

# Fly Ash Particles and Precipitated Silica as Fillers in Rubbers. III. Cure Characteristics and Mechanical and Oil-Resistance Properties of Acrylonitrile–Butadiene Rubber

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Received 10 October 2007; accepted 2 June 2008

DOI 10.1002/app.28842

Published online 2 September 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** This study investigated the cure characteristics, mechanical properties, and oil resistance of acrylonitrile–butadiene rubber (NBR) filled with 60 phr carbon black (CB) and different amounts of silica from fly ash [fly ash silica (FASi)] and precipitated silica (PSi). Loadings of CB and PSi silica in NBR vulcanizates reduced the scorch and cure times. An increase in the cure time of FASi–CB–NBR vulcanizates was probably caused by an interaction between the polarity of NBR and the metal oxide activators in FASi, which could retard the curing. The tensile modulus of NBR vulcanizates increased with the addition of CB and silica fillers and with immersion in hydraulic oil at 125°C. CB exhibited a more pronounced effect on

the NBR reinforcement versus the PSi and FASi fillers. The tensile and tear strengths and elongation at break decreased under thermal aging in hydraulic oil. The PSi system showed better reinforcement of CB–NBR vulcanizates than the FASi system. The hardness of NBR vulcanizates increased with CB and silica. The results in this work suggest that silica from fly ash particles could be used as an extender for cost savings in NBR compounds. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2877–2883, 2008

**Key words:** mechanical properties; reinforcement; rubber; silicas; swelling

## INTRODUCTION

Acrylonitrile–butadiene rubber (NBR), or nitrile rubber, is a copolymer of acrylonitrile and butadiene that has excellent oil resistance. Through the variation of the acrylonitrile content, the polarity of NBR can be adjusted to suit the applications of the final rubber products: the greater the acrylonitrile content, the higher the oil resistance. Apart from the oil resistance, the glass-transition temperature of NBR rises together with the brittleness temperature as the acrylonitrile content is increased. An unfilled NBR vulcanizate suffers mainly from low mechanical properties because of the absence of strain-induced crystallization, and so the incorporation of a reinforcing filler is usually required. Carbon black (CB) and silica are the most widely used fillers for rubber

reinforcement. The only limitation of using CB is black final products. Silica fillers are applicable to both black and light products, and silica has a small primary particle size that gives rise to noticeably high reinforcing efficiency in comparison with other white fillers. Because silica contains a large number of silanol groups (Si–OH) on its surface, it can be considered as highly polar and reactive filler.<sup>1</sup> Many published works have studied silica–rubber interactions and their influence on the properties of rubbers via primary chemical bonds with functionalized polymers, such as chlorosulfonated polyethylene,<sup>2</sup> epoxidized natural rubber,<sup>3</sup> carboxylated nitrile rubber,<sup>4</sup> chloroprene rubber,<sup>5,6</sup> and chlorinated polyethylene.<sup>7,8</sup> However, the presence of silanol groups on the surface of silica causes the formation of a strong filler–filler network via hydrogen bonds and thus poor silica dispersion. Moreover, the silanol groups cause the adsorption of curatives, which leads to a delay of the vulcanization reaction and a reduction of the crosslink density.<sup>9</sup> Consequently, the use of silane coupling agents has rapidly gained interest in rubber industries. In theory, silanes can deactivate the silanol groups via a chemical reaction between the alkoxy groups of silanes and silanol groups. In this way, improvements in the silica

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Contract grant sponsor: Commission on Higher Education (Center for Utilization of Polymers and NATURAL REsources, CUP-NATURE).

Contract grant sponsor: Compound Professional Co., Ltd.

dispersion and cure efficiency could be achieved. This would, in turn, enhance the mechanical properties.<sup>10–16</sup> The common silanes used in rubber industries include bis(3-triethoxysilylpropyl)tetrasulfide and bis(3-triethoxysilylpropyl) disulfide. The former has attracted more interest because it not only deactivates silanol groups on silica surfaces but also increases the cure efficiency on account of the release of free sulfur during the vulcanization process.

