

The Effect of Second Filler on Cure Characteristic and Mechanical Properties of Si-69 treated Precipitate Silica/NR Composite

C. Thongpin^{1,2,3}, C. Sripetdee^{1,2}, N. Papaka^{1,2}, N. Pongsathornviwat^{1,2}
and N. Sombatsompop³

¹ Materials Science and Engineering Department, Faculty of Engineering and Industrial Technology, Silpakorn University, Sanamchandra Palace Campus, Nakorn Pathom, 73000, Thailand.

² Center of Excellence for Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University, Bangkok 10350, Thailand.

³ Centre for Utilizations of Polymers and Natural Resources, CUP-NATURE, School of Energy, Environment, and Materials, King Mongkut's University of Technology Thonburi (KMUTT), Bangmod, Thungkru, Bangkok 10140 Thailand

Corresponding author: chanchai@su.ac.th

Abstract

Silica has been widely used as non-black reinforcing filler, however, the filler-filler interaction has been an important issue. Cure characteristic and mechanical properties of the rubber compound and rubber vulcanizate were affected both by filler-rubber interaction and filler-filler interaction. There have been, presently, a number of natural fillers which are also used as fillers for the rubber, i.e. fly ash, sawdust and zeolite. This work therefore will study the effect of second filler added into the 13% Si-69 treated precipitate silica (PSi) filled natural rubber compounds. It was revealed that the scorch and cure time of the rubber compound increased with the content of treated PSi. This was the effect of excess of the silane treated onto PSi which would agglomerate and form the cluster of polysiloxane and would then be able to absorb vulcanizing accelerator resulting in extending the scorch and cure time of the rubber compounds. However, this effect was over ruled with the reinforcing effect as could be seen by the increasing, with the contents of PSi, of maximum torque and mechanical properties of the vulcanizates. The NR compounded with treated PSi content of 20 phr selected to study the effect of excess silane on the cure characteristic of hybrid fillers NR composite. The addition of sawdust led to longer scorch time and cure time but not much change of the maximum torque. As expected, the modulus of the rubber vulcanizate increased with the sawdust content whereas the tensile strength and elongation at break decreased with the sawdust content. The incorporation of zeolite could accelerate the cure reaction therefore both scorch time and cure time decreased. The maximum torque also increased with the content of zeolite. Both modulus and tensile strength increased with the content of the zeolite whereas elongation at break tended to be unchanged. In the case of using fly ash as the second filler, the cure time tended to be unchanged. However, the maximum torque tended to be increased with the content of fly ash. It was found that the modulus, tensile strength increased but elongation at break decreased. Interestingly, the excess of Si-69 used effect pronouncedly for the addition of zeolite and fly ash cases as the excess silane could promote the interaction between fillers surface and rubber molecule accept for sawdust.

Introduction

Natural fillers have attracted rubber technologist, in both natural and synthetic rubber, for their environmental issue, good mechanical properties, better dimension stability and sustainable resources. The excellent properties over carbon black are tear strength, abrasion resistance, aging resistance and adhesion properties [1-6]. Silica containing fillers are naturally available especially zeolite and fly ash (FA). They have been being interested for a decade [1-6]. Sombatsompop et al. [1,6] studied the effect of various types of FA, available in Thailand, on both curing and mechanical properties. They found that all types of fly ash could be used as reinforcing fillers in NR for silica supplement. The advantage of using FA was on its high loading in rubber compounding without suffering flow in other word minimum torque and cure times of the rubber compound. In terms of mechanical properties of the vulcanizates, modulus at 100 % elongation was not much affected by the addition of FA compared to that of fumed silica used as filler. However, tensile strength of the FA/NR vulcanizate was much suffered by its large particle size. The advantage of spherical shape in FA over commercial silica was that gave great elasticity which responsible for resilience and

rebound characteristic. The suffering from using silica containing fillers is its hydrophilic property at surface. This results for the physical interaction between filler and rubber matrix. Filler-filler interaction and acidic property on the surface of silica causes long cure time and slow cure rate. To disperse and compatibilize the silica into rubber matrix, silane coupling agents were introduced. For FA filled NR, as mentioned, the FA used effectively was at the content of 30 phr. At above this concentration, FA functioned as an extender. The modification of FA surface with bis(3-triethoxysilyl propyl) tetrasulfane (Si-69) [6] was found to enhance FA-filled NR properties. The uses of Si69 modified FA was also found to effectively improve elastic behavior, compression set and resilience. Sawdust is very considerate as natural fiber used as hybrid reinforcement in carbon black/natural rubber composite [1,6], mainly for the economically reason. However, zeolite is a natural filler containing silica has not been studied much. It appears to enhance the properties of both compound and vulcanizate [8], modification is needed. The second filler in the matrix will also improve some missing properties of the single filler rubber composite [8]. The research is hence aimed to investigate the hybrid fillers reinforcing in rubber matrix system by studying the effect of second filler on the system containing excess Si-69.

