

The behavior of natural rubber–epoxidized natural rubber–silica composites based on wet masterbatch technique

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ABSTRACT: Natural rubber–epoxidized natural rubber–silica composites were prepared by the wet masterbatch technique and the traditional dry mixing method. Performances of the composites based on different preparation methods were investigated with a moving die rheometer, an electronic universal testing machine, a dynamic mechanical analyzer, a nuclear magnetic resonance crosslink density analyzer, a rubber processing analyzer (RPA), a scanning electron microscope (SEM), and a transmission electron microscope (TEM). The RPA, SEM, and TEM analyses indicated that silica has better dispersion, lower filler–filler interaction, and better filler–rubber interaction in compounds based on the wet masterbatch technique, leading to improvements in mechanical strength and the dynamic mechanical and compression properties of the composites. It also indicates that composites prepared by the wet masterbatch technique have shorter scorch time, faster curing velocity, and higher crosslink density. The composites prepared by the wet masterbatch technique also have lower rolling resistance, which is an important property for their use as a green material for the tire industry. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43571.

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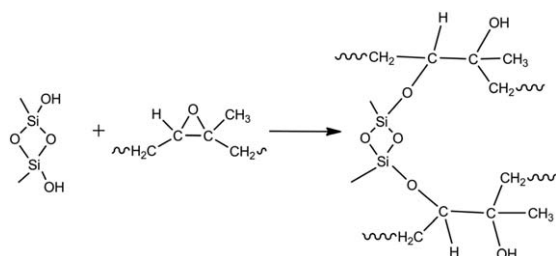
INTRODUCTION

Natural rubber (NR) is one of the green polymer materials with large-scale applications that is directly produced from the biological processes of plants. The properties of strain-induced crystallization, high tear resistance, and high elasticity make NR irreplaceable in many important engineering fields, although it has been substituted for by synthetic rubber in some applications. For example, NR has been replaced by styrene-butadiene rubber (SBR) and butadiene rubber (BR) in car tires, but in truck tires, off-road tires, and aircraft tires, NR is always the first choice.¹

Unlike other polymer materials, to attain good mechanical properties in accordance with the final application, elastomers have to be reinforced with fillers and chemical crosslinkages. Carbon black is the major reinforcing filler in the tire industry, but, since the introduction of “green tire technology,” carbon black has been completely replaced by silica in high-performance car tires.² Silica reduces the rolling resistance and improves the wet traction

of tire tread compounds significantly. Hence, it improves fuel efficiency and driving safety.³ Because silica has a strong tendency to agglomerate and poorly disperse in a natural rubber matrix, it cannot act as a reinforcing filler in the NR industry. And the general technology to improve silica dispersion in SBR/BR-based car tire tread compounds with silane coupling agents, specifically bis-(3-triethoxysilylpropyl) tetrasulfide (Si-69), has not been successful in industrial applications for NR,⁴ which prevents silica from being used as the main reinforcement filler in truck tires.⁵ Moreover, there is also a disadvantage in using Si-69: a high processing temperature is needed to obtain the chemical reactions, which consume more energy.⁶

Epoxidized NR (ENR) is a kind of non-petroleum-based elastomer from NR modification. Its special molecular structure leads to both good compatibility with NR and a reactive possibility with silica. When using ENR as a rubber matrix, it can significantly improve the silica dispersion and processability through an interfacial reaction between epoxy and silanol groups even in the



Scheme 1. Mechanism of interaction between ENR and silica.^{10,12}

absence of a silane coupling agent,^{6–12} as shown in Scheme 1.^{10,12} Although its application has been limited by its high cost and poor aging properties,^{13–15} there are still reports of ENR being employed as a compatibilizer for silica-filled rubber.^{10,12,16,17} The results show a substantial improvement in silica dispersion and mechanical properties, but still lower than when using Si-69. As a matter of fact, the interfacial bonding between ENR and silica was mainly achieved by long-term dry mixing under high temperature.⁷ The properties of the rubber compounds were damaged due to oxidative chain scission of the rubber matrix because of the vulnerability of the ENR process to high temperatures and severe damage to the rubber molecules by continuous mechanical shearing. Moreover, ENR was mixed with filler directly, which not only leads to flying dust and environmental pollution but also to more energy consumption.¹⁸

The wet masterbatch technique is a technology in which filler and rubber are mixed in the latex state to prepare masterbatches, and then masterbatches are mixed with accelerator and sulfur on an open two-roll mixing mill. The major benefits are shorter mixing time, better filler dispersion, and less damage to the rubber molecules, which significantly increase the performance of the rubber compounds compared with dry mixing.^{19–21} In the present study, NR/ENR/silica composites were prepared via the wet masterbatch technique, and the properties of the composites were studied.

EXPERIMENTAL

Materials

ENR-40 having 40 mol% epoxide and its latex are produced by the Agricultural Products Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences (Zhanjiang, China). Fumed silica with a particle size of 0.007 μm was provided by Sigma Co. (New York city, New York, America). NR latex with 60% dry rubber content was provided by Guangdong Guangken Rubber Group Co. (Guangzhou, China). NR gum was prepared from the NR latex in the laboratory. Other additives used were industrial grades.

