Application of Nano-Zinc Oxide Master Batch in Polybutadiene Styrene Rubber System

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ABSTRACT: The properties of nano-zinc oxide master batch filled butadiene styrene rubber (SBR) systems were researched in comparison with those of common zinc oxide and nano-zinc oxide filled systems. First, the nano-zinc oxide master batch was prepared and the cure characteristics of three different kinds of zinc oxide filled SBR composites were studied; second, the mechanical properties and wear resistance were compared; then, the improved mechanical properties were confirmed by dynamic mechanical properties and transmission electron microscopy. Finally, the zinc oxide amount reducing mechanism was analyzed. Results show that nano-zinc oxide master batch filled SBR system has better mechanical properties than those of nano-zinc oxide and common zinc oxide filled systems, which is due to the improved dispersion by master batch mixing technology. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 922–930, 2006

Key words: nano-zinc oxide; master batch; polybutadiene styrene rubber; dispersion

INTRODUCTION

Commercial applications of elastomers often require the use of activators in the system to obtain the desired reinforcement and make rubber compounds useful for a variety of applications.[1,2] It has been reported that nano-zinc oxides are effective activators and reinforcing agents in rubber systems because of their "little size effect," "surface effect," and "quantum effect."[3–11] The effects of addition agents on the mechanical and other properties of the composites depend not only on filler origin, particle shape, and size, but also strongly on filler aggregate size, surface characteristics, and degree of dispersion.[12] The reinforcement of composites by master batch is one of the most important technologies used for the finer dispersion of fillers presently.[13–15]

In this work, the application of nano-zinc oxide into butadiene styrene rubber (SBR) system by master batch technology was studied. First, the nano-zinc oxide master batch was prepared and the cure characteristic of three different kinds of zinc oxide filled SBR systems was researched by experiments; then, the mechanical properties such as tensile strength at break, elongation at break, and wear resistance were compared and studied. Finally, the mechanism of improved dispersion and improved mechanical properties were confirmed by dynamic mechanical properties (DMA) and transmission electron microscopy (TEM). Results show that nano-zinc oxide master batch filled SBR system has better mechanical properties than those of nano-zinc oxide and common zinc oxide filled systems, which is due to the improved dispersion of master batch mixing technology.

EXPERIMENTAL

Preparation of nano-zinc oxide master batch

Nano-zinc oxide (30 phr) was mixed into 70 phr SBR and the master batch was prepared on a double roller plasticator operating at 20°C. The compounds were then conditioned at 20°C for 24 h before use.

The nano-zinc oxide powder shows a hexagonal crystalline pattern with characteristic peaks at $2\theta = 31$, 34, and 36 (shown in Fig. 1), which is in good agreement with the chemical formula ZnO. The average size is 70 nm according to ASTM diffraction data.

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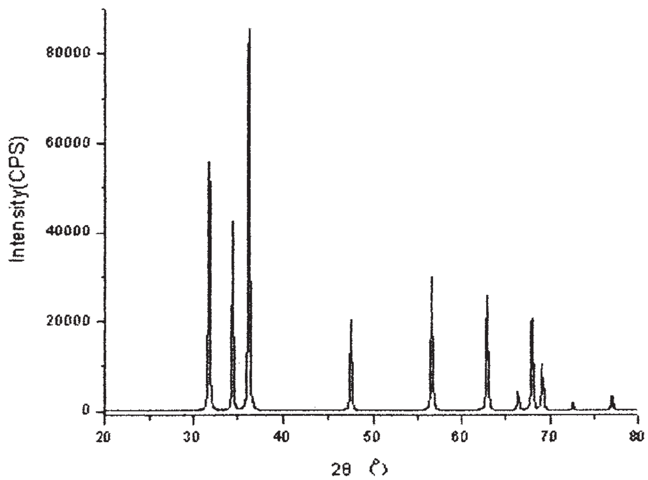


Figure 1 X-ray diffraction of nano-zinc oxide powder.

