# Structure, Morphology, and Properties of HNBR Filled with N550, SiO$_2$, ZDMA, and Two of Three Kinds of Fillers

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**ABSTRACT:** The vulcanization properties, mechanical properties of hydrogenated nitrile rubber (HNBR) filled with carbon black (N550), zinc dimethacrylate (ZDMA), SiO$_2$ independently and two of three kinds of fillers together were investigated, respectively. The filler-dispersion was characterized by the transmission electron microscopy (TEM) and dynamic mechanical properties. The results showed that HNBR composite filled with SiO$_2$ or ZDMA displayed high tensile strength, elongation at break and compression set. The HNBR composite filled with N550 displayed low compression set, tensile strength and elongation at break. The dispersion of SiO$_2$ in HNBR compound was better than that in HNBR vulcanizates because of SiO$_2$ particles self-aggregation in vulcanizing processing. ZDMA particles with micron rod-like and silky shape in HNBR compounds changed into near-spherical poly-ZDMA particles with nano size in HNBR vulcanizates by *in situ* polymerization reaction. The N550 particles morphology exhibited no much change between HNBR compounds and vulcanizates. N550/ZDMA have the most effective reinforcement to HNBR and the appropriate amount of ZDMA is about 25% of total filler amount by weights. The theory prediction for Payne effect (dispersion of the filler) shown by the dynamic properties is identical with actual state observed by TEM. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 421–427, 2010

**Key words:** fillers; HNBR; morphology; reinforcement; TEM

## INTRODUCTION

In 1980s, German Bayer and Japan Zeon Company developed a new type elastomer named hydrogenated nitrile butadiene rubber (HNBR) which is hydrogenated from nitrile butadiene rubber (NBR). HNBR not only keeps excellent oil and chemical resistance just the same as NBR, but also has good heat, pressure and ozone resistance, so HNBR is especially applied to the automobile, aviation, oil field, and other industries for the high performance rubber fittings, and the application of it is increasing year by year.[1,2]

The traditional reinforcing agents for HNBR are carbon black, SiO$_2$ powder, and other mineral fillers. Carbon black is a sort of nonpolar filler, but there were a few polar groups on its surface, such as carboxyl, hydroxyl, and quinonyl. So, it has affinity with polar rubber, such as HNBR.[3] But the reinforcing effect of carbon black on HNBR is weaker than that on the general nonpolar rubber. There are lots of hydroxyl groups on the surface of SiO$_2$ particles, and hydrogen bonds easily form between SiO$_2$ particles and nitrile groups of HNBR. Because of its strong self-aggregation it is hard to disperse SiO$_2$ powder into HNBR in nano scale. Moreover, SiO$_2$/ HNBR composites are set a limit to be used for the compression fittings materials for its high compression set, which results from slipping of the hydrogen bonds between the surface of SiO$_2$ particles and HNBR molecular chain in the force-field.[4] The comprehensive properties and service life of HNBR filled with other mineral filler could not meet the requirements of application in harsh environment.

In recent years, a new type of reinforcing filler—methacrylate salt, such as zinc dimethacrylate (ZDMA), magnesium dimethacrylate, and sodium dimethacrylate, were discovered.[5] The methacrylate salt particles, in whose molecular unsaturated bond existed, generally with micron-size were easily dispersed into HNBR and it could polymerized into polymethacrylate salt particles on nanoscale through radical polymerization reaction mechanism in the vulcanizing processing of rubber at high temperature. Besides, the co-crosslink interactions between polymethacrylate salt particles and HNBR could be produced, which improved the fillers dispersion

further more. Therefore, the polymethacrylate salt nanoparticles exhibited excellent dispersion in HNBR[6] and enhancement for HNBR,[7,8] and HNBR composites filled with methacrylate salt had high strength, elongation and good processability. However, there were plenty of ion bonds in polymethacrylate salt particles, which resulted in decreasing the properties of the composite at high temperature.

In summary, it is difficult to make HNBR composite filled with only one filler (such as carbon black, SiO$_2$ or methacrylate salt) obtain good comprehensive performance. Thus, using two or more kinds of filler together to reinforce HNBR could achieve a good effect. There are no reports about the structure, morphology and properties of HNBR filled with two of these three fillers together.

In this essay, the curing properties, mechanical properties, and compression set of HNBR composites filled with N550, SiO$_2$, ZDMA, N550/SiO$_2$, N550/ZDMA, and ZDMA/SiO$_2$ respectively were investigated. The dispersion of fillers in rubber matrix had been evaluated by Payne effect shown by dynamic mechanical properties, and observed by transmission electron microscopy (TEM), respectively. The useful data were obtained, and the study results would provide theoretical basis for preparing comprehensive performance HNBR composites.