Experimental Procedure

1 Materials

- *Rubber and curative additives:* Natural rubber (NR, STR 20) was received from Sinthong Thai Rubber Ltd. The curative additives, were kindly supplied by Chemical Innovation Ltd., Bangkok, Thailand.
- *Reinforcing Fillers:* The precipitated silica (PSi) was purchased from Siam Silica, Bangkok, Thailand, whereas fly-ash, with the particles less than 250 μm , supplied by Mae Moh Power Station of KNR Group Co., Ltd. (Lampang, Thailand). Zeolite, supplied by The PQ Chemical Co., Ltd. (Thailand). para wood particles which were obtained from carpentry and wood-working processes by V.P. Wood Co., Ltd. (Bangkok Thailand), were also used as the second fillers in rubber formulation. The average size of the particles used in this work was sieved in order to be in the range of 150-250 μm and was dried in a vacuum oven at 80 °C for 24 hours before used.
- *Modification Chemical:* PSi surface was chemically modified using bis(3triethoxysilylpropyl) tetrasulfane (Si-69), kindly supplied by Innovation Group, Bangkok, Thailand, as a surface modifying agent.

2 Surface Modification of Precipitated Silica (PS) with Si-69

The surface PSi was modified at the amount of 13 % Si-69. The modification method was carried out as follow: 6.5 grams of Si-69 was thoroughly dissolved in 400 cm^3 of ethanol and stirred with mechanical stirrer for 30 minutes then 50 grams of PSi was added slowly with stirring until PSi was very well dispersed in ethanol. The slurry was then mixed under stirring for further 15 minute before drying in a hot air oven at 100 °C for 12 hours. This part of experiment will result in 13 % Si-69 treated PSi.

3 Preparation and Vulcanization of Rubber Compounds

The rubber compounding was carried out by masticating the NR on a two roll mill (Hong Yow, China) for 5 minutes or until soft, the prepared fillers and chemicals stated in **Table 1**, except sulfur, were then masticated for further 20 minutes. The required sulfur was then added at the end of this state of compounding process and masticated for further 5 minutes. After mixing, cure characteristic properties of the compounds, i.e. minimum and maximum torques, scorch time and cure time, were evaluated in a Moving Die Rheometer (MDR, Model GT-M200, GOTECH Testing Machine, Ind., Taiwan) at 160 °C. The compounds were then compressed in a compression molding (Lab Tech. Co. Ltd Bangkok Thailand) to a 90 % cure, with the hydraulic pressure of 170 kg/cm^2 , using 160 C cure temperature and the cure time resulted from cure characteristic test, in order to obtain vulcanized rubber composites.

4 Testing of Rubber Vulcanizates

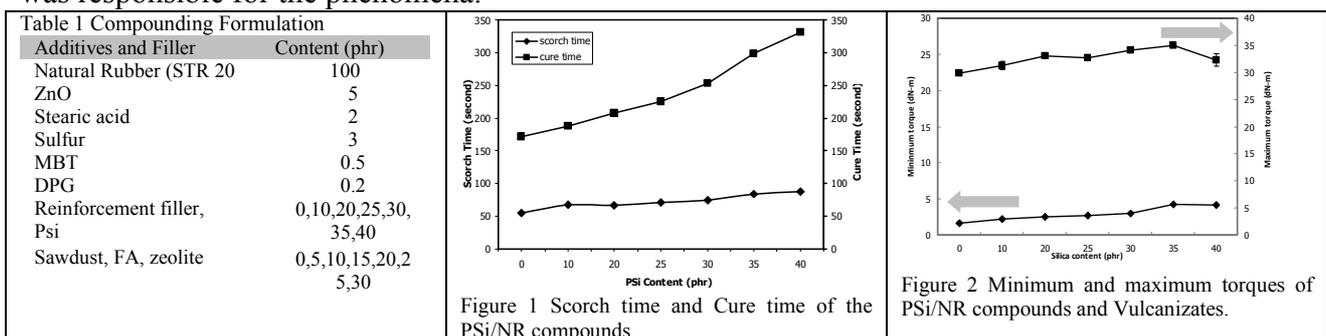
Tensile properties of the vulcanized rubber composites were monitored in terms of tensile modulus, tensile strength and elongation at break, according to ASTM D412-98 (1998) using dumbbell-shaped samples, the tests being carried out using the universal testing machine (Model LR50K, LLOYD Instruments, UK.) with the testing speed of 500 mm/min .