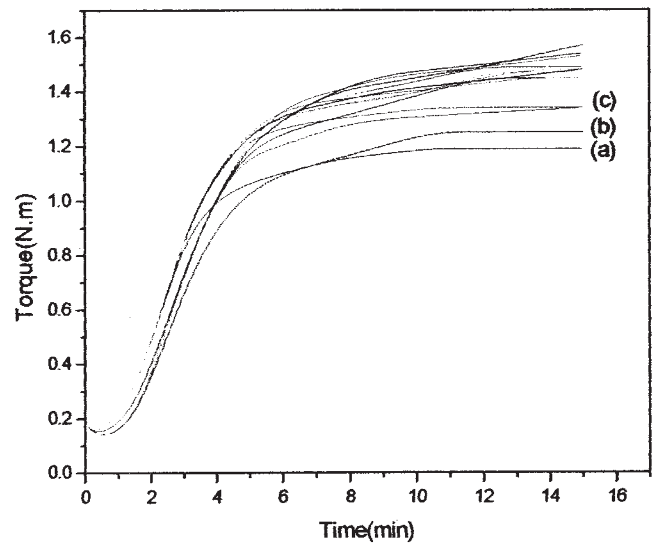


Figure 2 Rheographs of different zinc oxide filled SBR systems. (a) Common zinc oxide, (b) nano-zinc oxide, (c) nano-zinc oxide master batch.

Preparation of SBR vulcanizates

The formulation used in this study is presented in Table I.

SBR composites were prepared on a double roller plasticator operating at 20°C. The sheeted compounds were then conditioned at 20°C for 24 h before testing.

The curing parameters were then determined on an oscillating disk rheometer (MDR-2000, Wuxi, Liyuan, China) according to ASTM D 2084−81. The compositions were then vulcanized at 150°C during the respective optimum cure time under 15 MPa pressure on an electrically heated press. To compare test results conveniently, all the uncured mixes and vulcanizates used in this study were prepared using the conditions mentioned earlier as well as the formulation shown in Table I.

Determination of mechanical properties

The tensile properties of the vulcanizates were measured with dumbbell specimens (6 mm wide in cross section) according to the Chinese National Standard GB 528−82. The value for each sample was taken as the median value of five specimens. These tests were carried out at room temperature on an XL-250A universal testing machine, with a crosshead speed of 500 mm/min. The tensile specimens for each composition were tested and the stress and strain at break were determined. Hardness measurements were preformed according to GB 531−83 on a Shore A hardness tester.

The wear resistance tests of the vulcanized rubber composites were conducted on a WML-76 Akelon abrasion testing machine. The rotate velocities of the sample wheel and the empery wheel were 76 and 33 rpm, respectively, and the angle between the shafts of the two related wheels was 15°. A pressure of 26.7 N was loaded on the sample during the wearing. The

TABLE I
Formulations of SBR Vulcanizates

Components	phr
SBR	
Common zinc oxide filled system	100
Nano-zinc oxide filled system	100
Nano-zinc oxide master batch filled system	99.6, 99.2, 98.7, 98.3, 97.9
Sulfur	3
Stearic acid	1
2-bezothia-zolethiol	1.5
Diben zothiazole disulfide	2.0
N-phenyl-*β*-naphthylamine	1.0
Calcium carbonate	4.0
Semireinforcing carbon black	40
Zinc oxide	
Common zinc oxide	1, 2, 3, 4, 5
Nano-zinc oxide	1, 2, 3, 4, 5
Nano-zinc oxide master batch	1.4, 2.8, 4.3, 5.7, 7.1

TABLE II
Cure Characteristic of Different Zinc Oxide Filled SBR Vulcanizates

Formulations	Zinc oxide (phr)	t_{10} (min)	t_{90} (min)	M_0 (lb in.)	M_L (lb in.)	M_m (lb in.)
Common zinc oxide	1	0.72	2.98	0.105	0.098	1.105
	2	0.75	3.05	0.151	0.124	1.168
	3	0.79	3.08	0.191	0.324	1.246
	4	0.83	3.10	0.257	0.524	1.298
	5	0.87	3.22	0.348	0.652	1.368
Nano-zinc oxide	1	0.78	3.54	0.083	0.077	1.250
	2	0.82	3.64	0.121	0.099	1.311
	3	0.84	3.84	0.130	0.111	1.380
	4	0.92	4.04	0.141	0.127	1.484
	5	1.02	5.34	0.161	0.139	1.546
Nano-zinc oxide master batch	1	0.82	3.74	0.077	0.075	1.383
	2	0.88	3.90	0.102	0.096	1.425
	3	0.94	4.38	0.105	0.097	1.479
	4	0.99	5.60	0.111	0.099	1.527
	5	1.06	7.30	0.121	0.102	1.598

experiments were conducted at a temperature of 25°C and a humidity of 65%.