## EXPERIMENTAL

### Materials

HNBR were supplied by Zeon (Japan), as Zeptol 2010L grade, which contained 36% acrylonitrile and 5% residual double bonds. Carbon black (N550) was produced by Tianjin Dolphin Carbon Black Development (China). Zinc dimethacrylate (ZDMA) SR634 with a powder with micro-size were provided by Sartomer Company, USA. The precipitated silica (Tixosil 383) powder with an average particle diameter of about 20 nm comes from Rhodia Silica Qingdao, China. The other rubber additives are commercial grades.

### Formulation

The formulation of HNBR composites are as follows: HNBR 2010L 100, fillers 40 (shown in Table I), dicumyl peroxide (DCP) 5, other additives 9.5 phr.

### Preparation of the vulcanizates

The rubber compounds were prepared by a 6-inch mill (produced by Shanghai Rubber Machinery Works No. 1, Shanghai, China) with the conventional mixing technique. A plate vulcanization machine (produced by Shanghai Rubber Machinery

**TABLE I**
**The Ratio of Two Kinds of Fillers in HNBR**

| Contents | Ratio | | | | |
|---|---|---|---|---|---|
| | 40 : 0 | 30 : 10 | 20 : 20 | 10 : 30 | 0 : 40 |
| N550 : SiO$_2$ | N | NS1 | NS2 | NS3 | S |
| N550 : ZDMA | N | NZ1 | NZ2 | NZ3 | Z |
| ZDMA : SiO$_2$ | Z | ZS1 | ZS2 | ZS3 | S |

Works, Shanghai, China) was used to prepare the vulcanizates samples. The curing condition was 160°C × $t_{90}$ min (optimum curing time) and the post curing condition is 150°C × 9 h.

### Instruments and conditions

Transmission electron microscopy (TEM) observations were performed on an H-800-1 transmission electron microscope (Hitachi Corporation, Tokyo, Japan) with an acceleration voltage of 200 kV.

The mechanical properties of all vulcanizates were measured at 23 ± 2°C according to the Chinese National Standard 528–1998 with the material test machine (LLOYD, UK) at a stretching rate of 500 mm/min.

The Shore A hardness was determined using a rubber hardness apparatus made by the fourth Chemical Industry Machine Factory, Shanghai, China, according to Chinese National Standard 531–1999.

Compression set were measured according to the Chinese National Standard 7759-1996. The test condition was 150°C × 144 h and the precompression ratio is 25%.

Strain-sweep experiments were performed with an rubber process analyzer-RPA 2000 (produced by Alpha Technologies, USA). The test condition for the compounds: frequency 1 Hz, temperature 60°C, the strain 0.8–250%; The test condition for vulcanizates: the frequency 10 Hz temperature 60°C, the strain 0.28–40%.

## RESULTS AND DISCUSSION

### The effect of kinds of filler and the ratio between two fillers on the properties of HNBR composites

#### The effect of N550 and SiO$_2$

The curing, mechanical and compression set properties of HNBR composites filled with N550/SiO$_2$ in different ratio are shown in Table II.

From Table II, it could be seen that the scorch time ($t_{10}$) and optimum time ($t_{90}$) of HNBR composite are delayed with the increasing amount of SiO$_2$. The HNBR composite filled with SiO$_2$ (S) has higher tensile strength, elongation, and compression set at high temperature than that filled with N550 (N) observably, which indicates that the effect of

| Properties | N | NS1 | NS2 | NS3 | S |
|---|---|---|---|---|---|
| $t_{10}$ (min) | 2.07 | 2.13 | 2.93 | 3.23 | 4.32 |
| $t_{90}$ (min) | 15.17 | 14.43 | 16.27 | 17.40 | 24.48 |
| Hardness, Shore A | 73 | 72 | 74 | 73 | 79 |
| 300% Modulus (MPa) | – | 20.8 | 15.3 | 15.0 | 19.5 |
| Tensile strength (MPa) | 25.3 | 25.7 | 30.3 | 30.8 | 38.4 |
| Elongation at break (%) | 292 | 346 | 450 | 438 | 445 |
| Tensile set (%) | 5 | 9 | 11 | 11 | 11 |
| Compression set (%) | 30.9 | 45.3 | 73.4 | 73.2 | 77.9 |