Preparation of NR/ENR/Silica Masterbatches

To form a silica suspension, 20 g silica and 400 ml water were mixed and stirred and then further dispersed ultrasonically for 5 min to obtain a uniform silica slurry. ENR latex was added to NR latex by the ratio of 20 to 80 and stirred for 5 min. Then, the silica slurry was mixed with the blended latex and stirred for 5 min. Ethanol was poured into the mixture for coagulation. The coagula were sheeted with a creping machine, washed with water, and dried in an oven to produce NR/ENR/silica masterbatches.

Preparation of NR/ENR/Silica Compounds and Vulcanizates

The ingredients used to prepare the NR/ENR/silica compounds are shown in Table I. The letters “WE” and “DE” denote compounds prepared by the wet masterbatch technique and by dry mixing, respectively. The compounds were conducted on an XK-160 open two-roll mixing mill from Zhanjiang Machinery Factory (Zhanjiang, China) at 50–60 °C. For the WE compounds, masterbatches were rolled four times, and then ZnO, stearic acid (SA), accelerators, and sulfur were added to obtain homogeneous WE compounds. For the DE compounds, NR and ENR raw rubbers were blended and the silica was added in the open two-roll mixing mill, followed by the other ingredients to obtain homogeneous DE compounds. Then, the compounds were vulcanized for their optimum cure time (T_{90}) at 150 °C on a compression molding machine from Huzhou Hongqiao Rubber Machinery Co. (Huzhou, China) to prepare test sheets.

Characterization

Vulcanization Testing. The vulcanization properties of the composites were determined on an Alpha moving die rheometer (Alpha, Akron, Ohio, America) at 150 °C for 20 min or 25 min, and the optimum curing time T_{90} was determined by the rheometer.

Payne Effect. The Payne effect on uncured silica-filled compounds based on the different preparation methods was determined on an RPA 2000 rubber processing analyzer (Alpha). The storage shear moduli (G') of the compounds were measured under shear deformation. A strain sweep test was carried out in the range of 0.56–100% strain at 0.5 Hz and 100 °C. The difference between the storage moduli at low strain (0.56%) and high strain (100%) was reported.

Mechanical Properties. Tensile testing was conducted on an Instron Series IX automated material testing machine (Instron, Canton, Massachusetts, America) with C-type dumbbell samples according to ASTM D 412.

The dynamic mechanical analysis (DMA) was carried out on a Netzsch DMA 242 (Netzsch, Freistaat Bayern, Germany). The samples were tested in tension mode in the temperature range from –120 °C to 100 °C at 5 °C/min heating rate at 10 Hz frequency.

The dynamic mechanical properties in shearing mode of frequency sweep were determined on the RPA 2000 rubber processing analyzer (Alpha). The compounds were first vulcanized at 150 °C for their optimum curing time, and the frequency sweep was carried out in the range of 2 cpm to 1800 cpm at 60 °C with 1 degree shear angle.

The compression properties of NR/ENR/silica composites were determined on a GABOMeter 4000 machine (GABO, Ahlden, Germany) referring to the Chinese standard GB/T 1687, and there is a difference in compression frequency and die cavity temperature. Samples with a diameter of 17.5 mm and a height of 25 mm were vulcanized for 20 min longer than the optimum curing time. The testing conditions were as follows: die cavity temperature 30 \pm 1 °C, dynamic strain 5.71 mm, static load 250 N, compression frequency 50 Hz, and testing time 25 min. The rise in temperature ΔT was calculated from the temperature after 25 min compression, subtracting the constant die

Table I. Recipes of the Rubber Compounds

Samples	DE0	DE5	DE10	DE20	DE30	WE0	WE5	WE10	WE20	WE30
NR (phr)	100	95	90	80	70	100	95	90	80	70
ENR-40 (phr)	0	5	10	20	30	0	5	10	20	30
Silica (phr)	20	20	20	20	20	20	20	20	20	20
Zink oxide (phr)	4	4	4	4	4	4	4	4	4	4
Stearic acid (phr)	2	2	2	2	2	2	2	2	2	2
Accelerator CZ (phr)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Accelerator DM (phr)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur (phr)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

cavity temperature of 30 °C, and it was used to evaluate the anticompression properties of the composites.

Determination of Crosslink Density. Solid-state ^1H nuclear magnetic resonance (NMR) for characterizing crosslink density is based on the transverse of spin-spin (T_2) NMR relaxation. The T_2 relaxation time for an elastomer network is very sensitive to the conformational mean position of the network chains at temperatures about 100–150 °C above the glass transition temperature (T_g), which is affected by the chemical and physical network of the elastomer.^{22,23} For elastomer characterization, the Gotlib method for determining the mean molar mass between two crosslink points M_c is used.²⁴ Finally, the crosslink density was calculated from M_c . Physical crosslink densities that represent the entangled molecular chains are obtained from the nonvulcanized compounds, while chemical crosslink densities that represent the chemical crosslink chains are obtained from vulcanized compounds, removing the physical crosslink densities.