SEM analysis

An SEM analysis of fractured surfaces and morphology of rubber compounds was carried out using JSM-6360LV instrument. The samples used in SEM were gold coated in a vacuum chamber before examination.

Dynamic mechanical properties

The dynamic mechanical properties were measured using a rheometric scientific DMA analyzer (model MK III; Polymer Laboratories, Poole, UK) under the following conditions: frequency, 1 Hz; heating rate, 2°C/min; single-cantilever bending mode; and temperature ranging from −130 to 20°C.

TEM analysis

TEM micrographs were taken from an H-800 instrument using an accelerating voltage of 200 kV. The TEM samples were embedded in a capsule with an embedding agent polymerized at 60°C for 24 h. The embedded sample was ultrathin sectioned using a microtome equipped with a diamond knife in a liquid nitrogen trap. The thin sections were 60–80 nm thick.

TABLE III
Mechanical Properties of Different Zinc Oxide Filled SBR Vulcanizates

Formulations	Zinc oxide (phr)	Tensile strength (MPa)	Elongation at break (%)	Shore A hardness (ShA)
Common zinc oxide	1	4.52	270	55
	2	5.60	310	59
	3	7.09	360	60
	4	9.02	400	60
	5	9.69	430	60
Nano-zinc oxide	1	11.44	600	55
	2	10.78	470	60
	3	10.48	470	60
	4	8.17	400	60
	5	7.99	380	61
Nano-zinc oxide master batch	1	14.40	700	53
	2	12.08	550	59
	3	11.65	490	61
	4	11.03	460	61
	5	9.57	400	61

