

Mechanical and Dynamic Mechanical Properties of Natural Rubber Blended with Waste Rubber Powder Modified by Both Microwave and Sol-Gel Method

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ABSTRACT: Waste rubber powder (WRP) was modified by microwave, sol-gel method, and both microwave and sol-gel method, respectively. The mechanical and dynamic mechanical properties of natural rubber (NR)/modified WRP composite were investigated. The influence of bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) content on curing characteristics and mechanical properties of vulcanizate was also studied. The results showed that NR/WRP modified by both microwave and sol-gel method composite owned the best mechanical properties. Rubber processing analyzer was used to characterize the interaction between silica and rubber chains and the dispersion of silica. With increase of TESPT content, the Payne effect decreased. Scanning electron microscopy indicated the coherency and homogeneity of *in situ* generated silica filled vulcanizate. Dynamic mechanical analyzer showed that NR/WRP modified by both microwave and sol-gel method composite with 5 phr TESPT exhibited the lower $\tan \delta$ at temperature range of 50–80°C, compared with composite without TESPT and the higher $\tan \delta$ at temperature of 0°C, compared with the conventional modification of WRP. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2313–2320, 2013

KEYWORDS: rubber; recycling; composites; mechanical properties

Received 24 August 2012; accepted 21 December 2012; published online 17 January 2013

DOI: 10.1002/app.38954

INTRODUCTION

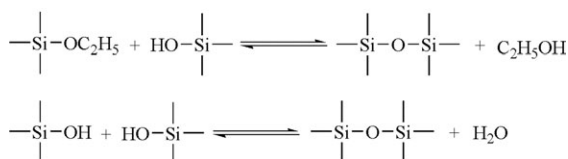
With the gradual increase of the rubber products, recycling of rubber materials has been an issue of environmental concern for some years. Recovery and recycle of rubber from used and scrap rubber products can save some precious petroleum resources as well as solve waste rubber disposal problems. Recently, great effort is put into improving recycling and finding new application for recycled rubber materials. In some developed countries, waste rubber is pulverized into powder to be a replacement of virgin rubber. This opens up a route for utilizing waste rubber and makes the rubber products cheaper. Unfortunately, the incorporation of waste rubber powder (WRP) into rubber matrix significantly impairs the mechanical and viscoelastic properties, because WRP with three-dimensional structure being insoluble and nonmelting does not blend with virgin rubber very well. For this reason, WRP has to be modified by some methods before it is added to virgin rubber. The purpose of WRP modification is to break the sulfur crosslink, allow the rubber to regain mobility for better reprocessability and remoldability and increase compatibility between virgin rubber and WRP. This modification of WRP can be

obtained by physical or chemical methods. Although much research on modification of WRP has been studied, all methods can be categorized into two groups that the first is the broken three-dimensional network and the second is the unbroken three-dimensional network. The former group mainly contains mechanochemical method,^{1–3} microwave,^{4,5} microbial devulcanization,^{6–9} and ultrasound.^{10–13} Through these methods, three-dimensional network of WRP is cut off and WRP can be easily compatible with the virgin rubber during compounding. The latter group mainly contains grafting method^{14–17} and sol-gel method.¹⁸ Compared with the former group, the latter technique does not break the three-dimensional network and sometimes provides WRP with some particular properties. However, when WRP is modified by former technique, the modification process is often accompanied with the main rubber chains degradation, which impairs the mechanical properties of virgin rubber/WRP composite. For example, mechanochemical modification method of WRP, carried out in an open two roll mixing in the presence of reclaiming agent, was a very conventional method. During this modification process, on one side milling action was able to promote the breakage of crosslinking network

Hydrolysis:



Condensation:



Overall reaction:



Figure 1. Hydrolysis and condensation reactions of TEOS.

by shear stress, which increased the compatibility between virgin rubber and WRP. On the other side, main rubber chains were also cut off by shear stress, which decreased the mechanical properties of rubber composite. Another technique named “microwave” was used to break crosslinking bonds by heating. The use of microwave for heating purpose had the advantage of volumetric heating, which was faster and promoted a more homogeneous heating than other methods based on convection and conduction. Scuracchio et al.⁵ used thermogravimetric analysis to understand ground tire rubber structure changing during microwave treatment. With increase of treatment time, the thermo-oxidation peak of the main rubber chains disappears gradually. Zanchet et al.⁴ realized that the microwave treatment of WRP caused both crosslink scission and main rubber chains degradation. The degradation of the main rubber chains created shorter rubber molecule chains and deterioration of the mechanical properties of virgin rubber/WRP composite.

