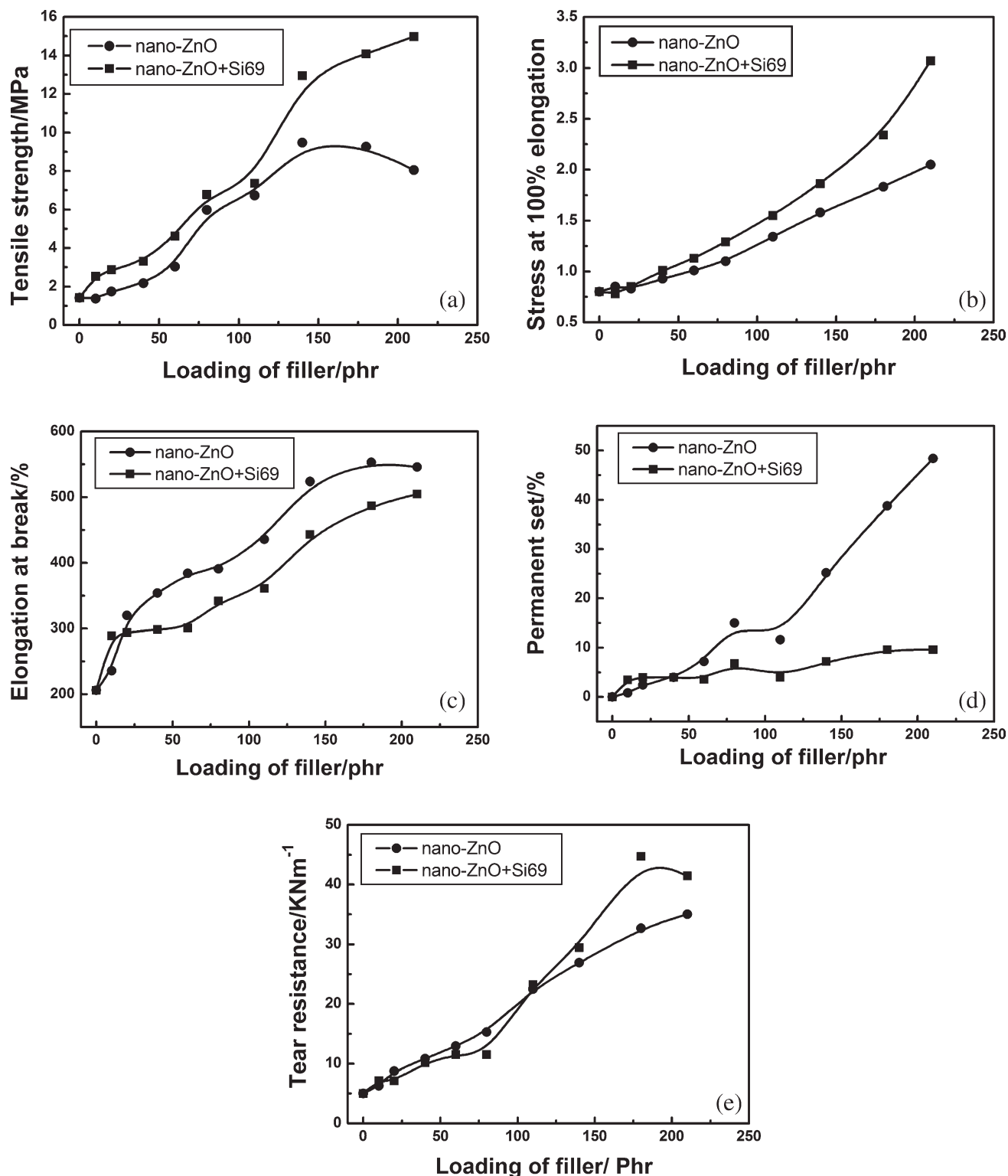
Figure 7 Influence of in-situ modification on the mechanical properties of nano-ZnO filled composites as a function of the filler loading: (a) tensile strength; (b) stress at 100% elongation; (c) elongation at break; (d) permanent set after tension; (e) tear resistance.