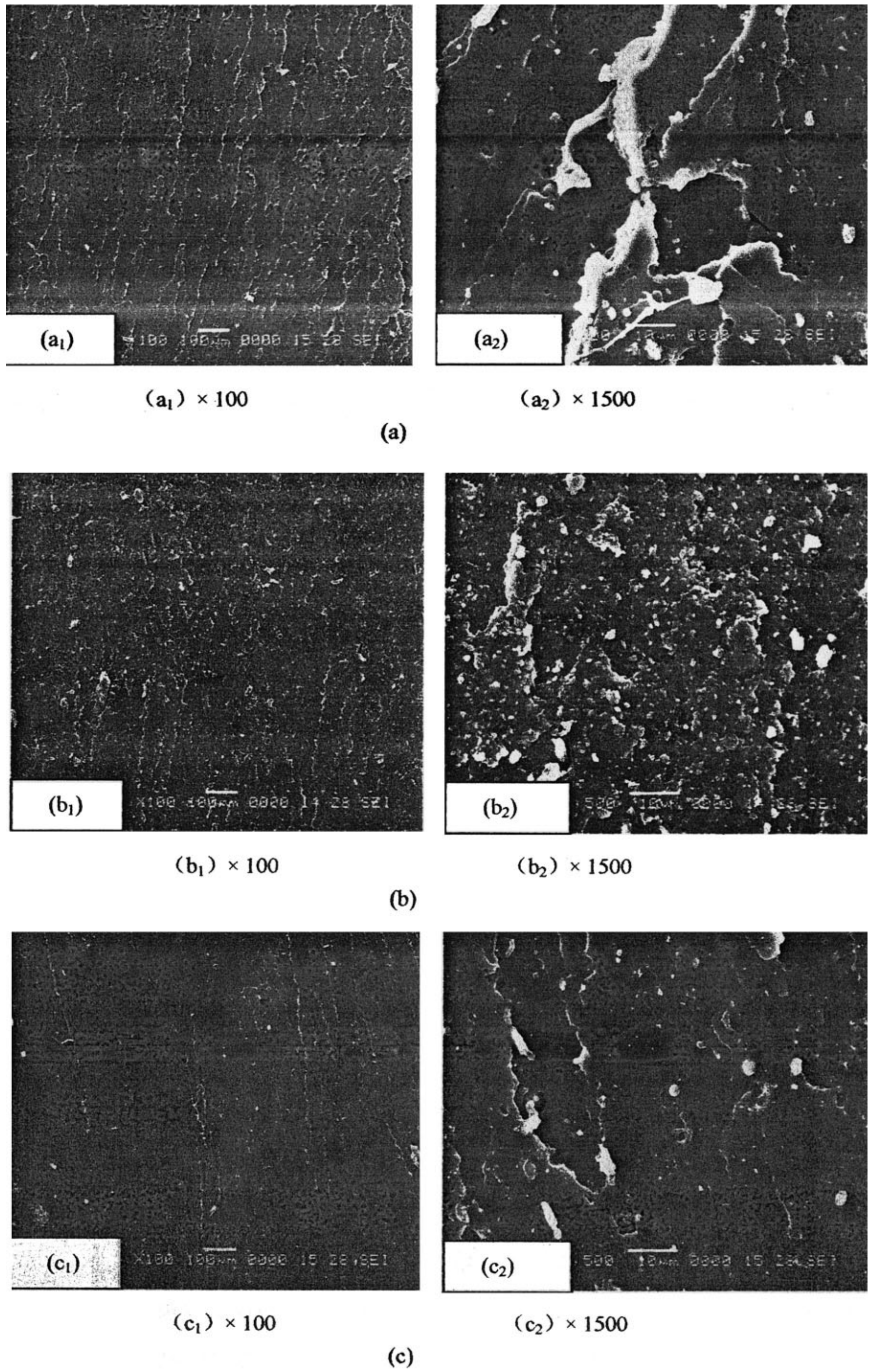


Figure 3 SEM images of the fracture surface of different zinc oxide filled SBR systems. (a) common zinc oxide, (b) nano-zinc oxide, (c) nano-zinc oxide master batch.

RESULTS AND DISCUSSION

Cure characteristics

Figure 2 shows the rheographs of different kinds and different amounts of zinc oxide filled SBR systems. The data of the cure characteristics are summarized in Table II.

From Table II, it can be seen that the addition of nano-zinc oxide master batch can prolong scorch time (t_{10}) and make processing safer compared with those of nano-zinc oxide and common zinc oxide filled SBR systems; also, it can be concluded that a retardation effect occurs in the vulcanization process deduced from the prolonged technical cure time (t_{90}). Meanwhile, the decrease of initial and minimum torque (M_0 and M_L), which shows a reduction of viscosity, can make the compounds easier to process. The maximum torque (M_m) can be taken as a measurement of crosslinking density, and the results suggest that the system of nano-zinc oxide master batch has higher crosslinking density than that of the systems of common zinc oxide and nano zinc-oxide.[16]

Mechanical properties

The mechanical properties of the common zinc oxide, nano-zinc oxide, and nano-zinc oxide master batch filled systems are listed in Table III. As expected, in common zinc oxide filled systems, the tensile strength and elongation at break of 5 phr system are the highest; also, it can be seen that the mechanical properties of 1 phr nano-zinc oxide and nano-zinc oxide master batch filled systems are the best among the five systems, respectively.

The mechanical properties of nano-zinc oxide master batch of 1 phr are better than that of nano-zinc oxide filled system. This is probably due to the improved dispersion of nano-zinc oxide in the master batch filled system, which can make the full embodiment of nano-effect such as little size effect, surface effect and quantum effect of nano-zinc oxide.

Figure 3 presents the images of the fracture surface of the three systems with common zinc oxide, nano-zinc oxide, and nano-zinc oxide master batch. The materials show fracture surfaces with different topographic aspects. The fracture surfaces of common zinc oxide and nano-zinc oxide filled system show microscopic features of surface roughness, characterizing a ductile fracture mechanism. The nano-zinc oxide master batch system presents flat regions with many cracks, characterizing a fragile behavior, which indicate an improvement of the plasticity of this system. These SEM observations agree well with the above tensile test results.[16]

Figure 4 shows the abrasion loss of various systems with different kinds and amounts of zinc oxide. In the common zinc oxide filled SBR system, the loss value decreases with the increase of common zinc oxide amount. As far as the systems of nano-zinc oxide and nano-zinc oxide master batch were concerned, the wear resistance property of 1 phr is the best among the five systems. Figure 5 shows the SEM images of the worn surfaces of common zinc oxide, nano-zinc oxide, and nano-zinc oxide master batch filled systems, respectively. It can be seen that the worn surface of common zinc oxide and nano-zinc oxide filled system accumulated stacks of shallow holes, while the composite containing master batch of nano-zinc oxide appears to have a relatively flat surface.