To avoid a large number of rubber chains degradation and further improve the mechanical properties of natural rubber (NR)/WRP composite, WRP can be modified by both the former technique and the latter technique. In this article, more emphasis was put on the preparation of WRP modified both by microwave and sol-gel method and the mechanical and dynamical mechanical properties of NR blended with WRP modified by both microwave and sol-gel method. First WRP was devulcanized by short time microwave treatment. This step caused the certain degree devulcanization of WRP, which increased the compatibility with NR, improved swelling degree, and did not result in a large number of rubber chains degradation. Second WRP-silica hybrid materials were prepared by sol-gel process. This step was achieved by immersing WRP modified by microwave in tetraethoxysilane (TEOS) together with catalyst. During hydrolysis and condensation process, inorganic silica was generated as shown in Figure 1. Then the modified WRP (MWRP) was added to NR. To improve the dispersion of *in situ* generated silica, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) was used. The dynamic mechanical properties and the filler network were also investigated by rubber processing analyzer (RPA) and dynamic mechanical analyzer (DMA). To directly observe the coherency and homogeneity of *in situ* generated silica filled vulcanizate, scanning electron microscopy (SEM) was used.

EXPERIMENTAL

Materials

NR was provided by Jincal Processing Co. (Sanya, China). WRP was supplied by Guangdong Hehong Rubber Material Factory (Guangdong, China). TEOS was used as precursor of silica, which was obtained from Aladdin Chemistry Co. Ltd. (Shanghai, China). The catalyst was *n*-butylamine which was provided by Aladdin Chemistry Co. Ltd. (Shanghai, China). TESPT was purchased from Guangzhou Jinshengchang Co. Ltd. (Guangdong, China). Other compounding ingredients were standard grade in the rubber industry.

Sample Preparation

Microwave Treatment of WRP. WRP was treated in an adapted microwave apparatus. The power of magnetron was set up to 800 W and the exposure time was 20 s.

***In Situ* Generation of Silica in WRP by Sol-Gel Method.** WRP and WRP modified by microwave were swollen in TEOS at 40°C for 48 h and then soaked in a 10% aqueous solution of *n*-butylamine at 40°C for 24 h. Then the samples were dried for several days at 50°C to constant weight under a reduced pressure.

Preparation of NR/WRP Composite. NR was masticated on a two-roll mill with 0.5 mm roller spacing and then blended with zinc oxide, stearic acid, accelerator diphenylguanidine (DPG), accelerator dibenzothiazyl disulfide (MBTS), sulfur, WRP, and different kinds of MWRP respectively. The basic formulation of the rubber compounds is listed in Tables I and II. The cure characteristics of the rubber compounds were determined by Moving Die Rheometer at 145°C. The rubber compounds were

Table I. Mix Formulation and Mechanical Properties of NR Blended with Different Kinds of MWRP Compound

	Sample 1	Sample 2	Sample 3	Sample 4
Ingredients (phr)				
NR	100	100	100	100
Zinc oxide	4	4	4	4
Stearic acid	2	2	2	2
DPG	0.6	0.6	0.6	0.6
MBTS	1.2	1.2	1.2	1.2
WRP	40			
MWRP		40	40	40
Sulfur	2	2	2	2
Mechanical properties				
300% modulus (MPa)	3.51	4.02	4.54	4.65
Tensile strength (MPa)	10.76	13.58	15.32	16.12
Tear strength (kN/m)	27.99	28.77	33.47	33.52
Elongation at break (%)	464.33	501.65	523.16	527.36

Sample 1 was the composite of NR with 40 phr WRP. Sample 2 was the composite of NR with 40 phr WRP modified by microwave. Sample 3 was the composite of NR with 40 phr WRP modified by sol-gel method. Sample 4 was the composite of NR with 40 phr WRP modified by both microwave and sol-gel method.

cured at 145°C by compression molding in a hydraulic press according to their optimum cure time obtained by Moving Die Rheometer. The vulcanized samples were stored at room temperature for at least 24 h before testing.

Characterization

Mechanical Tests. Electron tensile tester (WDW-0.5, Hualong) was used to measure the modulus, tensile strength, elongation at break, and tear strength of the vulcanizate according to ASTM D 412 (tensile strength) at a uniform speed of 500mm/min and ASTM D 624 (tear strength).

Fourier Transform Infrared Analysis. The Fourier transform infrared (FTIR) experiments were performed on a Perkin–Elmer spectrometer at room temperature and spectra were taken from 4000 to 650 wavenumbers (cm^{-1}).

Rubber Processing Analysis. The dynamic storage modulus and the loss factor ($\tan \delta$) of the vulcanizate were measured with RPA (MFR, Prescott, AZ). Strain sweep from 0.7% to 100% was operated at 60°C, 1 Hz.

SEM. SEM (S-4800, HITACHI) was used to observe the cryogenically fractured surface and the tensile surface of S_0 and S_5 vulcanizates.

Dynamic Mechanical Analysis. The dynamic mechanical analysis of vulcanizate was measured using DMA (2421/G, NETZSCH). The run condition for DMA was tension mode at a fixed frequency of 10 Hz. The temperature range was from –100 to 100°C, at a heating rate of 3°C/min.