reinforcing HNBR with SiO$_2$ is higher than that with N550, but the compression set of S composite is much larger. Only considering the rubber matrix, the compression set of HNBR vulcanizates cured by peroxide is very low for its C-C cross-linking bond. Therefore, the compression set of HNBR composites with the filler is originated from the deformation of filler aggregate and the change of interactions seat between rubber molecular chain and the surface of filler particles. There are some chemical bond force and weaker electrostatic adsorption force between HNBR molecular chains and a few of chemical groups, such as carboxyl, hydroxyl et al., on the surface of N550 particles. The elongation of N composite is low because the some bond force limits the high degree orientation of the molecular chains in the direction of external force and carbon black (N550) particles could not deform easily. During the recovery of deformation, there is little effect of electrostatic adsorption force on the relaxation of molecular chain, so the compression set of N composite is low. SiO$_2$ has good compatibility with HNBR due to the hydrogen bond formed between nitrile groups of HNBR and a lot of hydroxyl groups on the surface of SiO$_2$. Under the external force action, HNBR molecular chains slip easily on the surface of SiO$_2$ particles and new hydrogen bond at the new seat reforms, so HNBR molecular chain could not recover its original state. Second, SiO$_2$ could not disperse as single nano particles (about 20 nm), the aggregates will resplit under compression action force. Thereby, the compression set of HNBR filled with SiO$_2$ powder (S composite) is very high.

It could be concluded easily from Table II that with the increasing amount of SiO$_2$, $t_{10}$, $t_{90}$, tensile strength, elongation, and compression set of the HNBR composites increase and 300% modulus decreases as well. With the replacement of 10 phr N550 by 10 phr SiO$_2$ (compared N with NS1), the elongation of NS1composite increases by a factor of 18.5% but the compression set steps up to 146.6%. Therefore, the amount of SiO$_2$ in the HNBR composites used for seal products (low compression set) should be less than 25% of the total filler dosage.

The effect of N550 and ZDMA

As shown clearly in Table III, $t_{10}$ and $t_{90}$ of Z and N composites are nearly the same, which indicates that the effect of ZDMA is close to that of N550 on curing property of HNBR using DCP as the vulcanization system. The tensile strength and elongation of Z composite are higher than N, which shows that ZDMA has greater reinforcing abilities to HNBR than N550. This is because during the vulcanization ZDMA particles turn into poly-ZDMA particles through *in situ* polymerization and the electrostatic adsorption and chemical bond force between the poly-ZDMA particles and HNBR molecular chains are produced at the same time. So the molecular chains of Z composite could produce high orientating along the direction of external force. But the bunches of electrovalent bond formed by adsorption of Zn$^{2+}$ and –O$^-$ inside poly-ZDMA particles will deformed along external force. Moreover, the polymerization conversion rate of ZDMA could not

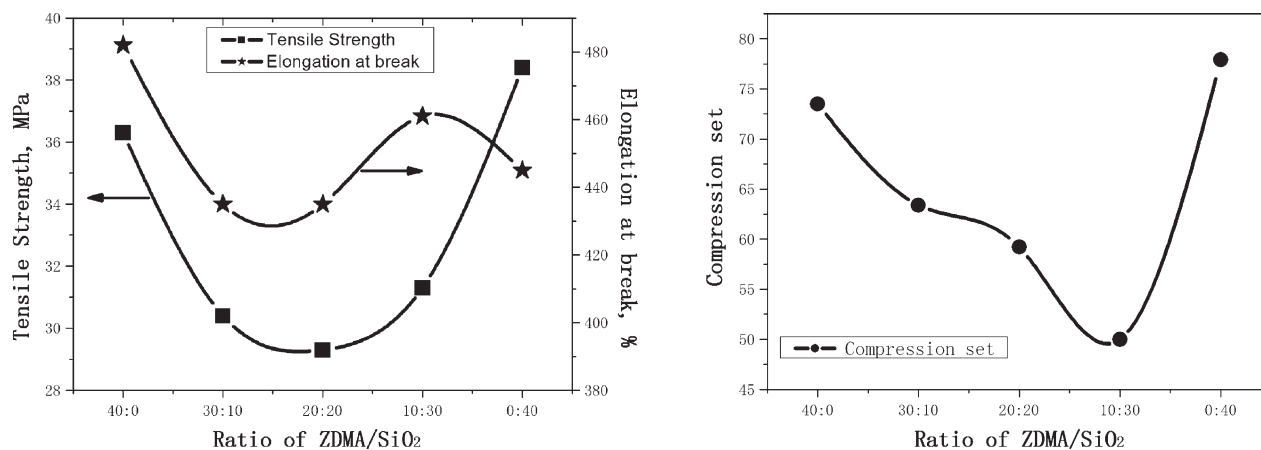| Properties | N | NZ1 | NZ2 | NZ3 | Z |
|---|---|---|---|---|---|
| $t_{10}$ (min) | 2.07 | 1.73 | 2.00 | 2.03 | 2.33 |
| $t_{90}$ (min) | 15.17 | 15.90 | 15.50 | 15.95 | 14.45 |
| Hardness, Shore A | 73 | 76 | 75 | 75 | 73 |
| 300% Modulus (MPa) | – | 21.0 | 17.4 | 14.4 | 11.7 |
| Tensile strength (MPa) | 25.3 | 29.8 | 31.6 | 31.7 | 34.4 |
| Elongation at break (%) | 292 | 419 | 472 | 502 | 499 |
| Tensile set (%) | 5 | 12 | 16 | 22 | 20 |
| Compression set (%) | 30.9 | 32.9 | 33.8 | 39.8 | 69.0 |