With very small size and very high surface energy, nano-zinc oxide easily agglomerates to large particles. By master batch technology, the agglomerated particles can evenly disperse in the rubber systems and

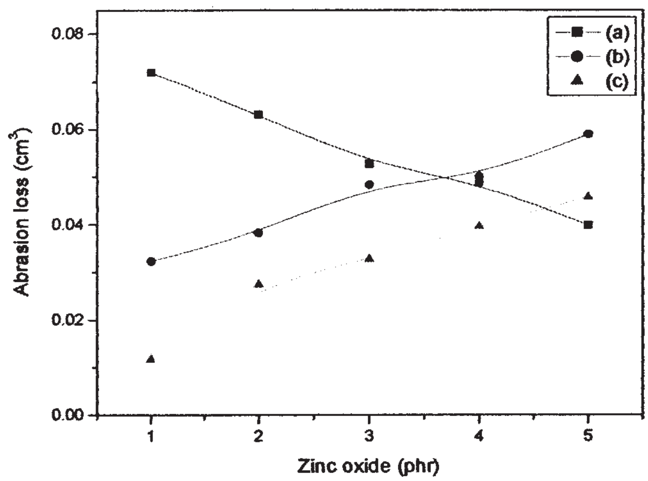


Figure 4 Abrasion loss of different zinc oxide filled SBR systems. (a) Common zinc oxide, (b) nano-zinc oxide, (c) nano-zinc oxide master batch.

have more chance to react with other addition agents, such as thiazole type activator, which can improve crosslinking level of the system. This crosslinking network may play an important role in preventing both the initiation and propagation of cracks that may occur in the rubber materials on the contact surface, which can decrease abrasion loss of the systems.[17]

Dynamic mechanical properties

Figure 6(a) shows the variation of storage modulus (E′) with temperature. The storage modulus of the rubber by master batch technology is relatively higher compared to that of the nano-zinc oxide and common zinc oxide filled systems. Having in mind that the working temperature of rubber is usually above their glass transition (T_g), the plateau values of the E′ in this region is of great importance. As shown in this figure, the stiffness of nano-zinc oxide master batch system above the T_g is relatively higher compared to the other two systems, which is due to better dispersion and higher crosslinking level of nano-zinc oxide by master batch.

As to the loss curves tan δ in Figure 6(b), at about −25 to −20°C, three intense peaks, due to the mobilization of the amorphous soft domains, appear in the corresponding main glass transition of the three systems. It can be seen that the tan δ peak of nano-zinc oxide master batch filled system is relatively lower, which can be concluded that the restricted mobility of the chains is due to the better dispersion improvement of nano-zinc oxide in the matrices.[18,19]

TEM analysis

Figure 7 shows the TEM images of the dispersion morphology of different zinc oxide filled uncuring systems