RESULTS AND DISCUSSION

Mechanical Properties of NR Blended with Different Kinds of MWRP

The mix formulation and mechanical properties of NR blended with different kinds of MWRP are shown in Table I. Sample 1 possessed the lowest mechanical properties. WRP with three-dimensional structure was insoluble and nonmelting and did not blend with NR very well. So the surface adhesion between NR and WRP was very low. In addition, during vulcanization process of NR/WRP composite, the postcure of WRP resulted in the reduction of sulfur in the rubber matrix and reduction of the mechanical properties of composite, due to the migration of sulfur from rubber matrix into WRP.^{19,20} So NR directly blended with WRP owned the lowest mechanical properties of rubber composite. WRP of Sample 2 was modified by microwave. Microwave, one of the most promising treatment, uses the source of energy radiation to cut off crosslinking bonds (the C–S and S–S linkages). After microwave treatment, some of crosslinking bonds were cut off, which increased the compatibility between NR and WRP. So Sample 2 owned higher mechanical properties than Sample 1. Silica offering better tear strength, better abrasion resistance, and less heat than carbon black was an important reinforcing filler. In Sample 3, *in situ* polymerization of TEOS on the surface of WRP was adopted and WRP filled with the *in situ* generated silica was prepared by sol–gel reaction. Through reinforcement of *in situ* generated silica, mechanical properties of Sample 3 improved. However, when WRP with three-dimensional structure was immersed in TEOS for

in situ generated silica, a few TEOS was penetrated into WRP and the effect of silica reinforcement was restricted. To overcome this problem and further improve properties of rubber composite, Sample 4 was treated by microwave first. During conventional microwave recycling process, the temperature of WRP with carbon black reached 260–350°C fast. This temperature can break both crosslinking bonds and carbon–carbon bonds. Macromolecular rubber chains were transformed into small molecular fragments. When NR was blended with this MWRP, small molecular fragments acted as stress concentration points and mechanical properties of rubber composite decreased. In Sample 4, the novel modification method used short time microwave treatment to devulcanizate WRP. On the one hand, a fraction of three-dimensional network was cut off by microwave, which improved the compatibility between NR and WRP. During short time microwave process, a large number of rubber main chains avoided degradation. On the other hand, devulcanization of WRP improved swelling in TEOS. Then WRP was modified by sol–gel method. Much more TEOS can be penetrated into WRP, due to the improvement of swelling in TEOS, and the number of *in situ* generated silica increased. Through reinforcement of *in situ* generated silica and improvement of the compatibility between NR and WRP, Sample 4 owned the highest mechanical properties.

Effect of Different TESPT Content on the Composite of NR/WRP Modified by Both Microwave and Sol–Gel Method

In this section, WRP was modified by both microwave and sol–gel method and then was added to NR. Silica has been increasingly used to reinforce rubber products. But a problem of silica reinforcing rubber was the incompatibility between hydrophilic silica and hydrophobic NR, which resulted in poor mechanical properties. TESPT, an organotriethoxysilane with tetrasulfide group, was investigated for its role as a coupling agent. Usually TESPT was used to prevent aggregation of silica particles in rubber and enhance compatibility between rubber and silica. The effect of different TESPT content (0–5 phr) on the curing characteristic of rubber compound and mechanical properties of vulcanizate is listed in Table II. With increase of TESPT content, optimum cure time (t_{90}) and scorch time (t_{10}) reduced and the torque increased. TESPT contained sulfur chain length varying from two to eight atoms and can be treated as a co-curing agent, which was the uniqueness of TESPT. From the sulfur crosslinking mechanism, the sulfur ring opened during vulcanization and reacted with the allylic hydrogens or the double bonds of the rubber to form sulfur crosslink. By the same chemistry, sulfur bridge of TESPT was broken and then reacted with the rubber chains. So the reaction between the organosilane and the rubber chains based on sulfur donation occurred during vulcanization, which led to premature scorch and higher crosslinking density. Usually silanol groups reduced the sulfur curing rate by adsorbing the curing chemicals onto their surface. After the incorporation of TESPT, the amount of silanol groups decreased. In addition, TESPT reacting as an accelerator accelerated vulcanization rate.^{18,21,22} So the t_{90} and t_{10} of rubber compound with TESPT reduced and the torque increased. From the result of mechanical properties, the modulus at 300%

Table II. Mix Formulation, Curing Characteristics, and Mechanical Properties of Rubber Compound with Different Content of TESPT