**Figure 1**  The mechanical properties and compression set of HNBR composites filled with different rate of ZDMA/SiO$_2$.

reach 100%, and the split of rest larger ZDMA aggregates would happen, so the tensile and compression set of Z composite are high.

With increasing the amount of ZDMA, the tensile strength, elongation and compression set of HNBR composites reinforced by N550/ZDMA increase, but the growth rate of compression set of them is far less than that of N550/SiO$_2$ composites with increasing the same amount of SiO$_2$. NZ1 and NZ2 composites exhibit lower compression set, higher tensile strength and larger elongation, so the preferred ratio of N550/ZDMA filled in HNBR composites is 30/10.

### The effect of ZDMA and SiO$_2$

From Table II and III, it could be seen that S composites has high tensile strength, elongation and compression set same as Z composites. But the tensile strength, elongation, and compression set of HNBR composites filled with ZDMA/SiO$_2$ decrease remarkably, as shown in Figure 1. The reason could be that the adsorption forces between electrovalent bonds in ZDMA particles and hydroxyl groups on

the surface of SiO$_2$ exists, and it is difficult for two kinds of fillers to disperse in HNBR at the same time. So the reinforcement of ZDMA and SiO$_2$ to HNBR is weakened. The mutual adsorption between ZDMA and SiO$_2$ particles drop down the splitting degree of filler particles so as to make compression set of each and every ZS series composites less than that of Z or S composites each., and that of ZS3 composite reaches the minimum value in ZS series.

In summary, these two fillers could not reinforce HNBR well together.

### The dispersion of fillers in HNBR

#### Fillers' dispersion characterized by dynamic mechanical properties

Figure 2 shows the relations between elastic modulus ($G'$) and strain ($\varepsilon$) of HNBR compounds and vulcanizates filled with SiO$_2$/N550 respectively.

In Figure 2 within the range of strain measured, the variation of $G'$ ($\Delta G'$) of S sample either compounds or vulcanizates is the biggest among these
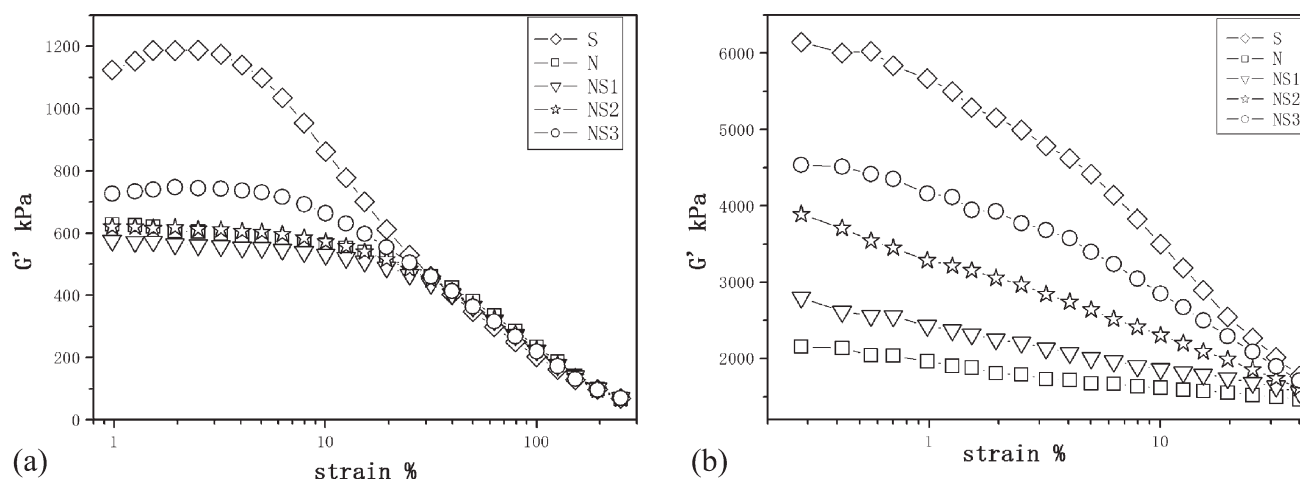