Mechanical properties

The influences of in-situ modification with Si69 on the tensile strength, stress at 100% elongation, elon-

gation at break, permanent set after tension, and tear resistance of nano-ZnO filled EPDM vulcanizates with respect to the filler loading are presented in Figure 7, respectively. Figure 7(a) shows that the

tensile strength of composites is enhanced with the increase of the nano-ZnO loading. The in-situ modified nano-ZnO filled composites exhibit greater tensile strength than that of untreated nano-ZnO filled system at the same filler content. It is noteworthy mentioning that the tensile strength of in-situ modified nano-ZnO filled EPDM vulcanizates reaches about 15 MPa at the filler loading of 210 phr, which is $\sim$ 15 times greater than that of pure rubber. As is well-known, nano-reinforcing is the predominant condition for the efficient reinforcement of rubber, which has been verified according to many researchers' work.[1,5–7] Worse dispersion state of filler and the existence of huge filler agglomerates in the vulcanizates will aggravate the mechanical properties, which causes that the tensile strength of untreated nano-ZnO filled composites slowly increases and then decreases over a high filler loading earlier in comparison with in-situ modified nano-ZnO filled system, just as shown in Figure 7(a).

Figure 7(b) indicates that after in-situ modification with Si69 the stress at 100% elongation of nano-ZnO filled composites increases at the same loading, which should be attributed to the formation of chemical bonding between nano-ZnO particles and rubber chains. The enhanced interfacial interaction results in the higher stress at low elongation. Additionally, the increase of the crosslink density of nano-ZnO particles' neighborhood is likely because of the incoming of multi-sulfur bond structure of the silane-coupling agent Si69, which contributes to the enhancement of the deformation resistance. For untreated nano-ZnO filled composites, rubber chains are adsorbed on the particle surface just through physical adsorption, and experience slippage during the stretching, which leads to the lower stress at 100% elongation. Figure 7(c) displays that elongation at break of both untreated and in-situ modified nano-ZnO filled system increases as a function of the filler loading. In most cases, the elongation at break of vulcanizates of in-situ modification is lower than that of untreated system. The probable reason should be attributed to the increase of the cross-linking density as well. Assisted by in-situ modification, the largest elongation at break is still up to $\sim$ 500% at the loading of 210 phr.

Figure 7(d) shows that the permanent set after tension of composites increases with the filler loading, and in-situ modification decreases the permanent set of vulcanizates remarkably. Compared with the untreated nanocomposites, the ratio of the permanent set of the untreated system to that of the modified one is $\sim$ 7 times at the loading of 210 phr. The reason why the permanent set of untreated nano-ZnO filled composites is so large mainly comes from two aspects: (1) the interaction between rubber chains and untreated nano-ZnO particles is mainly
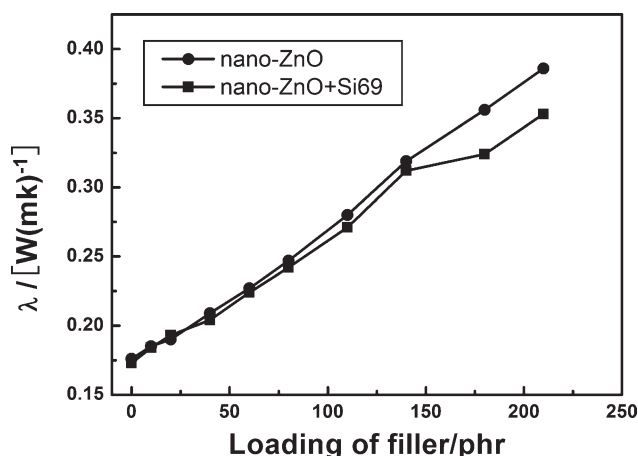

Figure 8 Influence of in-situ modification on the thermal conductivity (λ) of nano-ZnO filled composites as a function of the filler loading.

physical sorption and the rubber chains can slip easily on the particle surface during the stretch; (2) the huge agglomerates are broken into smaller ones under the external stress, which will accelerate the slippage of rubber chains. Additionally, the breakage of clusters is probably irreversible and new clusters would be formed again. Consequently, the rubber chains absorbed onto the surface of nano-ZnO particles could not return to the initial state, which makes the permanent set of untreated nanocomposties much larger. By contrast, the permanent set of the in-situ modification system is smaller, which is attributed to the fact that the chemical bonding between particle surfaces and rubber chains formed during the in-situ modification, will greatly limit the slippage of rubber chains on the particle surface during the tension. Furthermore, a better dispersion of filler particles as well decreases the occurrence and breakage of huge agglomerates during deformation. As shown in Figure 7(e), the tear resistance is not improved significantly by in-situ modification, because of the enhanced interfacial interaction and increased cross-linking density.