There have been attempts to use silica from natural resources, that is, rice husk ash.<sup>17–20</sup> In addition to rice husk ash, fly ash from thermal power plant stations has been reported as a natural silica providing good mechanical properties (particularly dynamic properties and compression set) when used with appropriate silane coupling agents.<sup>13,15,16,21–23</sup> According to previous works,<sup>15</sup> fly ash is approximately 40–45 wt % silica with similar silanol groups on its surface. When added to natural rubber (NR)<sup>13,15</sup> or NR/styrene-butadiene rubber (SBR) blends,<sup>16</sup> fly ash can not only function as a reinforcing filler similar to precipitated silica (PSi) but also yield superior vulcanizate elasticity. The reinforcement efficiency of fly ash can be enhanced remarkably by the treatment of its surface with silane coupling agents.<sup>15,16,24</sup>

This work was designed to extend our previous findings<sup>13,16</sup> on the use of fly ash particles as a reinforcing filler in NR and in NR/SBR blends. In this work, fly ash particles were loaded into an NBR compound, and their influence on the cure characteristics, mechanical properties, and oil resistance was examined. The results were then compared with those for commercial PSi.

## EXPERIMENTAL

### Raw materials

#### Rubber

The NBR used in this work was supplied by Zeon Advanced Polymix Co., Ltd. (Bangkok, Thailand), under the trade name N32; it had a bound acrylonitrile content of 33.5% and a Mooney viscosity of 44.5 (ML1+4 at 100°C).

#### Fillers

In this work, CB (HAF-N330), supplied by Thai Carbon Black Public Co., Ltd. (Bangkok, Thailand), was used as the primary reinforcing filler in NBR rubber at a fixed loading of 60 phr. Silica from fly ash particles [fly ash silica (FASi)] and commercial PSi were used as secondary fillers in CB-filled NBR compounds. The fly ash particles were supplied by the Mae Moh Power Station of KNR Group Co., Ltd.

(Lampang, Thailand). The characteristics (dimensions, average particle size, shape, surface area, density, and pH) of the fly ash particles can be found in previous works.<sup>13,16</sup> According to our previous results<sup>13,15,16</sup> for the chemical composition of fly ash particles in comparison with commercial-grade silica, the major component of the fly ash was SiO<sub>2</sub> (~ 46%). Both fly ash and commercial silica had the same functional groups (e.g., silanol and siloxane groups at wave numbers around 3400 and 1100 cm<sup>-1</sup>, respectively).<sup>16,24</sup> This work was intended to investigate the effects of the silica content and source on the cure and mechanical properties of NBR vulcanizates before and after conditioning in hydraulic oil. The required silica (FASi) content in the fly ash particles added to the rubber compounds had to be calculated on the basis of the fact that there was 46 wt % silica in the fly ash particles.

Filler surface treatment by bis(3-triethoxysilylpropyl) tetrasulfane (Si69)

Si69 [(C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>-Si-(CH<sub>2</sub>)<sub>3</sub>-S<sub>4</sub>-(CH<sub>2</sub>)<sub>3</sub>-Si-(C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>] was used as a chemical coupling agent; it was supplied by JJ-Degussa Co., Ltd. (Bangkok, Thailand). The experimental procedures for the surface treatment by Si69 can be found in our previous studies.<sup>15,16,24</sup> In this work, the Si69 concentration of 4.0 wt % with respect to silica was selected.

### Sample preparation: compounding and vulcanization of NBR

In this work, the formulation of the NBR compounds reinforced with fly ash and commercial silicas, in parts per hundred parts of rubber, is given in Table I. The compounding process was commenced by the mastication of NBR on a laboratory two-roll mill supplied by Yong Fong Machinery Co., Ltd. (Samutsakon, Thailand), for 2 min. The NBR was then compounded with prepared chemicals on the two-roll mill for another 32 min, and the compound was then kept at 25°C and 50% humidity before further use. The resultant rubber compound was then compression-molded to a 90% cure with a hydraulic press supplied by Lab Tech Co., Ltd. (Bangkok, Thailand), at 17 MPa with a cure temperature of 160°C to produce vulcanized NBR. The cure time used for any individual compound was predetermined with an oscillating die rheometer (ODR-GT 7070-S2) supplied by Gotech Testing Machine, Inc. (Taichung, Taiwan), before the vulcanization process proceeded.