**Figure 2**  $G' \sim \varepsilon$ curves of HNBR filled with different SiO$_2$/N550 (a-compounds, b-vulcanizates).
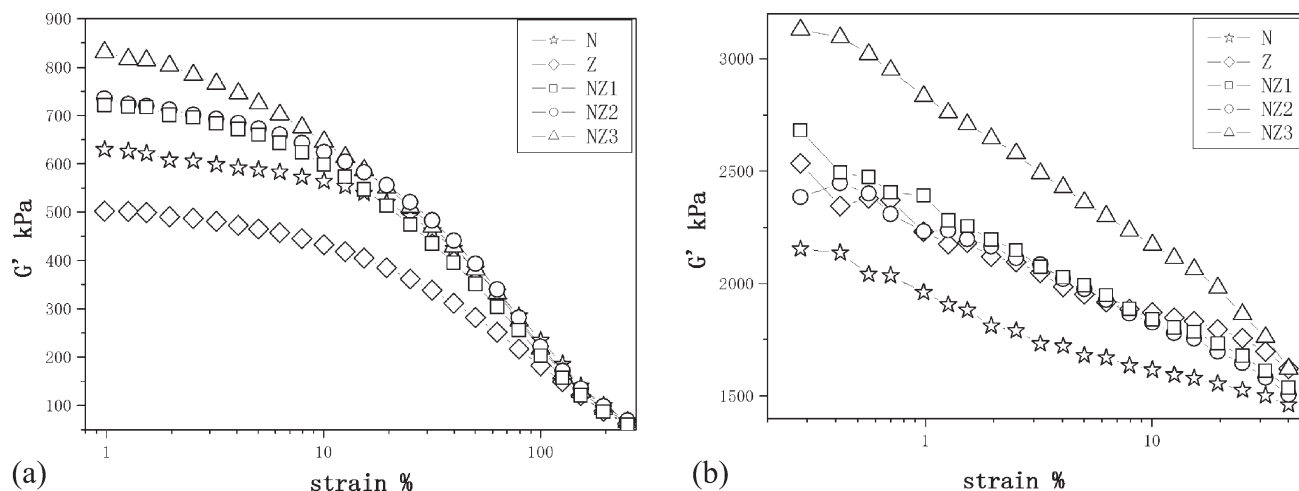
**Figure 3** $G' \sim \varepsilon$ curves of HNBR filled with different N550/ZDMA (a-compounds, b-vulcanizates).

five samples mentioned earlier. That is to say that the Payne effect characterized by $\Delta G'$ value (The higher $\Delta G'$ value is, the more obvious the Payne effect is[9,10]) of HNBR filled with $SiO_2$ is obvious, which indicates the dispersion of $SiO_2$ in HNBR is not changed during vulcanization. $\Delta G'$ of N sample in either compound or vulcanizates is lower than that of S sample, and so the dispersion of N550 in HNBR is much better. $\Delta G'$ of N vulcanizates is smallest among five vulcanizates, which shows that dispersion of N550 has been improved in vulcanization processing. It associates with the bigger particles size of N550 and good affinity with HNBR.

With the increasing amount of $SiO_2$, $\Delta G'$ of HNBR filled with $N550/SiO_2$ rises, especially that of the vulcanizates does. It is possible that some $SiO_2$ particles tend to aggregate during vulcanization due to the molecular random heat movement, which strengthens the Payne effect.

Figure 3 shows the curves between $G'$ and $\varepsilon$ of HNBR compounds and vulcanizates filled with N550/ZDMA, respectively.

Figure 3(a) shows that $G'$ and $\Delta G'$ of Z compounds are the lowest among five compounds, and those of N compounds are higher than those of Z compounds. It is indicated that ZDMA with bigger particle size has better dispersion in HNBR compounds. $G'$ and $\Delta G'$ of HNBR compounds filled with ZDMA/N550 increase along with the increasing amount of ZDMA. It is because there is little interaction between ZDMA and N550 during mixing process, both different filler particles bump and rub each other, and particle refinement occurs. The particles refined are easily to form filler network,[11] so the Payne effect of compounds becomes more obvious.