Thermal conductivity

Figure 8 displays the influence of in-situ modification on the thermal conductivity of nano-ZnO filled composites. It is observed that the thermal conductivity of both untreated and in-situ modified nano-ZnO filled vulcanizates increases approximately linearly with the filler loading. The maximum thermal conductivity value is up to 0.386 W mK^{-1} at the loading of 210 phr, about over two times greater than that of 10 phr nano-ZnO filled vulcanizate. Furthermore, according to our work the thermal conductivity of nano-ZnO filled composites is much greater than that of traditional reinforcing fillers

filled composites, which will be discussed later. However, excessive pursuit of higher thermal conductivity will deteriorate the mechanical properties of composites and good processing performance, which is a contradiction between them.[29] We also observe, at the same filler content, the thermal conductivity of untreated nano-ZnO filled vulcanizate is a little higher than that of in-situ modified nano-ZnO filled system, but the largest difference is no more than 10%. One probable reason is that in-situ modification improves the dispersion state, which does harm to the formation of thermal conductive chains composed of filler particles and increases the total quantity of filler-rubber interface thermal resistance. Additionally, the other probable reason is that parts of the Si69 molecules grafted on the particle surface during the in-situ modification will enhance the original thermal resistance and decrease the thermal conductivity of nano-ZnO filled composites.

Dynamic mechanical properties

As is well-known, the dynamic mechanical properties are more significant for rubber composites in some sense, especially for the rubber products serving in the dynamic conditions. In general, tanδ and compression fatigue properties of vulcanizates are two important indicators in characterizing the dynamic mechanical properties of rubber composites. Usually tanδ increases with the applied strain, which is attributed to the intrinsic hysteresis nature of rubber and internal frictions of various networks at the molecular level. Tanδ can be used to characterize the dynamic heat build-up property. The less the tanδ is, the less the energy loss under cyclic stress is. As shown in Figure 9(a,b), tanδ of untreated and in-situ modified nano-ZnO filled systems both increases with the applied strain, and meanwhile at the same applied strain tanδ also enhances with the increase of filler loading. For the untreated nano-ZnO filled composites, tanδ of vulcanizates rises more rapidly with the applied strain and is much greater at the same applied strain in comparison with the in-situ modified nano-ZnO filled systems, especially at the high filler content. Because of the strong filler-filler interaction, nanofillers increase tanδ greatly, and the dynamic heat build-up. In fundamental, dynamic heat build-up mainly results from the frictions of various networks such as rubber-rubber, filler-rubber, and filler-filler friction. In theory, steadier filler network will decrease the friction between filler particles effectively, and stronger interfacial interactions between filler particles and rubber chains will decrease the relative slippage and the filler-rubber friction. On the basis of these analyzes, the lower tanδ of in-situ modified nano-ZnO filled composites should be attributed to in-situ modification by enhancing the interactions between filler particles and
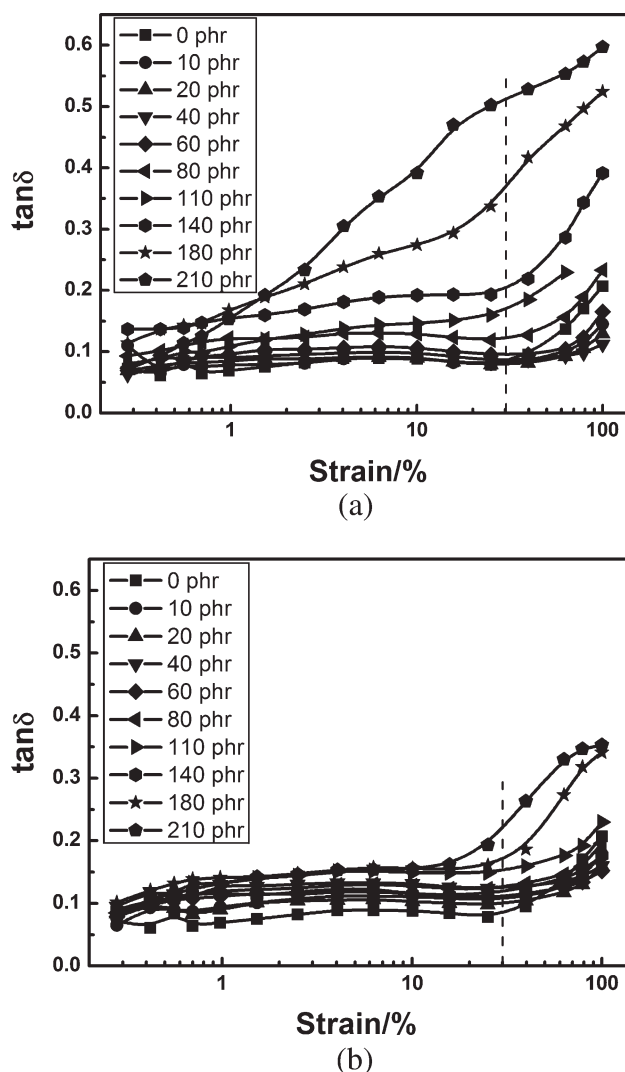