	S ₀	S ₁	S ₂	S ₃	S ₄	S ₅
Ingredients(phr)						
NR	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2
DPG	0.6	0.6	0.6	0.6	0.6	0.6
MBTS	1.2	1.2	1.2	1.2	1.2	1.2
TESPT	0	1	2	3	4	5
MWRP	40	40	40	40	40	40
Sulfur	2	2	2	2	2	2
Curing characteristics						
Scorch time (t_{10} , min)	0.85	0.82	0.8	0.78	0.74	0.72
Optimum cure time (t_{90} , min)	6.22	5.95	4.93	4.77	4.35	4.23
Δ Torque ($M_H - M_L$, dNm)	5.03	5.14	5.68	6.14	6.54	6.70
Mechanical properties						
300% modulus (MPa)	4.65	4.72	5.21	5.27	5.33	5.77
Tensile strength (MPa)	16.12	17.03	17.45	17.73	18.01	18.83
Tear strength (kN/m)	33.52	33.57	33.64	33.72	34.46	34.61
Elongation at break (%)	527.36	523.81	519.03	515.51	512.69	510.32

The composite of NR/WRP modified by both microwave and sol-gel method with different TESPT content (0 phr, 1 phr, 2 phr, 3 phr, 4 phr, and 5 phr) was abbreviated to S₀, S₁, S₂, S₃, S₄, and S₅, respectively.

elongation and tensile strength of NR/MWRP composite with TESPT improved. The ethoxy group (CH₃CH₂O-) of TESPT was capable of reaction with the silanol groups on silica surface, which prevented aggregation of silica particles, and the sulfide (-S-) can participate in sulfur vulcanization, which led to a strong chemical linkage between TESPT and the rubber molecule. TESPT can function as a bridge between hydrophilic silica and hydrophobic rubber, as represented in Figure 2.²³ For this reason, the rubber-silica interaction improved and the number of agglomerated silica in vulcanizate remaining as weak sites for stress transmission to its surrounding became less and less. According to the research of Gibala and Hamed,²⁰ sulfur added to the rubber matrix migrated from the matrix into WRP,

which reduced sulfur content in rubber matrix. TESPT participating in vulcanization can increase crosslinking density of rubber matrix. So the modulus at 300% elongation and tensile strength improved. However, the elongation at break of vulcanizate with TESPT decreased. Because of the increase of crosslinking density in rubber composite, rubber chains mobility and flexibility of composite decreased, which resulted in lower elongation at break.

To further prove disappearance of silanol groups, Figure 3 shows FTIR spectra of NR/MWRP composite with varied TESPT content. The peak around 3400 cm⁻¹ was assigned as stretching vibration of silanol groups whose wavenumber shifted to the lower one, due to the hydrogen bonds between silanol groups. With increase of TESPT content, the intensity of the peak at around 3400 cm⁻¹ disappeared gradually. This result implied that the reaction between TESPT and *in situ* generated silica caused a reduction in density of silanol groups on the silica surface.

Payne Effect

The famous effect of amplitude dependence of the dynamic viscoelastic properties of filled polymer was often referred as Payne effect and the concept of filler network yielded a good interpretation of the Payne effect for filled elastomer.²⁴ The amplitude dependence of the modulus was essentially determined by the agglomeration and de-agglomeration of the filler network.²⁵ At a set frequency and temperature, storage modulus (G') of filler rubber compound decreased from a high value G'_0 at low strain amplitude to a low value G'_∞ at high strain amplitude. The ($G'_0 - G'_\infty$) value was usually used to characterize

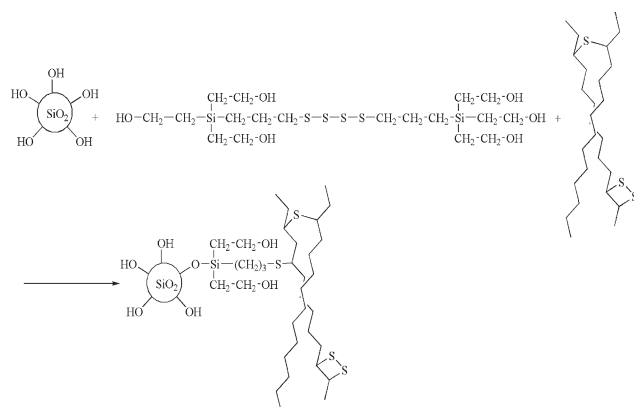


Figure 2. Illustration of a bridge between hydrophilic silica and hydrophobic rubber.