Figure 3(b) indicates that Payne effect of N vulcanizates is the lowest, and that of Z vulcanizates is higher than that of N vulcanizates. This shows that

after vulcanization the dispersion of N550 in HNBR gets a little improvement, and the state with nano poly-ZDMA and micron ZDMA particles multiphase coexisting makes Payne effect of Z vulcanizates a little higher. The $\Delta G'$ values (Payne effect) of NZ1 and NZ2 vulcanizates are higher than Z vulcanizates slightly, and that of NZ3 vulcanizates is the highest. The reason might be that a small amount of N550 makes against the polymerization and dispersion of ZDMA and the further research is still in progress.

Figure 4 shows $G' \sim \varepsilon$ curves of HNBR compounds and vulcanizates filled with ZDMA and $SiO_2$.

It could be seen from Figure 4(a) that Payne effect of S compounds is significant while that of the others compounds is much lower and close each other, which indicates that ZDMA could adsorb $SiO_2$ to form bigger filler particles and disperse more easily in HNBR. In Figure 4(b) ZDMA particles in vulcanizates are polymerized into poly-ZDMA particles which have weaker adsorbing abilities for $SiO_2$, and $SiO_2$ particles released makes the filler-dispersion worse. Hence, with the increasing amount of $SiO_2$ powder, the Payne effect is more obvious, which is in accordance with the conclusion from Figure 1.

### The morphology of HNBR filled with the fillers

Figure 5 shows TEM photographs of HNBR filled with N550, ZDMA and $SiO_2$ respectively.

As shown in Figures 5a1, b1, N550 particles aggregate together in N compounds and their morphology could not be picked out, while N550 particles in N vulcanizates shaped like the sphere with 50 to 60 nm and some of them form bead-chain structure. In Z compound [Fig. 5($a_2$)] ZDMA particles present different morphologies: Some display rod and silky, some appear lumpish aggregates above 100 nm size. In Z vulcanizates [Fig. 5($b_2$)] most poly-ZDMA
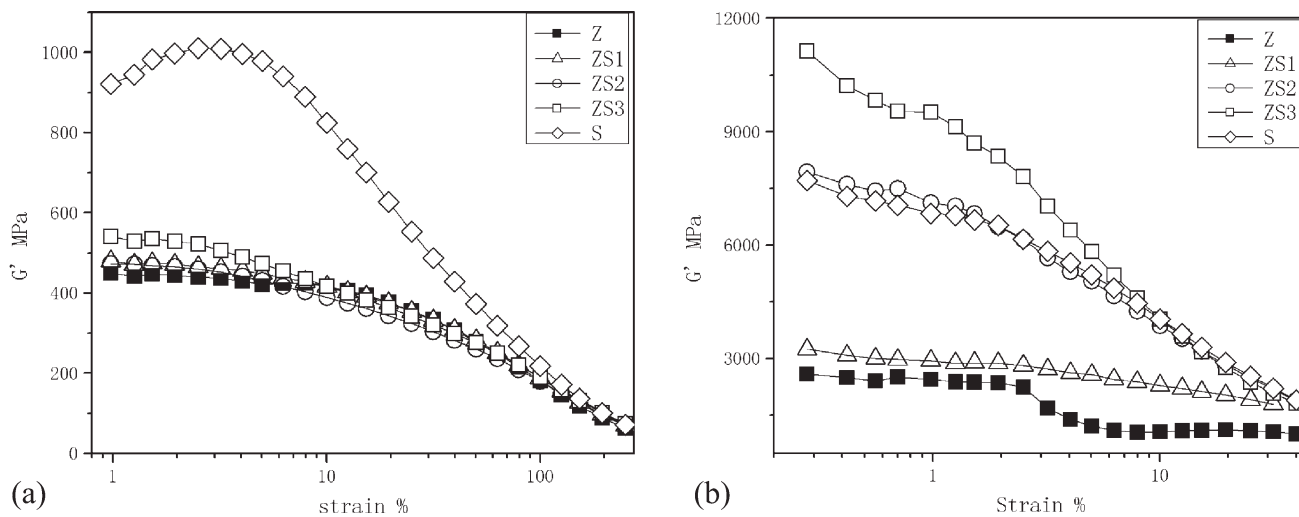
(a)

(b)