Samples were cut from rubber sheets about 2 mm thick and 8 mm long and put into a glass tube. The T_2 relaxation decays of the composites and the crosslink density measurements were tested on a MR-CDS3500 NMR Crosslink Density instrument (IIC Corp., Blieskastel, Germany) with 315 A/m at 15 MHz and 60 ± 0.1 °C. The 90° and 180° pulse angles were 2 μs and 4 μs , respectively. Each signal decay covered 512 data points over an acquisition time of 10.24 ms. To determine the relaxation times, 64 measurements at different tau values (T_2 , XLD) or variation delays (T_1) were carried out. The data analysis was performed with the IIC analysis software package using a nonlinear Marquardt-Levenberg algorithm.

Morphology Analysis. Scanning electron micrographs (SEM) of the composites was characterized by a Hitachi S-4800 scanning electron microscope (Hitachi, Tokyo, Japan). The samples were immersed in liquid nitrogen and were fractured. The cross sections were investigated to evaluate the dispersion of silica.

Transmission electron microscopy (TEM) was performed with a JEM-2100F (JEOL, Tokyo, Japan) at 100 kV. For solid samples, thin sections (about 70 nm) were cut using an EM-UC6 + FC6 cryoultramicrotome (Leica Microsystems, Wetzlar, Germany) by a diamond knife. The chamber temperature was -120 °C, and

the knife was -95 °C. The sections were collected on a copper network to test.

RESULTS AND DISCUSSION

Vulcanization Properties

The vulcanization curves of the NR/ENR/silica compounds with different preparation techniques are shown in Figure 1. It is

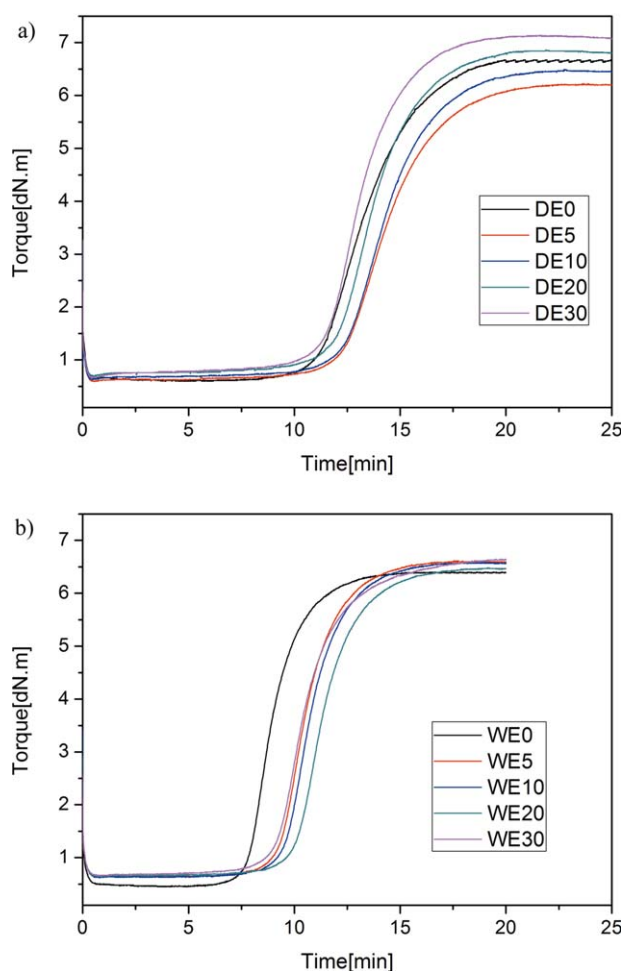


Figure 1. Vulcanization curves of NR/silica and NR/ENR/silica compounds: (a) vulcanization curves of DE compounds; (b) vulcanization curves of WE compounds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Vulcanization Parameters of NR/Silica and NR/ENR/Silica Compounds

Samples	T_{S1} (min)	T_{S2} (min)	T_{10} (min)	T_{90} (min)	S_{min} (N m)	S_{max} (N m)	ΔS (N m)
DE0	11.4	12.2	11.1	16.3	0.6	6.67	6.07
DE5	12.4	13.3	12.1	17.3	0.59	6.22	5.63
DE10	12.4	13.2	12.1	17.2	0.63	6.49	5.86
DE20	12.1	12.5	11.4	16.3	0.69	6.86	6.17
DE30	11.4	12.1	11.1	15.5	0.67	7.14	6.47
WE0	8.0	8.2	7.5	10.6	0.45	6.40	5.95
WE5	9.3	9.6	9.1	12.4	0.63	6.61	5.98
WE10	9.4	10.1	9.2	12.6	0.62	6.58	5.96
WE20	10.1	10.4	9.5	13.4	0.64	6.48	5.84
WE30	9.2	9.5	9.0	13.2	0.66	6.67	6.01

well known that silica has a vulcanization-retarding effect because it absorbs the curing activators and accelerators during processing.^{25–27} However, in this study, it is obvious that WE compounds have shorter vulcanization times than do DE compounds. Table II gives the vulcanization parameters of WE and DE with or without ENR. When ENR is added, the compounds have longer scorch time and optimum curing time. It is obvious that the scorch time and optimum curing time of WE are dramatically shorter than for DE, decreasing by 29.8% and 35.0% for compounds without ENR, respectively. The same trend can be also seen in the compounds with ENR. During dry mixing, silica is mixed into dry rubber, and silica absorbs the cure accelerator, which prolongs the curing time. However, in wet masterbatch compounds, the silica emulsion disperses in the rubber latex, and more silica particles combine with the rubber molecular chain and consequently absorb less cure accelerator. So compounds based on the wet masterbatch technique have shorter curing time than those based on dry mixing.