### Characterization

#### Cure characteristics

Scorch times and cure times of the rubber compounds were measured with an oscillating disk

TABLE I  
Compounding Recipes for CB-Filled NBR Vulcanizates

Ingredient	Function	Content (phr)
NBR (ACN33.5%)	Matrix	100
Zinc oxide	Activator	2.5
Stearic acid	Activator	0.75
Tetramethylthiuram disulfide	Accelerator	1.25
2-Mercaptobenzothiazole	Accelerator	0.35
CB (N330)	Reinforcing filler	60
PSi or FASi	Reinforcing filler	Varied (0, 15, 30, and 45)
Si69	Coupling agent	4 wt % silica
Poly(ethylene glycol) (#4000)	Activator	5 wt % added silica
Aromatic oil	Processing aid	3.0
Sulfur	Crosslinker	1

rheometer (ODR-GT 7070-S2) supplied by Gotech Testing Machine at a test temperature of 160°C.

#### Mechanical properties

The tensile properties of the NBR composites were monitored in terms of the modulus at 30% elongation, tensile strength, and elongation at break according to ASTM D 412-98 (1998) with dumbbell-shaped samples; the tests were carried out with a universal testing machine (Autograph AG-I, Shimadzu, Tokyo, Japan). The tear strength was determined according to ASTM D 624-00 (2000) with angle specimens (die C) and a Shimadzu tear strength testing machine. For both the tensile and tear properties, a testing speed of 500 mm/min was used. A model 475 hardness durometer (Shore A), supplied by PTC Instruments Co., Ltd. (Boylston, MA), was used for the hardness tests, the test conditions being in accordance with ASTM D 2240-03 (2003).

#### Oil resistance

The silica-filled NBRs were immersed in hydraulic oil (AW ISO32L, Penzoi, Bangkok, Thailand) in accordance with ASTM D 471-06 (2006) at room temperature (25°C) and at 125°C for 168 h, and the changes in the mechanical properties (tensile modulus, tensile strength, elongation at break, tear strength, and hardness) before and after oil aging conditions were also evaluated.

## RESULTS AND DISCUSSION

#### Cure characteristics

Figure 1 shows the relationship between the scorch time and silica content for CB-filled NBR (i.e., CB-NBR) vulcanizates loaded with commercial PSi and FASi. The scorch time for the neat NBR vulcanizate is also given. The loading of CB in the NBR vulcanizate clearly reduced the scorch time. This reduction

was associated with the increase in the compound viscosity and thus the shear heating effect together with some surface alkalinity and the good thermal conduction property of CB. Considering the effect of the silica content, we found that with the silica content increasing, the scorch time of black-filled NBR vulcanizates slightly decreased for reasons similar to those given for the effect of the black loading, as stated earlier. However, it was observed that the reduction of the scorch time for the FASi-filled CB-NBR vulcanizate was less pronounced than that for the PSi-filled CB-NBR vulcanizate. This was caused by the physically rounded shape of the ash particles, which could produce a solid-lubrication effect to promote the flowability of the rubber molecules during the deformation.<sup>13,16</sup> This statement is supported by the minimum torque results in Figure 2, which