**Figure 4**  $G' \sim \varepsilon$ curves of HNBR filled with different ZDMA/SiO$_2$ (a-compounds, b-vulcanizates).
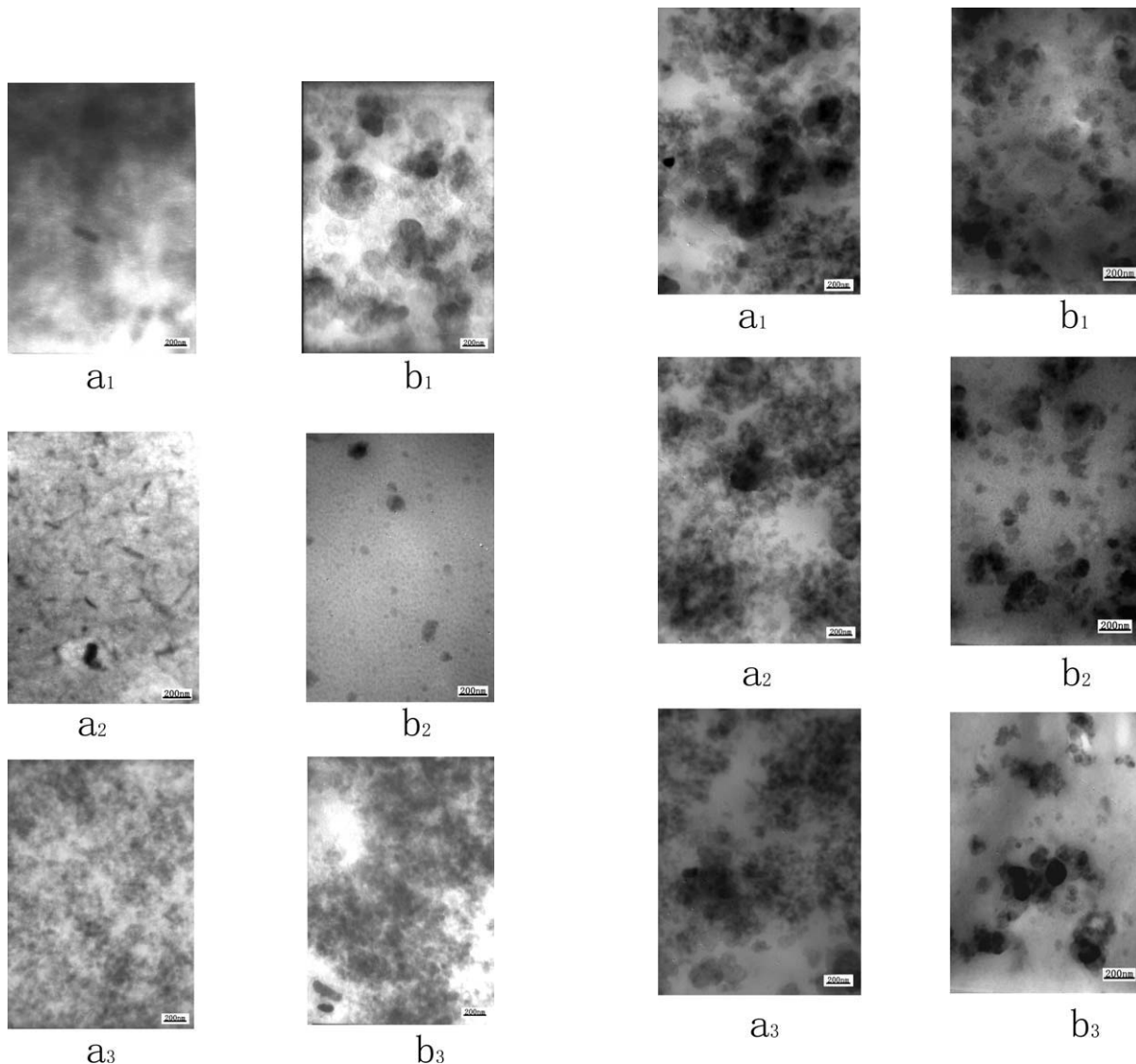


**Figure 5** TEM photographs of HNBR filled with N550, ZDMA, and SiO$_2$ separately (a$_1$, a$_2$, a$_3$–N, Z, S compounds; b$_1$, b$_2$, b$_3$–N, Z, S vulcanizates).