Payne Effect

The Payne effect, which refers to the difference in moduli at small and large deformations, can reflect the filler–filler interaction in compounds. Therefore, the storage moduli of compounds at 0.56% and 100% strain were measured, and the

difference in moduli at small deformation 0.56% and large deformation 100% is shown in Figure 2.²⁸ As shown in Figure 2, compared to DE compounds, WE composites incur a strong decrease in the Payne effect, which indicates that the wet masterbatch technique can lower filler–filler interaction in NR/silica and NR/EN/silica compounds. There is a different Payne effect trend in DE and WE compounds with increasing ENR content. In the DE compounds, the addition of ENR decreases the filler–filler interaction dramatically; 10 phr ENR has the optimal effect, and more ENR content has an adverse effect. That is because large amounts of epoxide groups can create additional interactions or linkages between themselves, as previously reported by Kaewsakul *et al.*⁶ But, in WE composites, the Payne effect slightly increases with the addition of ENR, and this may be due to the additional interactions or linkages between ENR molecules. However, the Payne effects in WE compounds dramatically decrease compared to that in DE compounds. This indicates that the preparation method plays an important role in filler–filler interaction; for compounds prepared by the wet masterbatch technique, filler–filler interaction is optimized during both latex mixing and the mechanical mixing process, and the Payne effect is decreased dramatically compared to dry-mixed compounds.

Mechanical Properties

Tensile Properties. The mechanical properties of the composites prepared by different techniques are shown in Table III. The tensile strength increased with the increase in ENR loading. The 100%, 300%, and 500% moduli of NR/ENR/silica composites increase with an increase in ENR content that is no more than 20 phr, but when the ENR content is 30 phr, the modulus decreases. The reason is a phase split between NR and ENR. Silica is prone to disperse in the ENR matrix and less so in the continuous NR phase, and the resulting moduli of the composites decrease.²⁹

The preparation technique has a significant effect on the mechanical properties of composites. Compared to DE composites, WE composites had higher moduli at 100%, 300%, and 500% strain and stronger tensile strength, but lower elongation at break. For example, the 100%, 300%, 500% moduli, max strength, and elongation at break of DE30 are 0.99 MPa, 3.11 MPa, 21.94 MPa, and 732%, respectively, while those of WE30

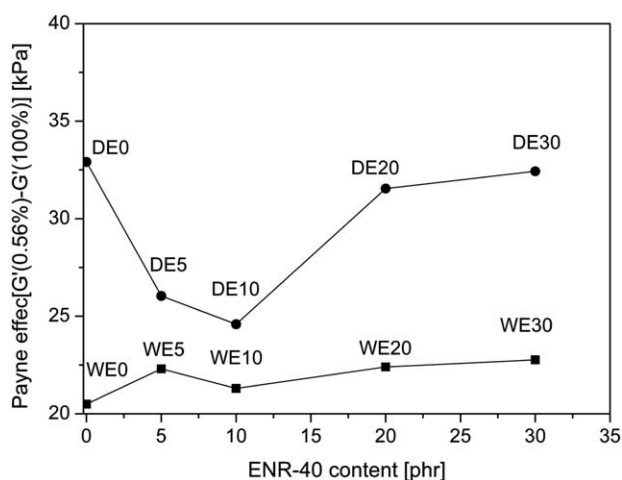
**Figure 2.** Payne effects on NR/silica and NR/ENR/silica compounds.

Table III. Tensile Properties and Crosslink Densities of the Studied Vulcanizates

Properties	Mod 100% (MPa)	Mod 300% (MPa)	Mod 500% (MPa)	Elongation at break (%)	Max strength (MPa)	Physical crosslink density (mol/cm ³)	Chemical crosslink density (mol/cm ³)
DE0	0.82	1.82	4.56	779	18.74	5.70×10^{-5}	8.84×10^{-5}
DE5	0.85	2.33	6.41	741	19.58	5.59×10^{-5}	9.78×10^{-5}
DE10	0.97	2.57	6.86	735	19.62	5.45×10^{-5}	9.15×10^{-5}
DE20	1.09	3.15	8.52	716	21.03	6.04×10^{-5}	8.60×10^{-5}
DE30	0.99	3.11	8.46	732	21.94	7.59×10^{-5}	7.41×10^{-5}
WE0	0.96	2.37	9.03	626	19.8	6.12×10^{-5}	9.53×10^{-5}
WE5	0.96	2.59	9.29	624	20.56	5.83×10^{-5}	9.65×10^{-5}
WE10	1.09	3.06	11.39	627	21.93	6.03×10^{-5}	9.79×10^{-5}
WE20	1.17	3.54	12.69	603	22.15	6.39×10^{-5}	10.35×10^{-5}
WE30	1.11	3.26	11.32	662	27.20	6.93×10^{-5}	10.61×10^{-5}

are 1.11 MPa, 3.26 MPa, 27.20 MPa, and 662%. The wet masterbatch technique obviously improves mechanical strength, which is related to its better filler dispersion and improved interaction with the rubber matrix, and that has been proved in the Payne effect analysis.