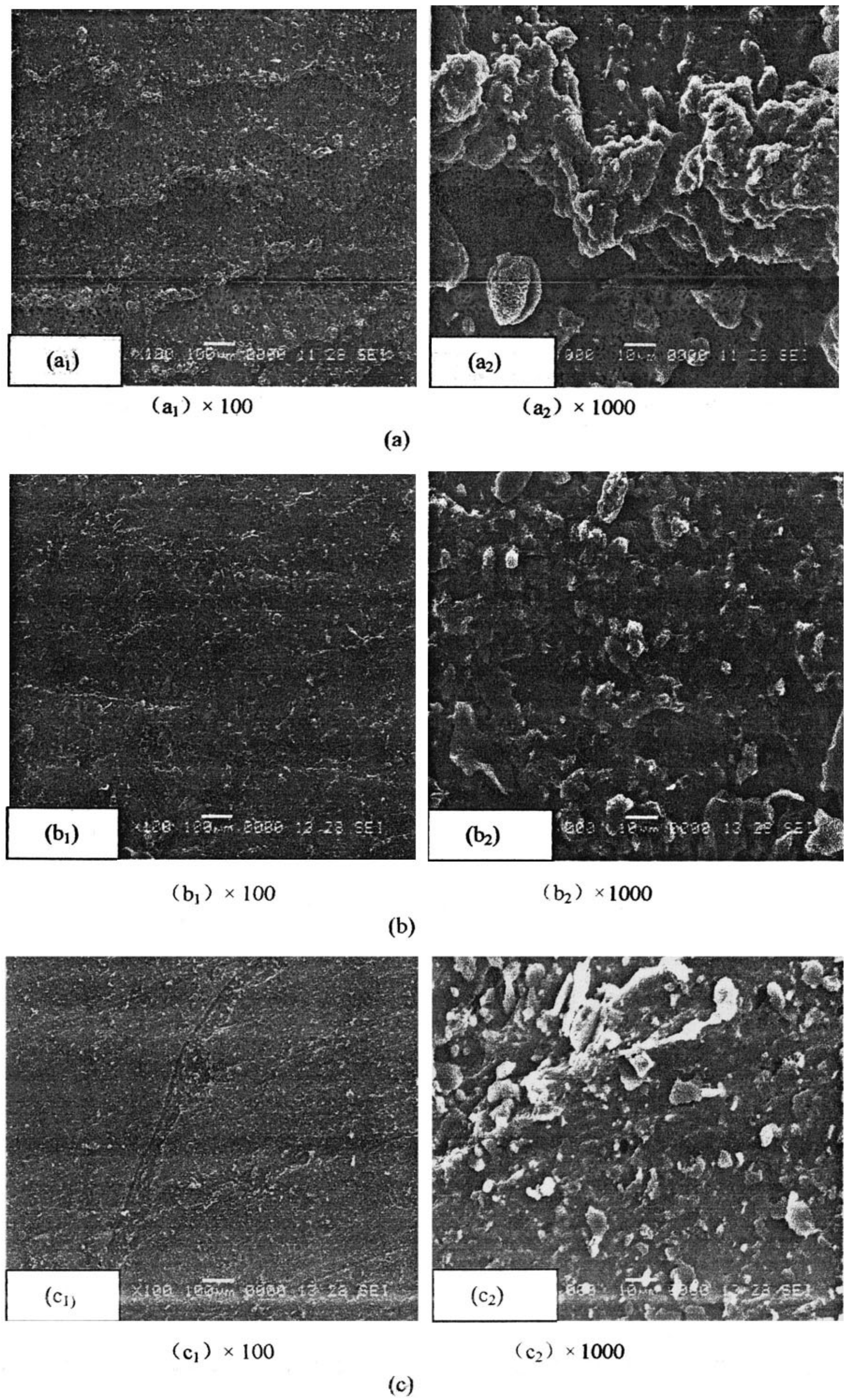


Figure 5 SEM images of different zinc oxide filled SBR systems. (a) Common zinc oxide, (b) nano-zinc oxide, (c) nano-zinc oxide master batch.

without other addition agents, in which (a) relates to the common zinc oxide, (b) nano-zinc oxide, and (c) nano-zinc oxide master batch filled composites. As can be seen from Figure 7(a), common zinc oxide can evenly disperse in the SBR system, while in Figure 7(b), the clustering of nano-zinc oxide can be clearly seen, which is due to its high surface energy. We also observed the morphology of SBR matrix with nano-zinc oxide by master batch, and the excellent dispersion of nano-zinc oxide may be explained by the application of master batch technology in the mixing procedure, which is beneficial for filler dispersion in composites.

General discussion of zinc oxide amount reducing mechanism

Zinc oxide is an important rubber additive, and it has an important effect on the development of sulfur bonds in rubber systems.

The mechanism for the sulfuration and activation is concluded as follows (XSH in the formula represents thiazole type activator, RH represents rubber molecules):

$$ZnO + 2XSH \rightarrow XZnX + \cdots \quad (1)$$

$$ZnX + \mathbf{2S}_n \rightarrow XS_nZnS_nX \quad (2)$$

$$XS_nZnS_nX + RH \rightarrow XS_nR + ZnS + HS_{n-1}X \quad (3)$$

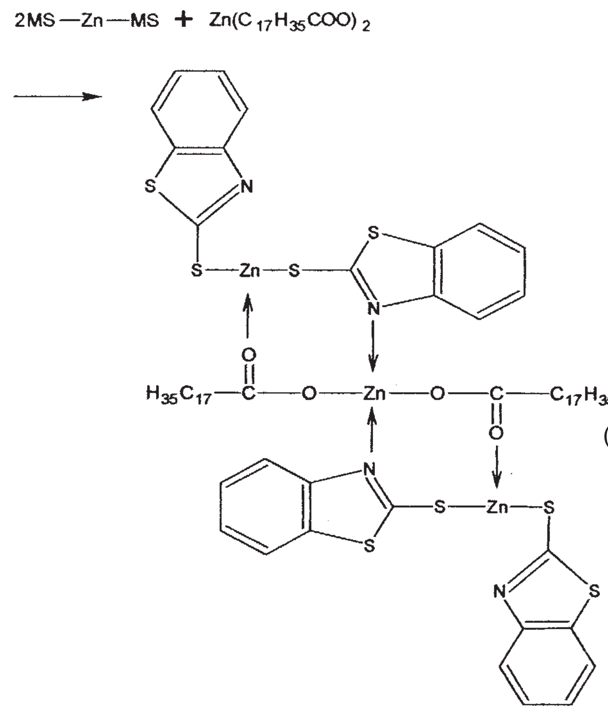
$$XS_nR + RH \rightarrow RS_{n-1}R + XSH \quad (4)$$

In this mechanism, the amount of zinc oxide used has something to do with S_n. The sulfur in this mechanism was considered eight-ring structure, and as a result, the amount of zinc oxide used will be $81 \times 3/(32 \times 16) = 0.48$ phr, if the amount of sulfur used is 3 phr.