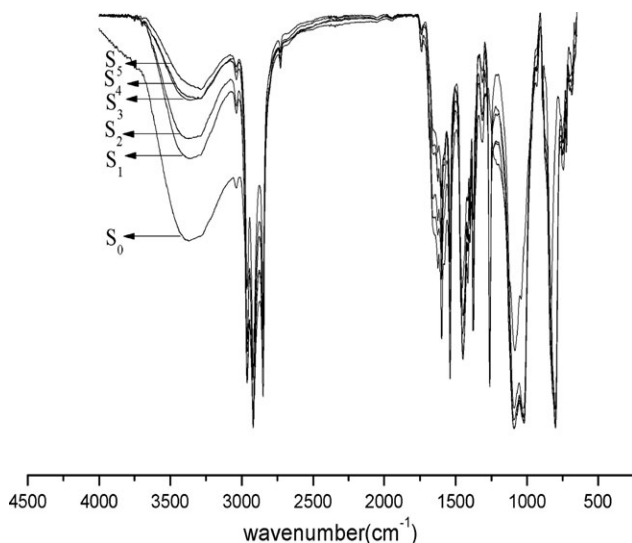


Figure 3. FTIR spectra of NR/MWRP composite with varied TESPT content.

the contribution of filler network. So this effect was closely related to the filler dispersion and rubber–filler interaction. The effect of the strain amplitude on G' at various TESPT concentrations for vulcanizate is shown in Figure 4. From Figure 4, the G' of all curves were the highest at small amplitude and gradually decreased to a low value. The drop of G' was ascribed to a progressive breaking of silica aggregates. The larger the amplitude of deformation, the larger the fraction of silica aggregates. So G' became lower and lower. Without TESPT, the interaction between silica particles was the strongest and the Payne effect was very evident. The $(G'_0 - G'_\infty)$ value of S_0 was much higher than others, which should be attributed to the fact that there were large amounts of direct filler–filler contacts and the poor dispersion of silica in S_0 . With increase of TESPT content, the interaction between silica particles weakened gradually, the chemical bonds between rubber and silica greatly prevented the

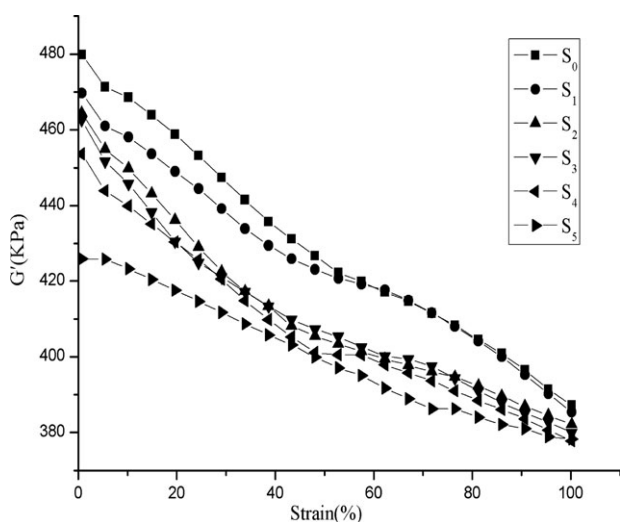


Figure 4. Effect of the strain amplitude on G' at various TESPT concentrations for vulcanizate.

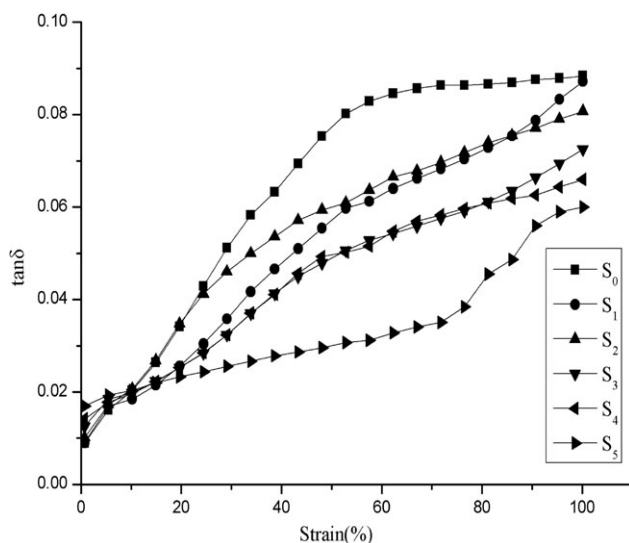


Figure 5. $\tan \delta$ of vulcanizate with various TESPT concentrations.

occurrence of flocculation of silica particles, flexible filler–rubber–filler contacts increased, and $(G'_0 - G'_\infty)$ value decreased, which was due to TESPT functioning as a bridge between hydrophilic silica and hydrophobic rubber. Because of the above mentioned fact, rubber compound with TESPT weakened Payne effect and improved the dispersion of silica particles in rubber matrix.