Crosslink Density. Crosslink densities of the composites based on different techniques are shown in Table III. There are a lot of silanol groups on the surface of the silica particles, which induce strong filler–filler interaction, leading to a strong tendency to filler agglomeration in the rubber matrix.³⁰ Furthermore, NR is a nonpolar polymer and is incompatible with polar silica particles. Therefore, ENR is employed to improve the interaction between NR and silica and has been proved efficient.¹⁰ As known, the chemical crosslink density represents the chemical molecular chain trapped in the matrix, while the physical crosslink density represents the entangled molecular chains of the rubber matrix. On the other hand, the chemical crosslink density can also reflect the interaction between rubber matrix and filler.

As seen in Table III, the trend of crosslink density with different ENR loading is dramatically different based on different techniques. The chemical crosslink densities of DE composites increase with ENR addition, and with increasing ENR content, the chemical crosslink densities first increase at no more than 5 phr ENR and then decrease when more than 5 phr ENR. Moreover, the physical crosslink densities of DE composites decrease at no more than 10 phr ENR and increase when more than 10 phr ENR. In the WE composites, the chemical crosslink densities increase with increasing ENR content, but the physical crosslink densities decrease at no more than 5 phr ENR and increase when more than 5 phr ENR. As a result, WE composites have higher chemical crosslink densities than DE composites, which indicates that WE composites have better filler–rubber interaction than do DE composites. And the results are in agreement with the Payne effect analysis of the compounds.

From the above results, it is noticeable that the processing technique plays an important role in the interaction between filler

and rubber. Silica disperses in NR/ENR gum through mechanical shear, and high mechanical shear breaks the rubber molecular chain under a dry mixing procedure. Because of the weak epoxy groups in ENR, it is more easily broken during mechanical mixing, and the broken molecular chain forms free, small molecular chains; thus, the physical crosslink densities increase while chemical crosslink densities decrease when there is more than 5 phr ENR in DE composites. In contrast, silica disperses more easily and uniformly in NR/ENR latex. During the mechanical mixing, the broken molecular chains not only form free, small molecular chains but also make up crosslink points to silica, which lead to an increase in chemical crosslink density. So WE composites have higher chemical crosslink densities than do DE composites.

Dynamic Mechanical Properties

Dynamic Mechanical Properties by DMA Analysis. The DMA curves of NR/silica and NR/ENR-40/silica composites are shown in Figure 3. Figure 3(a,b) shows the storage modulus of NR/silica and NR/ENR/silica composites. It indicates that the storage modulus increases with an increase in ENR loading, resulting from the higher modulus of ENR. The second glass transition plateau appears when ENR loading exceeds 10 phr, which indicates phase splitting between NR and ENR. Compared to DE composites, the storage modulus at the second plateau of WE composites is less obvious. That is because the wet masterbatch technique can improve the compatibility of the ENR and NR matrix.

Figure 3(c,d) shows the loss factor curves of the composites. In agreement with the storage modulus, the loss factor curves also display the second glass transition peak when ENR loading exceeds 10 phr. Compared to DE composites, WE composites have a lower loss factor at the second glass transition temperature peaks. Through the wet masterbatch technique, WE composites have better compatibility of NR and ENR matrix and have lower phase splitting (which can be seen in TEM photos), leading to a lower loss factor at the second peaks in the WE composites.