Figure 9 Influence of in-situ modification on tanδ of nano-ZnO filled composites as a function of the filler loading: (a) untreated nano-ZnO filled composites; (b) in-situ modified nano-ZnO filled composites.

rubber chains through chemical bonding, improving the dispersion of filler and forming the steadier filler network. Consequently, the tanδ of in-situ modified nano-ZnO filled system maintained within a lower plateau until the applied strain is over 30%.

Compression fatigue properties are usually used to measure the dynamic mechanical properties of rubber composites directly through compression heat build-up and dynamic compression deformation rate. As shown in Figure 10(a), compression heat build-up of untreated and in-situ modified nano-ZnO filled systems both increase with respect to the loading of nano-ZnO. The in-situ modified nano-ZnO filled composites possess the much lower compression heat build-up than untreated nano-ZnO filled system at the high loading. The compression heat build-up of untreated system is up to 43°C at the loading of 210 phr nano-ZnO, whereas for the
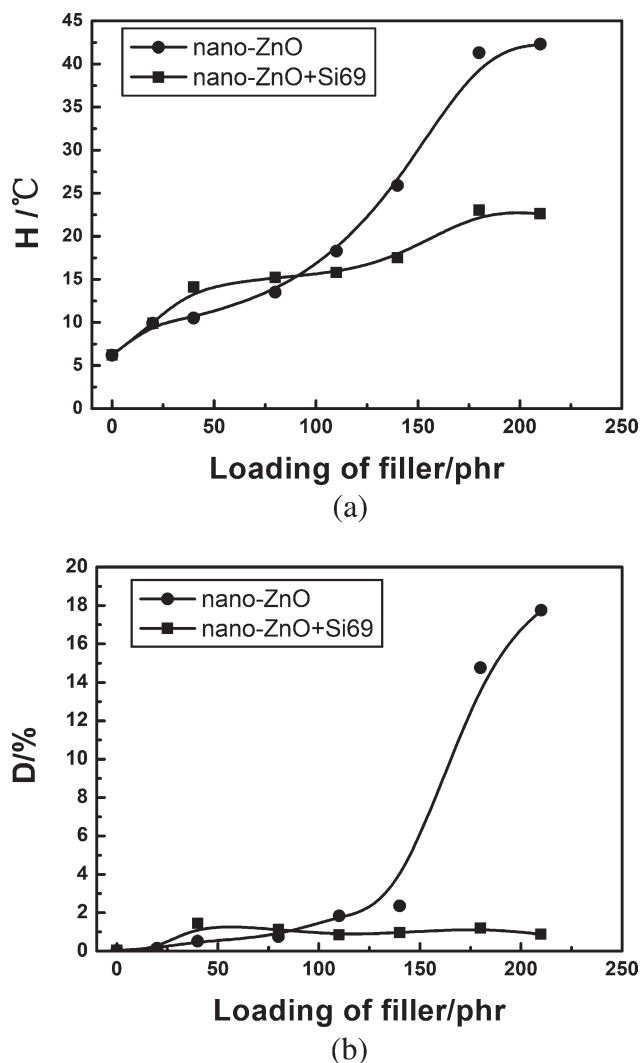
(a)