$\tan \delta$ of vulcanizate with various TESPT concentrations is shown in Figure 5. $\tan \delta$ was a ratio of loss modulus and storage modulus (G''/G'). From Figure 5, the order of $\tan \delta$ was $S_5 > S_4 > S_3 > S_2 > S_1 > S_0$ at low strain, whereas this trend reversed at high strain. The viscous nature of rubber was responsible for the energy dissipation. Without TESPT, the dispersion of silica in S_0 was poorest and filler clusters formed by filler–filler were most. At low strain, filler network was not destroyed and the rubber fraction entrapped within filler clusters was largest in S_0 , which was shielded from deformation and led to the reduced deformable rubber fraction. So the energy dissipation was lowest in S_0 . With increase of TESPT content, the restriction of filler decreased and the deformable rubber fraction increased, which increased $\tan \delta$. So the order of $\tan \delta$ was $S_5 > S_4 > S_3 > S_2 > S_1 > S_0$ at low strain. At high strain, the filler network was gradually destroyed and the viscous characteristic of rubber fraction released from filler clusters contributed to the hysteresis. In addition, the breakdown of filler clusters increased filler–filler friction and the weaker interfacial interaction also increased the interfacial friction between filler and rubber. Thus S_0 exhibited highest $\tan \delta$ at high strain. By contrast, with increase of TESPT content, the dispersion of silica and chemical interfacial interaction between rubber and silica improved. At high strain, rubber compound with TESPT exhibited low $\tan \delta$. So the order of $\tan \delta$ was $S_0 > S_1 > S_2 > S_3 > S_4 > S_5$ at high strain.^{26,27}

SEM

To further make sure of the *in situ* generated silica particles dispersion and also make clear idea of the interface of NR/MWRP

composite, the fracture surfaces of composites were observed by SEM.

Figure 6 shows the SEM micrographs taken from the cryogenically fractured surfaces of S_0 (a) and S_5 (b) vulcanizates. It can be seen clearly that S_0 possessed apparent agglomerates and the *in situ* generated silica particles were dispersed more homogeneously in S_5 compared with S_0 , which indicated that the dispersion of *in situ* generated silica in S_0 was poorer than that in S_5 .

Figure 7 shows the SEM micrographs taken from the tensile fractured surfaces of S_0 (a) and S_5 (b) vulcanizates. With the incorporation of TESPT into composite, the low concentration of silanol groups on the surface of silica particles improved the dispersion of silica and the silanized silica had higher wettability with rubber matrix. So the fracture surface of S_5 was smoother than that of S_0 , from Figure 7. Apart from that, S_0 had more pulled out silica compared with S_5 and some apparent holes were left on the fracture surface of S_0 , which resulted in the lower tensile strength, as shown in Table II. As explained before, the presence of TESPT improved the adhesion between *in situ* generated silica and rubber and the dispersion of silica particles. So the interfacial interaction between silica and rubber of S_5

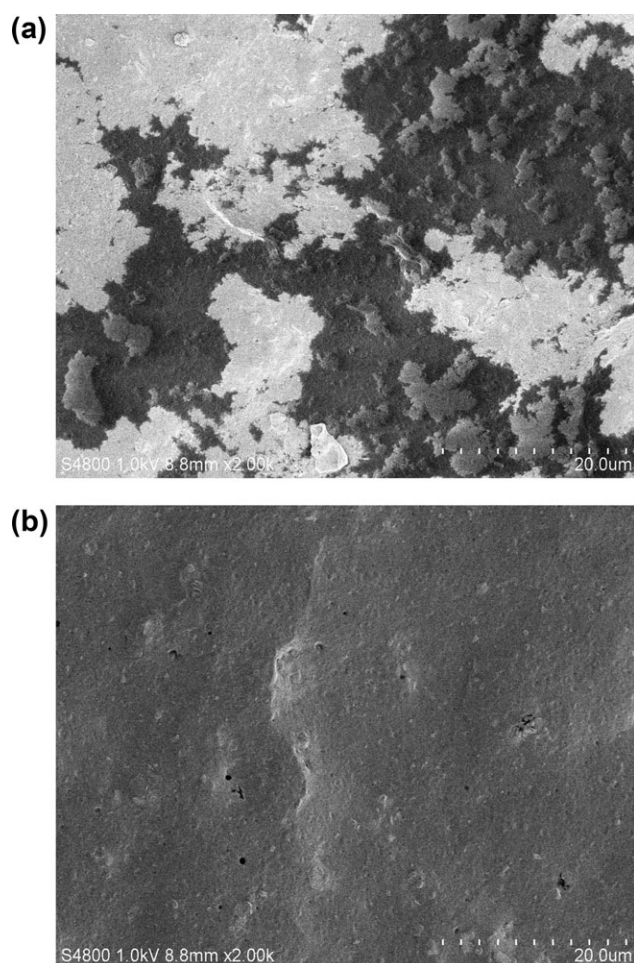


Figure 6. Cryogenically fractured SEM photographs of S_0 and S_5 vulcanizates: (a) S_0 ; (b) S_5 .