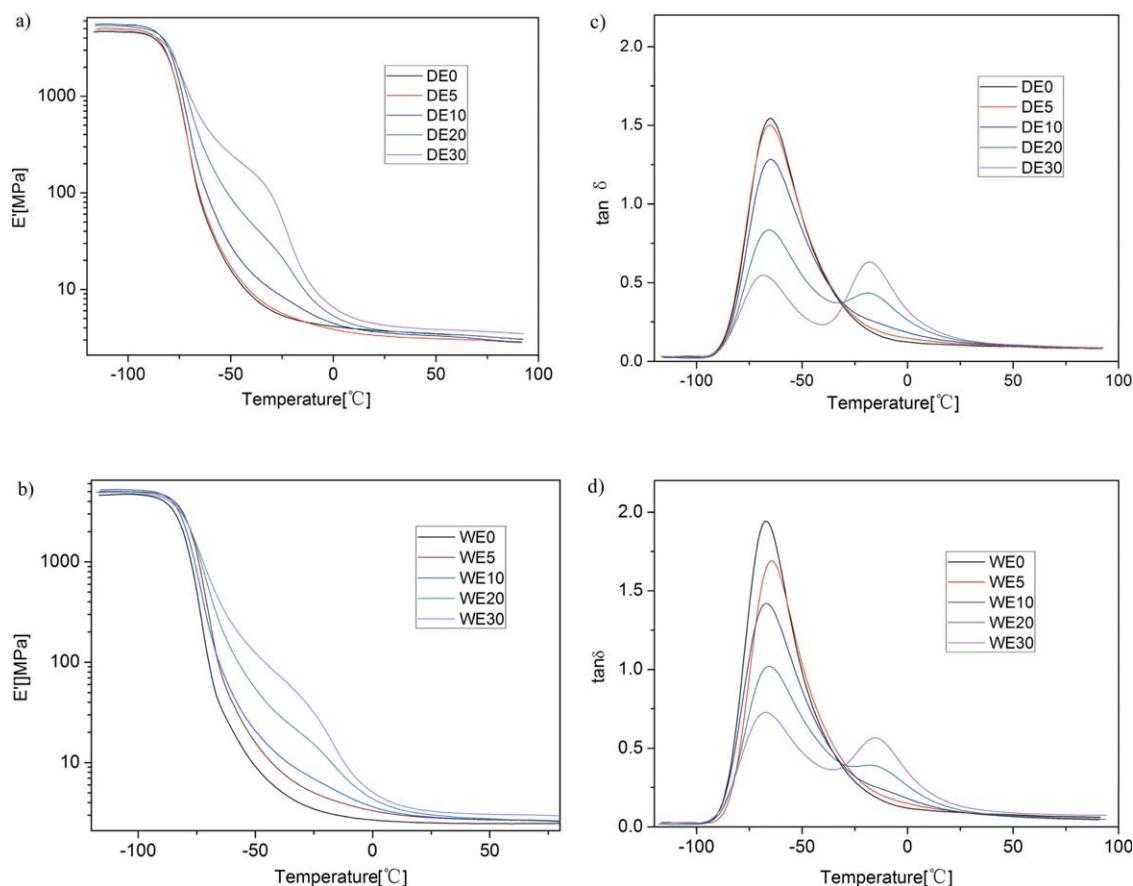


Figure 3. DMA curves of NR/silica and NR/ENR/silica composites: (a) storage moduli of DE composites; (b) storage moduli of WE composites; (c) loss factor of DE composites; (d) loss factor of WE composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV provides the DMA parameters of the composites. It is well known that hysteresis can be characterized by the loss factor $\tan\delta$, which has a good correlation with the rolling resistance and wet skidding resistance. Generally, $\tan\delta$ values at 0 °C

Table IV. DMA Parameters of NR/Silica and NR/ENR/Silica Composites

Samples	T_g at the first peak (°C)	T_g at the second peak (°C)	$\tan\delta$ at 0 °C	$\tan\delta$ at 60 °C
DE0	-65.1	-	0.1226	0.0881
DE5	-65.4	-	0.1481	0.0896
DE10	-65.0	-	0.1823	0.0947
DE20	-65.7	-18	0.2640	0.0970
DE30	-68.3	-18.9	0.3274	0.1006
WE0	-67.2	-	0.1193	0.0712
WE5	-64.5	-	0.1477	0.0656
WE10	-67.0	-	0.1816	0.0577
WE20	-65.6	-15.4	0.2601	0.0622
WE30	-67.2	-18.1	0.3454	0.0822

and 60 °C are used to evaluate wet skidding resistance and rolling resistance, respectively.^{31,32} It can be seen that $\tan\delta$ at 0 °C is increasing dramatically with an increase in the ENR amount in both DE and WE composites. The processing techniques have a significant effect on the loss factor. As shown in Table IV, the $\tan\delta$ values at 0 °C and 60 °C of the WE composites are lower than in the DE composites, which indicates that WE composites have lower rolling resistance than do DE ones.

Above all, the wet masterbatch technique not only improves the compatibility of ENR and NR but also helps to make a low-rolling-resistance material that is suitable for preparing green tire tread.

Dynamic Mechanical Properties by Rubber Processing Analysis. Figure 4 shows rubber processing analysis (RPA) curves of NR/silica and NR/ENR/silica composites, and it can be seen that the $\tan\delta$ of the WE composites is lower than for the DE composites by comparing the two curves. In shearing mode, $\tan\delta$ is the ratio of loss modulus (G'') to storage modulus (G'), which is relevant to the energy loss produced by the damage of the filler network and the filler–rubber network and the sliding friction between molecular chains and filler at a certain frequency. In WE composites, energy loss between filler