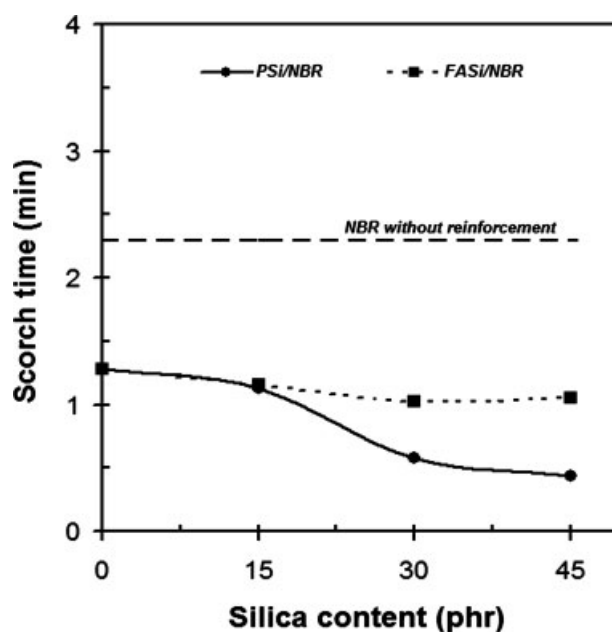
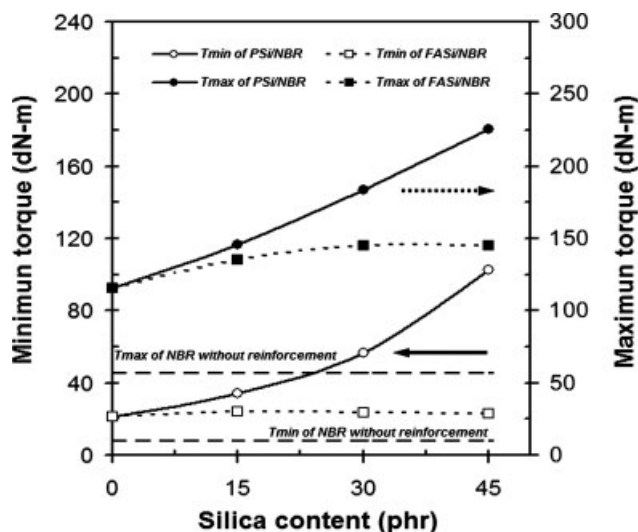


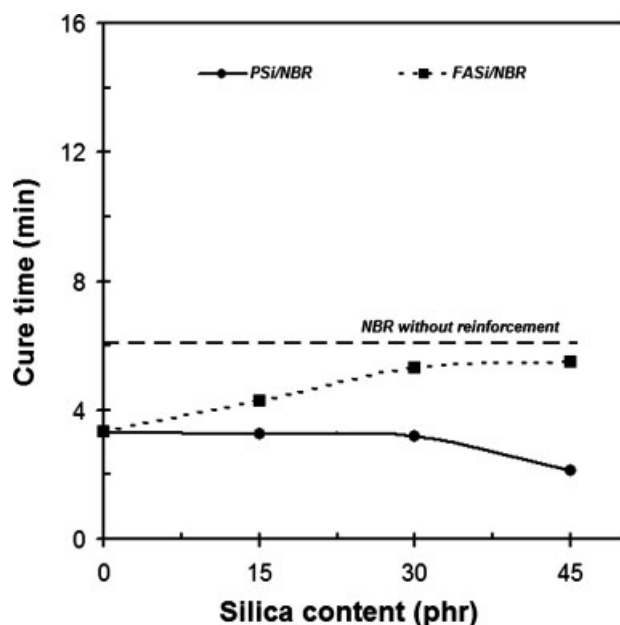
Figure 1 Relationship between the scorch time and silica content for CB-NBR vulcanizates filled with PSi and FASi.



**Figure 2** Effect of the silica content on the minimum torque ( $T_{min}$ ) and maximum torque ( $T_{max}$ ) for PSi-filled and FASi-filled CB-NBR vulcanizates.

shows that the viscosity of the FASi-filled CB-NBR vulcanizate was lower than that of the PSi-filled CB-NBR vulcanizate. The maximum torque in Figure 2 also suggests that the crosslinking level of the NBR vulcanizate increased with the addition of CB and silica, PSi exhibiting a more pronounced effect on the maximum torque than FASi.

Figure 3 shows the effect of the silica (PSi and FASi) loading on the cure time for CB-NBR vulcanizates. The cure time of NBR was reduced by the presence of CB. This was probably due to the fact that CB itself has a neutral to slightly alkali pH (ca. 7–8) with a low oxygen content, and this had an