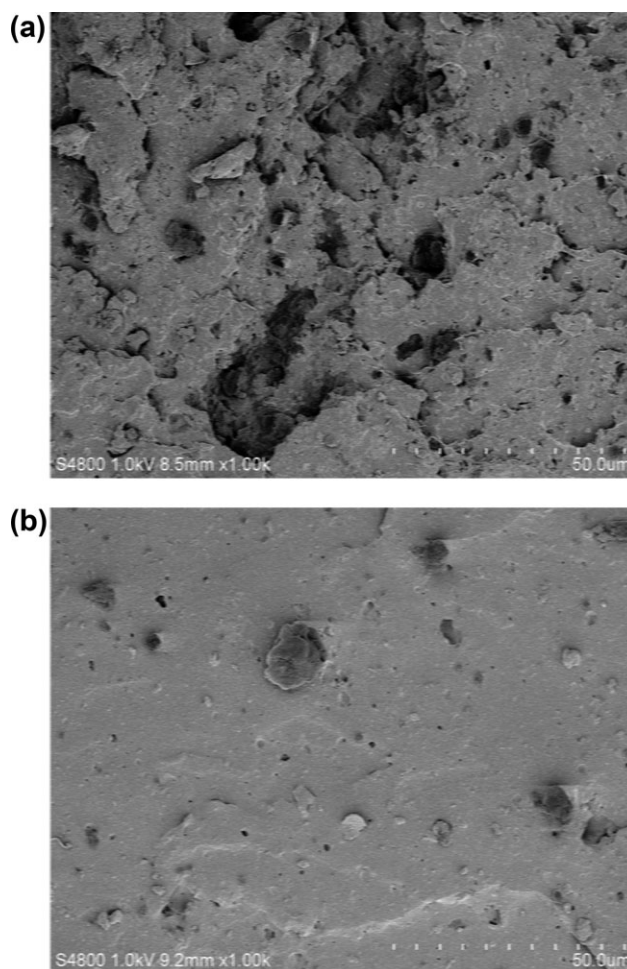


Figure 7. Tensile fractured SEM photographs of S_0 and S_5 vulcanizates: (a) S_0 ; (b) S_5 .

improved and the number of the pull-out *in situ* generated silica and the holes became less in S_5 .^{28,29}

DMA Analysis

The plots of $\tan \delta$ versus temperature of S_0 and S_5 vulcanizates tested by DMA are displayed in Figure 8. It can be seen that the temperature at glass transition temperature of S_0 and S_5 vulcanizate was not significantly different, being about -60 to -65°C . However, the glass transition region of S_5 became broader and the glass transition peak became higher, compared with S_0 . According to the above analysis, the dispersion of *in situ* generated silica in S_5 was better than that in S_0 and the number of rubber fraction entrapped within filler clusters became less in S_5 . The amount of rubber fraction participating in the glass transition in S_5 was more than that of S_0 . So the glass transition peak of S_5 was higher. The rolling resistance of tires was related to $\tan \delta$ value at temperature of 50 – 80°C . From Figure 8, S_5 possessed the lower $\tan \delta$ value than S_0 at temperature range of 50 – 80°C , which meant that S_5 vulcanizate owned lower rolling resistance than S_0 vulcanizate. In filler rubber system, the dynamic mechanical properties of the filled rubber were affected by several factors. The effect of the rubber shell that was formed surrounding the filler aggregate was one of the main factors.

The rubber shell, a layer of more or less immobilized rubber, was a result of an interaction between rubber chains and filler. Because of the filler–rubber interaction, the chains mobility in the rubber shell was low and increased gradually as rubber chains extended away from the filler surface. From above analysis of Payne effect, NR/MWRP composite with TESPT showed a higher filler–rubber interaction. That meant that a thicker rubber shell was formed for composite with TESPT.³⁰ So energy dissipation of vulcanizate without TESPT arose from a breakdown of filler transient network and loss of trapped rubber chains in the filler structure during dynamic test. In the presence of TESPT, the reduction in rolling resistance was clearly observed and this was attributed to the enhancement in degree of filler dispersion, rubber–filler interaction, and crosslinking density of the vulcanizate.^{31,32}

Figure 9 shows the plots of $\tan \delta$ versus temperature of S_5 , Sample 1, and Sample 2 vulcanizates tested by DMA. The WRP of S_5 was modified by sol–gel method. As a result of rubber–filler interaction, the absorption of rubber chains on the silica surface reduced the mobility of rubber chains. So S_5 owned the highest glass transition temperature. The wetting resistance property of tires was related to $\tan \delta$ value at temperature of 0°C. The absorption of rubber chains on the silica surface resulted in the rubber shell on the silica surface in which the spectrum of relaxation time was broadened. For one thing, the energy dissipation of the filled rubber originated from the breakdown and reformation of the filler network. For another thing, the joint shell rubber absorbed more energy resulting in higher hysteresis. So S_5 owned the best wetting resistance property, compared with Sample 1 and Sample 2. With the increase of temperature, S_5 possessed the lowest $\tan \delta$ at temperature range of 50–80°C, which meant that S_5 vulcanizate owned lowest rolling resistance.