(b)

Figure 10 Influence of in-situ modification on compression fatigue properties of nano-ZnO filled composites: (a) compression heat build-up; (b) the difference D. H represents the compression heat build-up and D represents the difference between ultimate compression deformation rate and initial one.

in-situ modified nano-ZnO filled system, the heat build-up is no more than 22°C at the same loading, ~ 50% lower. As mentioned before, heat build-up mainly comes from internal frictions of various networks, particularly filler-filler friction and filler-rub-

ber chain friction. The lower compression build-up of in-situ modified nano-ZnO filled system should be attributed to two aspects: (1) In-situ modification with Si69 enhances the filler-rubber interfacial interaction through chemical bonding and weakens the relative slippage and friction of filler-rubber. (2) The formation of steadier filler network induced by the improved dispersion state of filler decreases the filler-filler friction greatly.

Figure 10(b) displays the influence of in-situ modification with Si69 on the difference D of nano-ZnO filled composites. The difference D is defined as the ultimate dynamic compression deformation rate subtracting the initial one. The lower the difference D is, the better the dynamic mechanical properties and elasticity of composites are. As shown in Figure 10(b), compared with the untreated nano-ZnO filled composites, the difference D of in-situ modified nano-ZnO filled system is decreased significantly. For instance, the difference D remains around 1% even in the case of high filler loading for in-situ modified system. The results suggest that in-situ modification can improve the elasticity and dynamic compression fatigue xmechanical properties of nano-ZnO filled composites, which should be mainly attributed to improving the filler dispersion, enhancing the interfacial interaction, transporting the heat from inner to outside in time, and decreasing the internal temperature. For the untreated nano-ZnO filled system, although the generated heat is transported well from inner to outside, the internal high temperature still cannot be avoided because of much strong frictions, especially the filler-filler friction, which leads to the larger difference D indirectly. As a result, the rubber composites by only employing nano-ZnO without in-situ modification probably cannot possess the high performance in dynamic mechanical properties as expected, because of its higher compression heat build-up and larger difference D.

Comparisons to the traditional reinforcing fillers

As is well-known, both of carbon black and nano-sized precipitated silica are the traditional reinforcing fillers widely used in rubber industry. Here we

TABLE I
Comparison of Mechanical Properties and Thermal Conductivity of Composites
Compounded with Nano-ZnO and Traditional Reinforcing Fillers