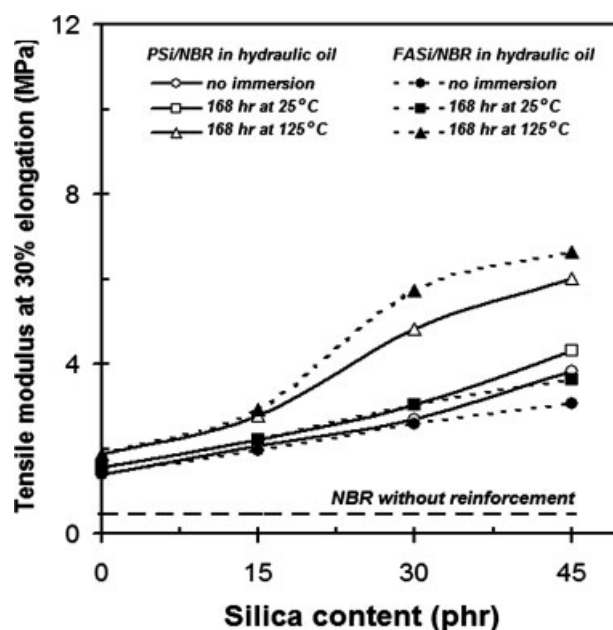


**Figure 3** Relationship between the cure time and silica content for CB-NBR vulcanizates filled with PSi and FASi.

acceleration effect on the vulcanization reaction; this view is supported by Lewis et al.<sup>25</sup> and Ansarifard et al.<sup>26</sup> It was surprising that when the silica filler was added to the CB-NBR compound, the cure time remained unchanged for the PSi system and appeared to increase for the FASi system. Previous works<sup>13,16</sup> have shown that adding FASi to NR or NR/SBR vulcanizates results in a reduction in the cure time because there are a number of metal oxides that can act as activators in NR or NR/SBR vulcanizates. The progressive increase in the cure time of the CB-NBR vulcanizates due to the addition of FASi was thought to be associated with an interaction between the polarity of NBR (—CN groups) and the metal oxide activators in FASi, which retarded the curing.

### Mechanical properties and oil resistance

In this work, the oil uptake was examined by the consideration of the percentage change in the mass of the CB-NBR vulcanizates with different concentrations of added PSi and FASi before and after aging in hydraulic oil for 168 h at 25 (room temperature) and 125°C. The results indicated that the percentage changes in the mass for NBR in all cases (with and without silica fillers) were extremely low, the values being less than 1.0% (thus, the results are not shown). Figure 4 shows the tensile modulus at 30% elongation of the NBR vulcanizates with different concentrations of added PSi and FASi before and after aging in hydraulic oil for 168 h at 25 and 125°C. The tensile modulus for the 60 phr CB filled



**Figure 4** Variations in the tensile modulus at 30% elongation for different silica contents in CB-filled NBR vulcanizates.

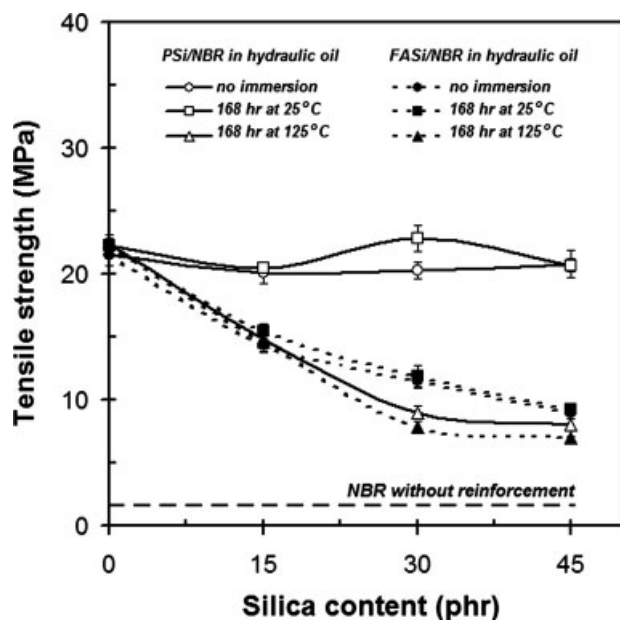


Figure 5 Variations in the tensile strength for different silica contents in CB-filled NBR vulcanizates.