CONCLUSIONS

The conventional WRP modification methods such as mechanochemical method, microwave, and so on were to break the sul-

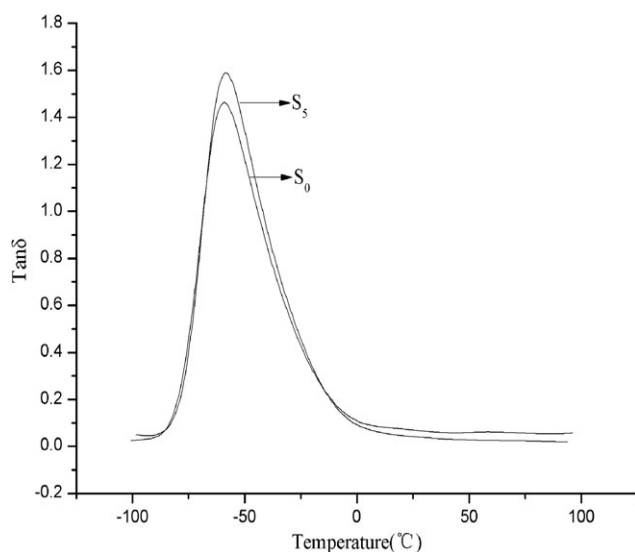


Figure 8. $\tan \delta$ versus temperature of S_0 and S_5 vulcanizates.

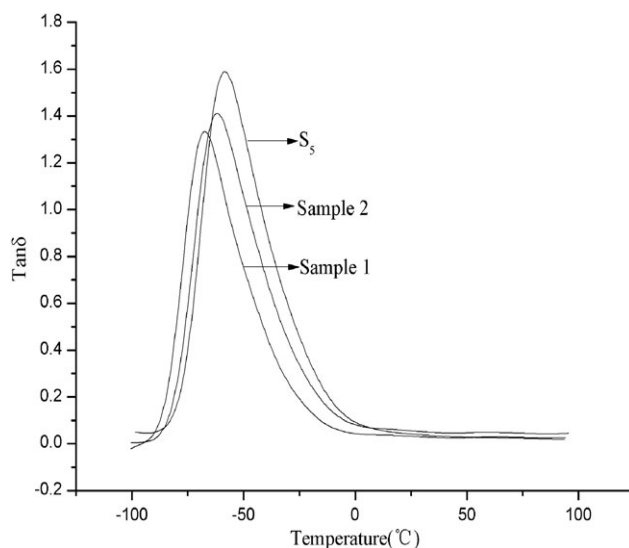


Figure 9. $\tan \delta$ versus temperature of S_5 , Sample 1, and Sample 2 vulcanizates.

fur crosslink. Through the rupture of crosslinking bonds, the strong permeability of inter-molecular chains and strong interfacial bonding between virgin rubber and WRP led to increment of mechanical properties. However, the conventional modification methods were often accompanied with the main rubber chains degradation, which impairs the mechanical properties of virgin rubber/WRP composite. To overcome this problem, this study showed the novel modification method of WRP. This novel modification method used short time microwave treatment to devulcanize WRP. On the one hand, a fraction of three-dimensional network was cut off by microwave, which improved the compatibility between NR and WRP. During short time microwave process, a large number of rubber main chains avoided degradation. On the other hand, devulcanization of WRP improved swelling in TEOS. Then WRP was modified by sol–gel method. Much more TEOS can be penetrated into WRP, due to the improvement of swelling in TEOS, and the number of *in situ* generated silica increased. Through reinforcement of *in situ* generated silica and improvement of the compatibility between NR and WRP, the results showed that the composite of NR/WRP modified by both microwave and sol–gel method owned the best mechanical properties. To enhance compatibility between rubber and silica and prevent aggregation of silica particles in rubber matrix, TESPT was used. With the incorporation of TESPT into composite, the silanol groups on the surface of silica particles became less and less and the Payne effect weakened. From SEM micrographs, TESPT improved coherency and homogeneity of *in situ* generated silica in rubber matrix. Compared with the composite without TESPT, NR/MWRP composite with 5 phr TESPT possessed the lower $\tan \delta$ value at temperature of 50–80°C, which meant that this composite owned the lower rolling resistance. Due to the absorption of rubber chains on the silica surface, the mobility of the rubber chains reduced. This absorption process resulted in the rubber shell on the silica surface in which the spectrum of relaxation time was broadened. For one thing, the energy dissipation of the filled rubber

originated from the breakdown and reformation of the filler network. For another thing, the joint shell rubber absorbed more energy resulting in higher hysteresis. So the composite of NR/MWRP composite with 5 phr TESPT owned the best wetting resistance property, compared with the conventional modification of WRP.

ACKNOWLEDGMENTS

Authors thank the High School Science Research Project of Hainan Provincial Department of Education (Hjkj2011-03) and Innovation Program of Hainan Province Graduate student (Hys2011-17) for financial support.

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