The mechanism shown earlier also has its defects, that is, the function of stearic acid is not embodied in this mechanism. The following mechanism can illustrate that only about 1 phr nano-zinc oxide is needed in the sulfuration process, if the activity of zinc oxide is fully embodied. (MSH in the formula represents MBT type activator).

$$2MSH + ZnO \rightarrow MS{-}Zn{-}SM + H_2O \quad (5)$$

$$2C_{17}H_{35}COOH + ZnO \rightarrow Zn(C_{17}H_{35}COO)_2 + H_2O \quad (6)$$



(7)

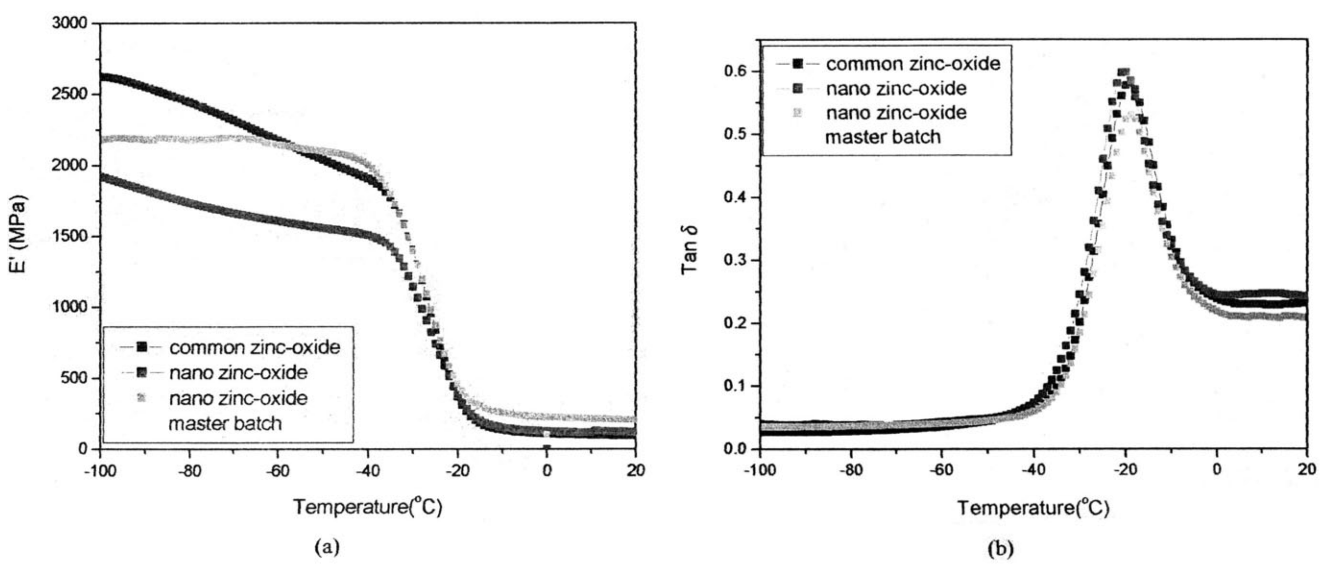
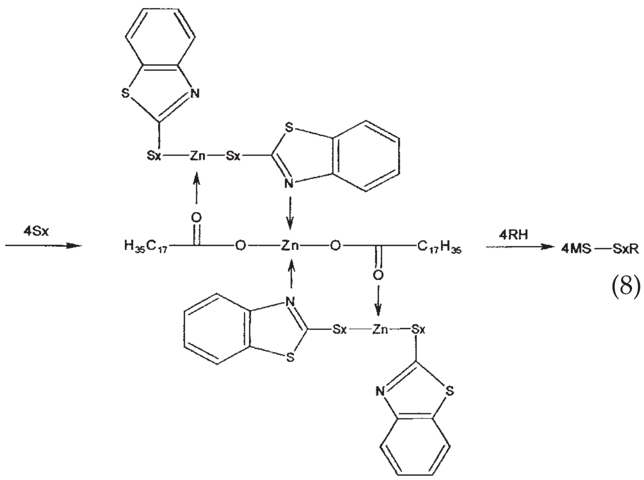


Figure 6 DMA curves of different zinc oxide systems. (a) Storage modulus versus temperature, (b) loss tangent versus temperature.