NBR vulcanizate was greater than that for the neat NBR vulcanizate, as expected because of the reinforcement effect and rigidity of CB in the NBR.<sup>27</sup> Loading the silica fillers resulted in a progressive improvement of the tensile modulus of the CB-NBR vulcanizates, the results being in line with the maximum torque results shown in Figure 2. Immersion of CB-NBR filled with PSi and FASi in hydraulic oil at 25°C did not significantly affect the tensile modulus, but in hydraulic oil at 125°C, the tensile modulus greatly increased. Because the NBR itself had high resistance to hydraulic oil, the increase in the tensile modulus was mainly caused by a thermal postcuring effect, which probably produced more crosslinks in the vulcanizates. Figure 5 shows the tensile strength of the NBR vulcanizates with various PSi and FASi contents before and after aging in hydraulic oil for 168 h at 25 and 125°C. Unlike the tensile modulus results, the tensile strength of the CB-filled NBR vulcanizate was much greater than that of the neat NBR. This was expected as a result of CB reinforcement. However, the incorporation of PSi or FASi did not increase the tensile strength of the CB-NBR vulcanizates; this implied that no reinforcement effects were obtained by the addition of the PSi or FASi filler. Furthermore, FASi appeared to behave as a diluent. It could be postulated that the black reinforcement had a dominant effect on the NBR vulcanizates. In other words, the effect of silica reinforcement was probably suppressed by that of CB reinforcement. After immersion of the NBR vulcanizates into hydraulic oil at 25 and 125°C for 168 h, the tensile strength progressively decreased. This may be due to the postcuring effect, which

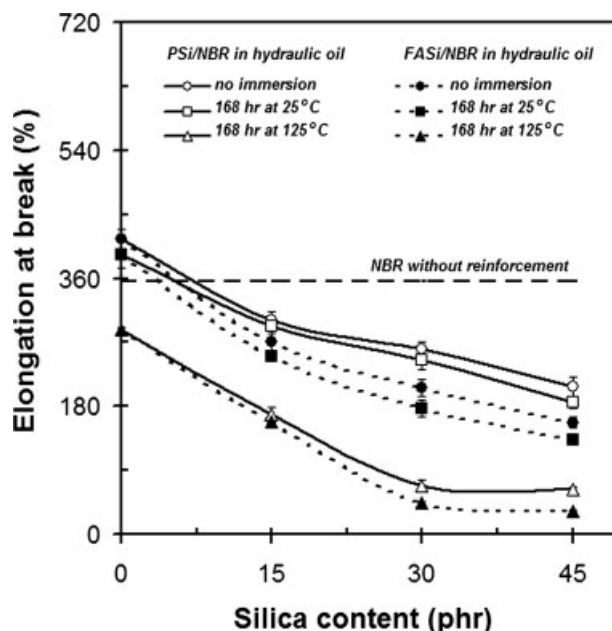


Figure 6 Effect of the silica content on the elongation at break for PSI-filled and FASI-filled CB-NBR vulcanizates.

might have produced too high a crosslink density, which in turn worsened the tensile strength; a decrease in the tensile strength as a result of an excessively high crosslink density was also proposed by Sirisinha and Sittichokchuchai.<sup>28</sup> Similar discussions could be used to explain the decrease in the elongation at break of NBR vulcanizates in the presence of CB at 60 phr and with various silica contents in Figure 6, the reduction of the elongation at break being in the range of 200–250%. It was observed that

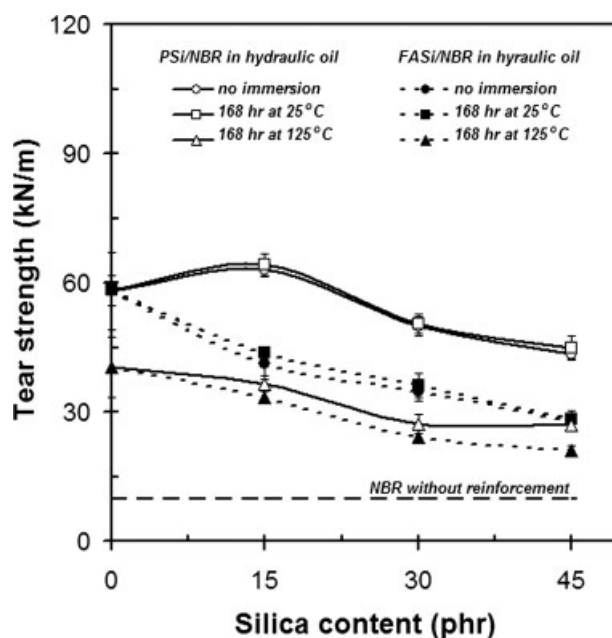
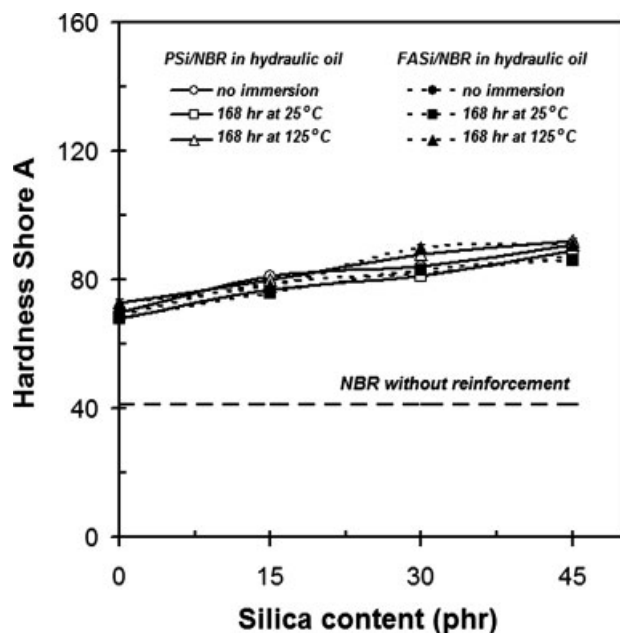