Result and Discussion

1. Vulcanizing Properties

It was reported that the present of unmodified silica in rubber matrix effect dispersion and compatible in most rubbers [6] and could also act as the accelerators absorber. This resulted in long scorch time (t_s) and cure time (t_{90c}). The Si69 modified silica would overcome the problem. In this work, the various contents of 13%Si-69 modified P*Si* was used in rubber compounding. It was shown that the effect on cure characteristic properties exhibited in different way. The results, i.e. t_s and t_{90c} , are shown in **Fig. 1**. It could be seen that t_s was slightly increased meanwhile t_{90c} steadily increased with the amount of silica added. It was understood that the excess Si-69 that did not couple with hydroxyl (OH) on the surface of silica would be able to polymerize to form polysiloxane. The hydroxyl group could absorb accelerator and consequently retarded the curing reaction. It was also observed that maximum and minimum torques tended to increase with the loading of modified P*Si*, as shown in **Fig. 2**. The torques increments were not sharply increased compared to the other rubber systems [1,6,7]. This may be because of the polysiloxane formed and could act as dispersed gel led to self interaction. Considering cure characteristic and mechanical properties, not shown here, the Si-69 modified P*Si* at 20 phr content was selected for the hybrid fillers composites. **Fig. 3** shows both t_s and t_{90c} of the hybrid rubber composite compounds and will be elucidated as follow:

- It was found that excess Si-69 would not effect dispersion and compatibility of sawdust with rubber matrix much compared to the other silane system [1,6]. The large particle size of this filler which can obstruct curing reaction and raise both t_s and t_{90c} as a consequence.
- Considering having fly ash as the second filler, t_s and t_{90c} of the hybrid NR compound were remain unchanged or slightly decreased with the additional fly ash. It could be explained that metal oxides containing in FA would be able to act as activator [1,6]. This can compensate the retardation effect of excess Si-69.
- For the zeolite case, it was found that both characteristic times of the compound decreased with the present of zeolite, however, they remained unchanged after the content of 10 phr. The reduction of t_s and t_{90c} could be due to the high content of the metal oxide on the porous surface and could also accelerate the curing reaction. After which, the agglomeration of the particles was responsive. The minimum torque, **Fig. 4**, was found to be slightly decreased with the contents of the second fillers especially for fly ash which will ease the rubber flow caused by the spherical shape of the fly ash particle. It was found in the sawdust/modified P*Si*/NR compounds that maximum torque decreased with contents of sawdust. As it was mentioned earlier that the large particle size of sawdust could obstruct the curing reaction and lowered crosslink density and consequently reduced maximum torque. No interaction between sawdust and rubber is also the reason for the torque reduction. It was not the case for fly ash and zeolite, of which maximum torques increased with the content of the second fillers, which due to the fact that the fillers are able to disperse, by the excess Si-69 presenting in the matrix, and induce crosslinking reaction. The aggregation of the second filler would also occur, particularly for zeolite, at the high filler content, i.e. 25 phr. It was noticeable that this specific behavior was in the same manner as having P*Si* alone, of which at the P*Si* content of 40 phr the torques was reduced again. The aggregation of zeolite and excess Si-69 was responsible for the phenomena.



The tensile properties of the hybrid fillers filled vulcanized rubber are shown in **Fig. 5a-5c**. Considering secant modulus in the vulcanizates, of which are dependent upon both crosslink density

and the reinforcement effect of the fillers. It was explained here that the reinforcement effect was evident for sawdust, as can be seen that at high elongation where elongation of rubber molecule was interrupted by the large particle of sawdust. This can be elucidated by tensile strength and elongation at break. It was not the case for fly ash and zeolite. Particles dispersion, crosslink density and reinforcement effect are the factors governing vulcanizates properties even so the present of fly ash was not much effect mechanical properties the composite. The spherical shape of fly ash might responsible for the different behavior among these silica containing fillers.

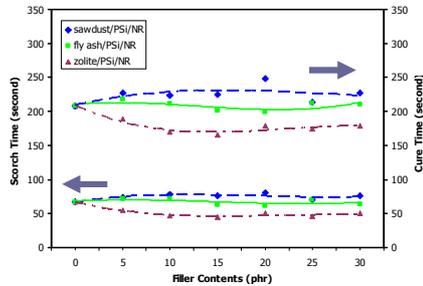


Figure 3 Scorch time and cure time of 2nd filler/PSi/NR compounds

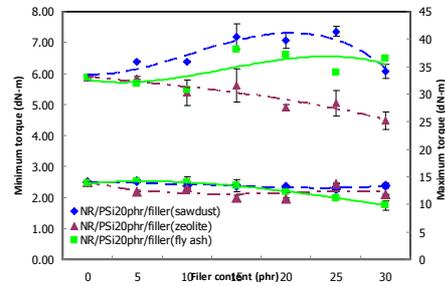


Figure 4 Minimum and maximum torques of 2nd filler/PSi/NR compounds and Vulcanizates.