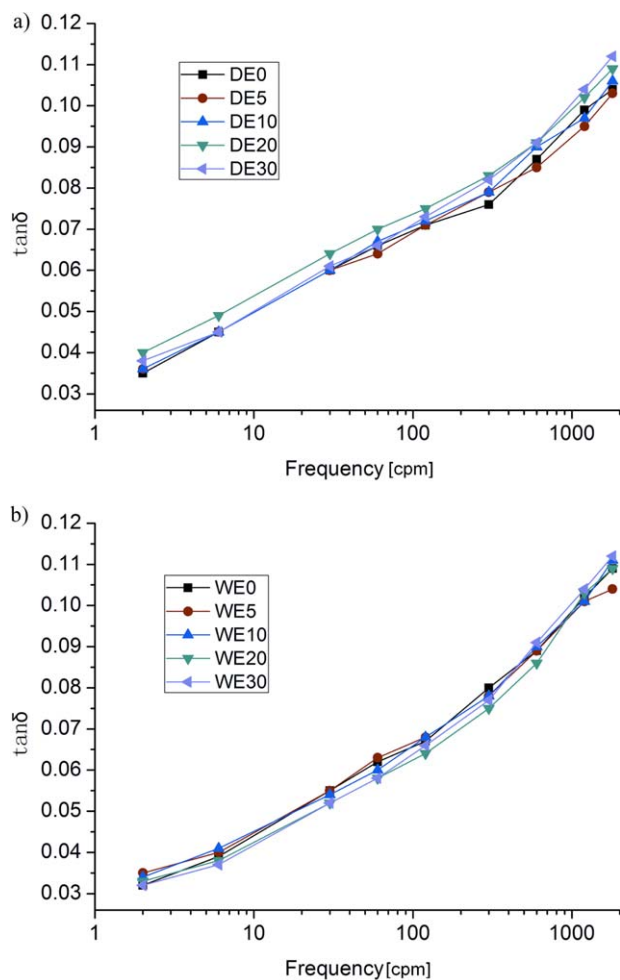


Figure 4. RPA curves of NR/silica and NR/ENR/silica composites: (a) RPA curves of DE composites; (b) RPA curves of WE composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

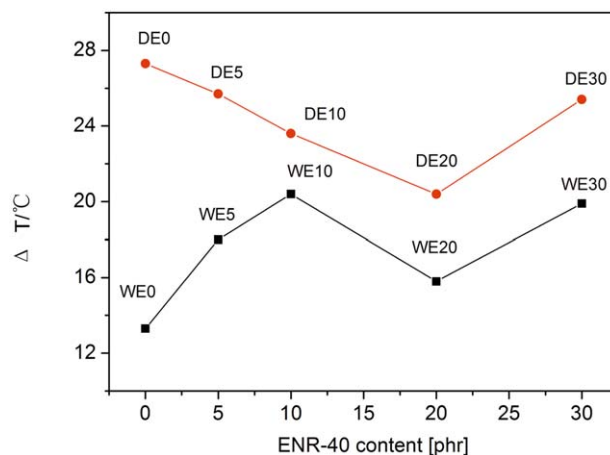


Figure 5. Temperature rise by compression of DE and WE composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

network and sliding fraction between molecular chains and filler have been decreased by decreasing filler–filler interaction and increasing chemical crosslink densities that have been proved by the Payne effect and crosslink densities analysis, consequently resulting in a lower loss factor than in DE composites at 60°C . The result also gives the information that WE composites have lower rolling resistance, which is in accordance with the DMA analysis.

Compression Test. It is believed that heat buildup by compression not only can be used to characterize the resistance to fatigue of composites but can also reflect the filler–matrix network and filler–filler networks.³⁰ Figure 5 shows a temperature rise by heat buildup after compression of composites. It can be seen that WE composites have lower temperature rises than do DE ones, and the temperature rise of WE composites reduces by 3.2°C to 14°C compared to DE composites. During compression, heat generation is mostly due to the friction between filler and matrix and filler particles.³³ The wet masterbatch

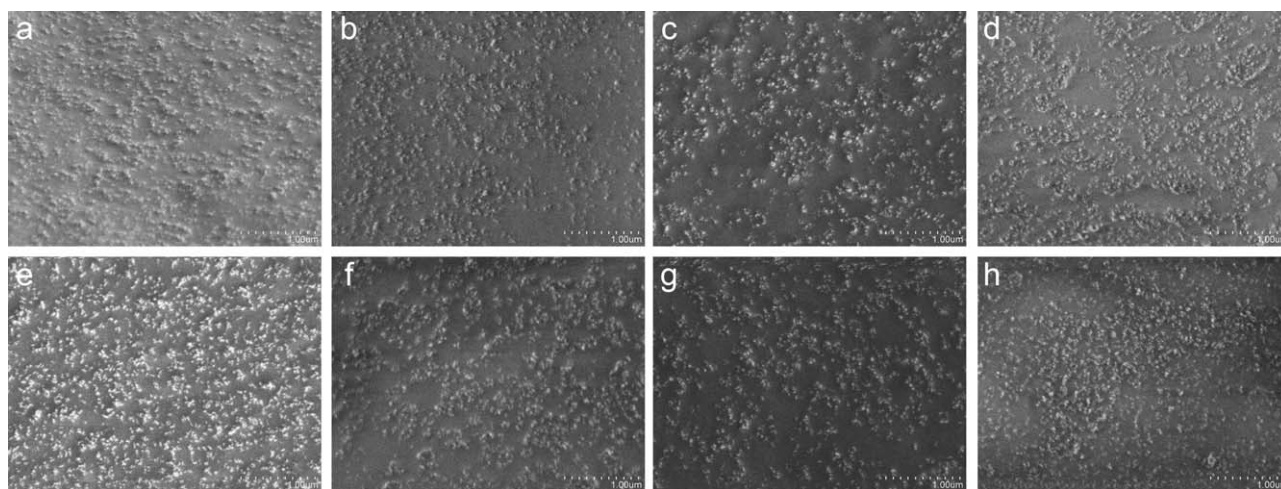


Figure 6. SEM photographs of NR/silica and NR/ENR/silica composites: (a) DE0; (b) DE10; (c) DE20; (d) DE30; (e) WE0; (f) WE10; (g) WE20; (h) WE30.