Figure 7 Effect of the silica content on the tear strength for PSI-filled and FASI-filled CB-NBR vulcanizates.



**Figure 8** Hardness of PSi-filled and FASI-filled CB-NBR vulcanizates at different silica loadings.

for a given silica content, PSi showed better reinforcement of CB-NBR vulcanizates than FASI. This was associated with the differences in the particle size and number of functional groups (Si-OH groups) on the silica surfaces.<sup>15,24</sup> Previous works<sup>15,29,30</sup> have suggested that the particle size and the dilution level for a given silica content for fly ash particles are greater than those for the PSi filler. Taking the overall tensile properties of the NBR vulcanizates into account, we believe that FASI could be used as an extender for cost savings.

Figure 7 shows the tear strength of the NBR vulcanizates with various contents of PSi and FASI before and after aging in hydraulic oil for 168 h at 25 and 125°C. The tear strength of the NBR vulcanizate was much improved by the addition of CB as expected. Again, the incorporation of PSi or FASI did not improve the tear strength of the CB-NBR vulcanizates as expected. This was probably due to the dominant reinforcement effect of CB, as stated earlier. The tear strength was also decreased after thermal aging in hydraulic oil.

Figure 8 shows the effect of the silica loading on the hardness for CB-NBR vulcanizates before and after aging in hydraulic oil for 168 h at 25 and 125°C. The hardness of the NBR vulcanizates increased in the presence of CB and with increasing silica content, the results corresponding well to the tensile modulus results in Figure 4. The effects of thermal and hydraulic oil aging on the hardness of NBR vulcanizates appeared very small in comparison with the changes in the modulus.

## CONCLUSIONS

The cure characteristics, mechanical properties, and oil resistance of CB-reinforced NBR vulcanizates filled with various contents of PSi and fly ash particles were studied. The main findings of this work were as follows:

1. The addition of CB and silica to NBR vulcanizates reduced the scorch time. The cure time of NBR was reduced by the presence of CB but remained unchanged when the PSi filler was added. The increase in the cure time of CB-NBR vulcanizates due to the addition of FASI was associated with an interaction between the polarity of NBR (-CN groups) and the metal oxide activators in FASI, which could retard the curing.
2. The tensile modulus of NBR vulcanizates increased with the addition of CB and silica fillers, the effect becoming very pronounced when the vulcanizates were immersed in hydraulic oil at 125°C. The tensile strength of the NBR vulcanizate increased with CB but decreased with the PSi and FASI loadings. CB was observed to have a dominant effect on the NBR reinforcement versus PSi and FASI for all loadings of interest. The ultimate mechanical properties (tensile and tear strengths and elongation at break) decreased under thermal aging in hydraulic oil. PSi showed better reinforcement of CB-NBR vulcanizates than FASI because of differences in the particle size and number of functional groups (Si-OH groups) on the silica surfaces. The hardness of NBR vulcanizates increased with CB and silica but was not affected by thermal aging in hydraulic oil. Taking the overall properties of NBR vulcanizates into account, we believe that FASI could be used as an extender for cost savings.