**Figure 6** TEM photographs of HNBR filled with N550/SiO$_2$ and N550/ZDMA respectively (a$_1$, a$_2$, a$_3$–NS1, NS2, NS3 vulcanizates respectively; b$_1$,b$_2$, b$_3$–NZ1, NZ2, NZ3 vulcanizates, respectively).

particles with the diameter of about 10 nm disperse evenly in HNBR, and only a few loose particles in 50 to 150 nm size which could be ZDMA particles unpolymerized. $SiO_2$ particles display barely passable dispersion but form filler-net in the compound [Fig. 5($a_3$)], and aggregate very significantly in the vulcanizates [Fig. 5($b_3$)]. The dispersion of each of these three fillers in either the compound or the vulcanizates is consistent with the predicted results by dynamic mechanical properties, same as the study results of other investigator.[12,13]

The photos $a_1$, $a_2$ and $a_3$ in Figure 6 show that with the increasing amount of $SiO_2$, the size of carbon black aggregates becomes smaller and its dispersion get improvement gradually. $SiO_2$ particles dispersed more evenly in three samples. So $SiO_2$ and N550 do not interfere with each other in HNBR and reinforce HNBR with superimposing effect. Therefore, with increasing the load of $SiO_2$ tensile strength, compression set and elongation at break of NS series vulcanizates increase. It is not appropriate to use N550 and $SiO_2$ together to reinforce HNBR due to large compression set of the composites.

It could be seen from photo $b_1$ and $b_2$ in Figure 6 that N550 particle size in NZ1 and NZ2 vulcanizates is about 50 to 100 nm and poly-ZDMA particle size is about 10–20 nm, and both fillers have good dispersion in HNBR. The photo b3 in Figure 6 shows that there are some aggregates of filler in NZ3 vulcanizates. It fit for the conclusion from dynamic mechanic properties, in which the dispersion of fillers in NZ3 vulcanizate is in a bad state. The mechanical properties and compression set of HNBR composites being considered, the suitable amount of ZDMA should be 25% of total filler parts when N550 and ZDMA are filled together to HNBR.

## CONCLUSIONS

1. The HNBR composite filled with $SiO_2$ or ZDMA has high tensile strength, elongation and compression set. HNBR composite filled with N550 exhibits low compression set, tensile strength, and elongation. It is necessary to reinforce HNBR with different kinds of fillers to-

gether in order to get HNBR composite with good overall properties.

2. The dispersion of $SiO_2$ particles in HNBR compound is better than that in vulcanizates, which indicates that $SiO_2$ particles aggregate itself easily during vulcanization. The dispersion of N550 in HNBR vulcanizates is better than that in its compound. During vulcanizing micro ZDMA particles with rod-like and silky shape in HNBR polymerize to form near-spherical nano P-ZDMA particles dispersed evenly.

3. $SiO_2$ and N550, ZDMA, and N550 do not interfere with each other in HNBR and reinforce HNBR with superimposing effect. There are strong adsorption between ZDMA and $SiO_2$ particles, so the dispersion of these two fillers in HNBR get worse. Filling N550/ZDMA to HNBR makes HNBR composites get good comprehensive performance, and the suitable amount of ZDMA is 25% of total amount of fillers.

4. The theory prediction for Payne effect (dispersion of the filler) shown by the dynamic properties is identical with actual state observed by TEM.

## References

1. Gatos, K. G.; Sawanis, N. S.; Apostolov, A. A.; Thomann, R.; József, K. K. Marcromol Mater Eng 2004, 289, 1079.
2. Gatos, K. G.; László, S.; Béla, P.; József, K. K. Marcromol Rapid Comm 2005, 26, 915.
3. Sirisinha, C.; Prayoonchatphan, N. J Appl Polym Sci 2001, 81, 3198.
4. Samui, A. B.; Dalvi, V. G.; Chandrasekhar, L.; Patri, M.; Chakraborty, B. C. J Appl Polym Sci 2006, 99, 2542.
5. Ikeda, T.; Yamada, B.; Tsuji, M.; Sakurai, S. Polym Int 1999, 48, 446.
6. Peng, Z. L.; Liang, X.; Zhang, Y. X.; Zhang, Y. J Appl Polym Sci 2002, 84, 1339.
7. Ikeda, T.; Yamada, B. Polym Int 1999, 48, 367.
8. Wu, J. H.; Li, C. H.; Chiu, H. T.; Shong, Z. J. J Appl Polym Sci 2008, 108, 4114.
9. Lin, C. R.; Lee, Y. D. Macromol Theor Simul 1996, 5, 1075.
10. Scott, C.; Ishida, H.; Maurer, F. H. J. Polym Compos 1992, 13, 237.
11. Suzuki, N.; Ito, M.; Ono, S. J Appl Polym Sci 2005, 95, 74.
12. Drozdov, A. D.; Dorfmann, A. Polym Eng Sci 2002, 42, 591.
13. Lu., Y. L.; Liu, L.; Tian, M.; Geng, H. P.; Zhang, L. Q. Eur Polym J 2005, 41, 589.