(8)

$$MS\text{-}S_X\text{-}R \rightarrow RS_a^{+} + MS_b^{-} \quad (a+b=x+1)$$

From the above, $0.48 + 81 \times 3/(2 \times 284) = 0.91$ phr zinc oxide is needed if the amounts of zinc oxide, which participates both in sulfuration and in the reaction with stearic acid, are all considered. That is why SBR composites with 1 phr nano-zinc oxide and 1 phr nano-zinc oxide master batch has the best mechanical properties.

CONCLUSIONS

The master batch mixing technology of nano-zinc oxide is an effective way for improving the mechanical properties of SBR composites. In comparison with common and nano-zinc oxide filled SBR systems, nano-zinc oxide master batch filled composite shows better tensile and wear resistance properties.

A combination of DMA, TEM, and sulfuration process analyses shows that master batch technology is of great importance for the better dispersion of nano-zinc oxide in SBR matrix, which is beneficial for the improvement of crosslinking level and me-

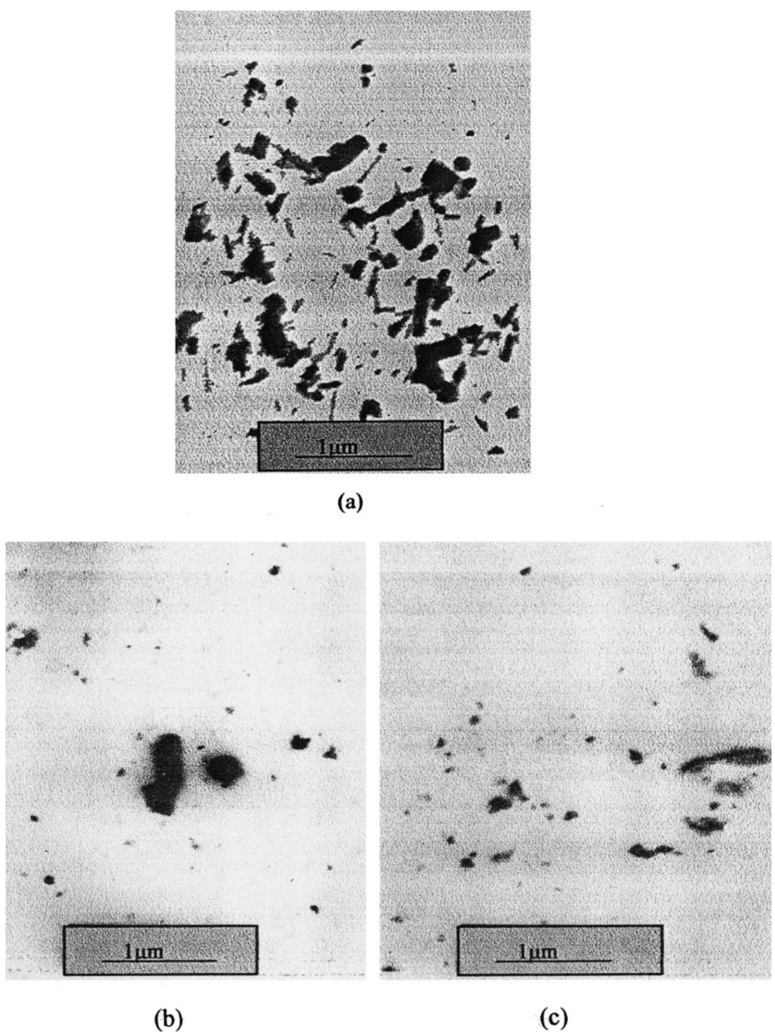


Figure 7 TEM of different zinc oxide filled SBR systems (×30,000). (a) Common zinc oxide, (b) nano-zinc oxide, (c) nano-zinc oxide master batch.

chanical properties. Thus, it can be concluded that the amount of zinc oxide used can be reduced to 1 phr or even less due to the full embodiment of the nano-effect by the master batch technology.

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