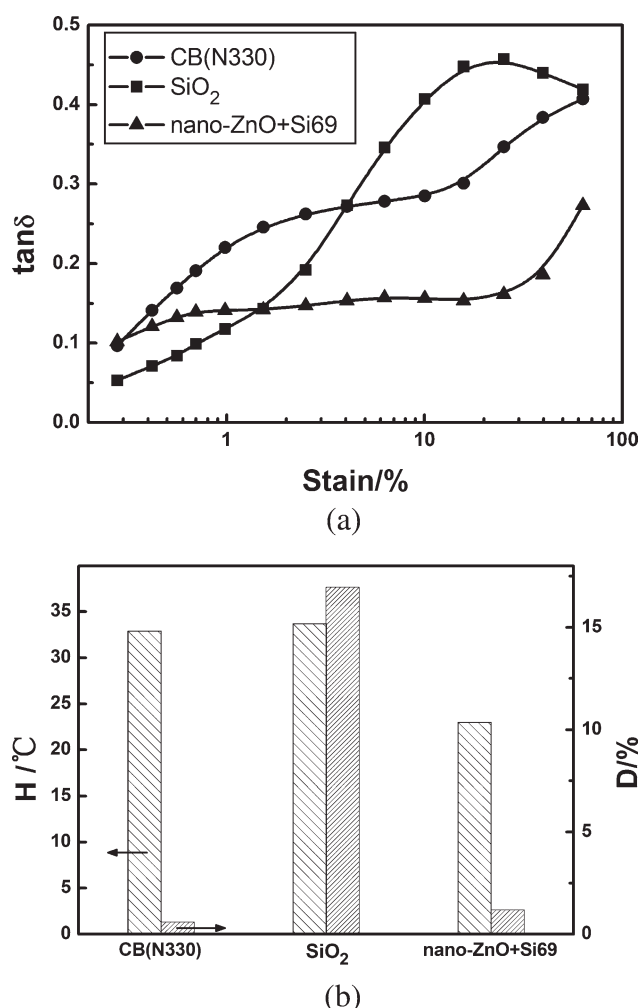|	N330	SiO$_2$	Nano-ZnO+Si69
Loading of filler (phr)	80	80	210
Volume fraction (%)	22.6	20.5	19.8
Tensile strength (MPa)	17.1	15.9	15.0
Tear resistance (KN m^{-1})	41	42	41
Elongation at break (%)	716	670	503
Permanent set (%)	22	15	10
Thermal conductivity λ [W m^{-1}K^{-1}]	0.284	0.262	0.353

(a)

(b)

Figure 11 Comparison of dynamic mechanical properties among composites compounded with nano-ZnO and traditional reinforcing fillers: (a) tanδ; (b) compression fatigue properties. H represents the compression heat build-up and D represents the difference between ultimate compression deformation rate and initial one.

compare the mechanical properties, thermal conductivity, and dynamic mechanical properties of composites by employing the similar filler volume fraction of in-situ modified nano-ZnO, carbon black N330, and nano-silica, respectively. As shown in Table I, the filler volume fractions are chosen within a small range around 20%, and the nano-ZnO volume fraction is about 19.8%. The tensile strength of in-situ modified nano-ZnO filled composite is up to 15.0 MPa, and the tear resistance is 41 KN m^{-1}, which is close to that of traditional reinforcing fillers filled composites. Additionally, the elongation at break of nano-ZnO filled system is up to 503%, and meanwhile the permanent set is only 10%, the smallest one of the three vulcanizates. The thermal conductivity of nano-ZnO filled composite is $\sim$ 25% higher than that of carbon black N330 filled composite and 35% higher

than nano-silica filled composite at the similar volume fraction.

Figure 11 displays tanδ and compression fatigue properties of various composites by employing in-situ modified nano-ZnO and traditional reinforcing fillers. As shown in Figure 11, the tanδ of in-situ modified nano-ZnO filled composite is lower than that of traditional reinforcing fillers filled composites at a certain strain, as well as the much lower compression heat build-up and the smaller difference D. The result is in good agreement with those illustrated in Figures 9 and 10. Based on the comparisons above, it can be concluded that in-situ modified nano-ZnO is successful in enhancing the thermal conductivity of composites more remarkably than traditional reinforcing fillers such as carbon black N330 and silica, and meanwhile it can reinforce the EPDM well, which can probably satisfy the mechanical performance requirements of rubber products in most cases. Consequently, because of all these better performance, especially the dynamic mechanical properties, nano-ZnO can be considered as a kind of novel potential thermal conductive reinforcing filler, which is a better candidate for reinforcing rubber products serving in the dynamic conditions.

CONCLUSIONS

1. Nano-ZnO can enhance the thermal conductivity greatly, and perform well in the reinforcement of EPDM rubber as well. The dynamic mechanical properties are not good enough, because of the strong filler-filler interaction.
2. In-situ modification with Si69 can improve the static and dynamic mechanical properties of nano-ZnO filled composites effectively by enhancing the interfacial interaction, without influencing the thermal conductivity obviously.
3. Compared with the traditional reinforcing fillers such as carbon black N330 and silica, nano-ZnO particles assisted by in-situ modification increase the thermal conductivity greatly and perform well in reinforcing the EPDM matrix. As a result, it can be expected that nano-ZnO should be suitable for rubber products serving in dynamic conditions, extending the service life significantly.

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