## References

1. Byers, J. T. *Rubber World* 1998, 218, 38.
2. Roychoudhury, A.; De, P. P.; Roychoudhury, N.; Vidal, A. *Rubber Chem Technol* 1995, 68, 815.
3. Varughese, S.; Tripathy, D. K. *J Appl Polym Sci* 1992, 44, 1847.
4. Bandyopadhyay, S.; De, P. P.; Tripathy, D. K.; De, S. K. *Rubber Chem Technol* 1996, 69, 637.
5. Choi, S. S. *J Appl Polym Sci* 2002, 83, 2609.
6. Sae-Oui, P.; Sirisinha, C.; Thepsuwan, U.; Hatthapanit, K. *Eur Polym J* 2006, 43, 185.
7. Pattanawanidchai, S.; Sae-Oui, P.; Sirisinha, C. *J Appl Polym Sci* 2005, 96, 2218.
8. Phewthongin, N.; Sae-Oui, P.; Sirisinha, C. *J Appl Polym Sci* 2006, 100, 2565.
9. Wolff, S.; Wang, M. J. *Rubber Chem Technol* 1992, 65, 329.
10. Waddell, W. H.; O'Haver, J. H.; Evans, L. R.; Harwell, J. H. *J Appl Polym Sci* 1995, 55, 1627.
11. Goerl, U.; Hunsche, A.; Mueller, A.; Koban, H. G. *Rubber Chem Technol* 1997, 70, 608.

12. Sae-Oui, P.; Sirisinha, C.; Thepsuwan, U.; Hatthapanit, K. *Polym Test* 2004, 23, 871.
13. Sombatsompop, N.; Thongsang, S.; Markpin, T.; Wimolmala, E. *J Appl Polym Sci* 2004, 93, 2119.
14. Sae-Oui, P.; Sirisinha, C.; Thepsuwan, U.; Hatthapanit, K. *Polym Test* 2005, 24, 439.
15. Thongsang, S.; Sombatsompop, N. *Polym Compos* 2006, 27, 1, 30.
16. Sombatsompop, N.; Wimolmala, E.; Markpin, T. *J Appl Polym Sci* 2007, 104, 3396.
17. Ishak, Z. A. M.; Bakar, A. A. *Eur Polym J* 1995, 31, 259.
18. Saeoui, P.; Rakdee, C.; Thanmathorn, P. *J Appl Polym Sci* 2002, 83, 2485.
19. Da Costa, H. M.; Visconte, L. L. Y.; Nunes, R. C. R.; Furtado, C. R. G. *J Appl Polym Sci* 2002, 83, 2331.
20. Sereda, L.; Lopez-Gonzalez, M. M.; Visconte, L. L. Y.; Nunes, R. C. R.; Furtado, C. R. G.; Riande, E. *Polymer* 2003, 44, 3085.
21. Garde, K.; McGill, W. J.; Woolard, C. D. *Plast Rubber Comp Proc Appl* 1999, 28, 1.
22. Alkadasi, N. A. N.; Hundiwale, D. G.; Kapadi, U. R. *J Appl Polym Sci* 2004, 91, 1322.
23. Mishra, S.; Sonawane, S. H.; Badgujar, N.; Gurav, K.; Patil, D. *J Appl Polym Sci* 2005, 96, 6.
24. Thongsang, S.; Sombatsompop, N. *J Macromol Sci Polym Phys* 2007, 46, 825.
25. Lewis, C.; Buanpa, R.; Kiatkamjornwong, S. *J Appl Polym Sci* 2003, 90, 3059.
26. Ansarifar, A.; Lim, M. P.; Nijhawan, R. *Int J Adhes Adhes* 2004, 24, 9.
27. Park, S.-J.; Cho, K.-S.; Ryu, S.-K. *Carbon* 2003, 41, 1437.
28. Sirisinha, C.; Sittichokchuchai, W. *J Appl Polym Sci* 2001, 80, 2474.
29. Leblanc, J. L. *Prog Polym Sci* 2002, 27, 627.
30. Choi, S. S. *J Appl Polym Sci* 2004, 93, 1001.