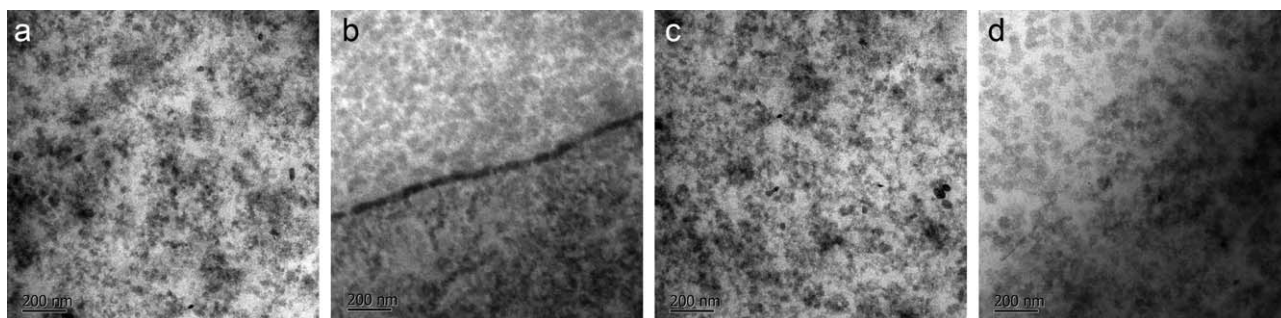


Figure 7. TEM photographs of NR/silica and NR/ENR/silica composites: (a) DE0; (b) DE20; (c) WE0; (d) WE20.

technique improves the interaction between filler and rubber matrix, lessens the agglomeration of silica, and weakens filler–filler networks. Hence, the friction between filler and rubber and filler and filler was reduced, leading to less heat being produced during compression. Furthermore, the WE composites have a lower loss factor than do DE composites at 60 °C in the DMA and RPA tests; the compression test also agrees with these results.

Morphology Characterization

SEM. The dispersion of silica in NR and NR/ENR matrixes based on different techniques is shown in Figure 6. It shows that silica particles aggregate together, forming clusters in DE composites [Figure 6(a–d)], and when silica loading is increased to 20 phr and 30 phr [Figure 6(c,d)], there is an obvious phase split between NR and ENR, and silica has an orientation dispersion. However, in WE composites, the phase split of NR and ENR becomes less obvious, and the silica orientation dispersion is weakened [Figure 6(g,h)]. Especially in Figure 6(d) and Figure 6(h), the silica in DE30 disperses as clusters, while in WE30 it disperses as particles. Above all, it can be concluded that the wet masterbatch technique can promote the compatibility of NR and ENR, which leads to better dispersion of silica.

TEM. Figure 7 shows the morphology and dispersion of silica in NR and NR/ENR matrixes based on the different preparation methods. It can be seen in a comparison of Figure 7(a) and Figure 7(c) that the dispersion of silica is more uniform and has less aggregation in the WE0 composites. There is also an enormous difference between DE20 and WE20 in morphology and silica dispersion. As shown in DE20 [Figure 7(b)], there is an obvious interface line between NR and ENR, while in WE20 [Figure 7(d)], the interface between NR and ENR is fuzzy and has a transition region between them, which indicates better compatibility of ENR and NR. Moreover, the silica dispersion in WE20 is more uniform and has less aggregation than in DE20. Hence, it turns out that the wet masterbatch technique can improve the silica dispersion and the compatibility of NR and ENR rubber matrix, a conclusion that agrees with the SEM, crosslink density, Payne effect, and mechanical results.

CONCLUSIONS

The behavior of NR/silica and NR/ENR/silica composites prepared by the wet masterbatch technique was investigated. The results indicate that compounds prepared by the wet masterbatch technique have shorter optimum curing time and need

less energy during processing. According to the SEM and TEM photographs, a Payne effect analysis, and NMR tests, it can be concluded that the wet masterbatch technique can improve silica dispersion, lower filler–filler interaction, increase chemical crosslink density, and promote the compatibility of NR and ENR. Therefore, the wet masterbatch technique can enhance tensile moduli and tensile strengths, raise dynamic mechanical properties, and lower the heat produced during compression. Moreover, from DMA and RPA analyses, composites based on the wet masterbatch technique have lower rolling resistance while retaining similar wet skidding resistance, which is significant for a material to be used in a high-performance green tire tread.

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