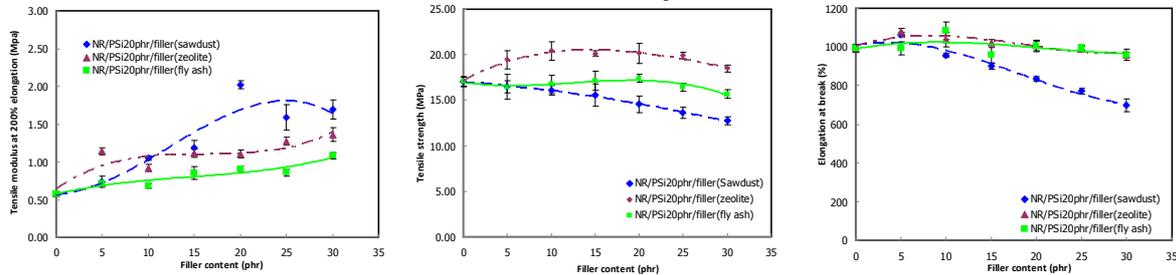


Figure 5 Modulus, tensile strength and Elongation at break of 2nd filler/PSi/NR vulcanizates.

Conclusion

The excess Si-69 in single filler could perform as both vulcanizing additive absorber and induce crosslinking by sulfur distributed. The excess Si69 also could enhance, fillers distribution, filler -rubber interaction, in the hybrid filler system, especially for the system having silica containing fillers.

Acknowledgement

The authors would like to thank Department of Material Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Thailand for their facilities used throughout the work.

References

1. N. Sombatsompop, S. Thongsang, T. Markpin and E. Wimolmala: *J. of Apply. Polym. Sci.* Vol. 93 (2004) p. 2119-2130.
2. M. Castellano, L. Conzatti, G. Costa, L. Falqui, A. Turturro, B. Valenti and F. Negroni: *Polymer* Vol. 46 (2005) p. 695-703.
3. A. Ansarifar, S.F. Shiah and M. Bennett: *International J. of Adhesion & Adhesives* Vol. 26 (2006) p. 454-463.
4. B. Meissner and L. Matejka: *European Polymer Journal* Vol. 44 (2008) p. 1940-1948.
5. N. Sombatsompop, E. Wimolmala and T. Markpin: *J. Appli. Polym. Sci.* Vol. 204 (2007) p. 3396-3405.
6. P. Sae-oui, C. Sirisinha, K. Hatthapanit and U. Thepsuwan: *Polymer Testing* Vol. 24 (2005) p. 439-446.
7. N. Sombatompop, C. Kantala and E. Wimolmala: *Polymers and Polymer Composites* Vol. 14 No. 4 (2006) p. 331-347.
8. N. Rattanasoma, T. Saowapark and C. Deprasertkul: *Polymer Testing* Vol. 26 (2007) p. 369-377.

Multi-Functional Materials and Structures II

doi:10.4028/www.scientific.net/AMR.79-82

The Effect of Second Filler on Cure Characteristic and Mechanical Properties of Si-69 Treated Precipitate Silica/NR Composite

doi:10.4028/www.scientific.net/AMR.79-82.2183

References

1. N. Sombatsompop, S. Thongsang, T. Markpin and E. Wimolmala: J. of Apply. Polym. Sci. Vol. 93 (2004) p. 2119-2130.
doi:10.1002/app.20693
2. M. Castellano, L. Conzatti, G. Costa, L. Falqui, A. Turturro, B. Valenti and F. Negroni: Polymer Vol. 46 (2005) p. 695-703.
doi:10.1016/j.polymer.2004.11.010
3. A. Ansarifar, S.F. Shiah and M. Bennett: International J. of Adhesion & Adhesives Vol. 26 (2006) p. 454-463.
doi:10.1016/j.ijadhadh.2005.06.008
4. B. Meissner and L. Matejka: European Polymer Journal Vol. 44 (2008) p. 1940-1948.
doi:10.1016/j.eurpolymj.2008.04.006
5. N. Sombatsompop, E. Wimolmala and T. Markpin: J. Appli. Polym. Sci. Vol. 204 (2007) p. 3396-3405.
doi:10.1002/app.25973
6. P. Sae-oui, C. Sirisinha, K. Hatthapanit and U. Thepsuwan: Polymer Testing Vol. 24 (2005) p. 439-446.
doi:10.1016/j.polymertesting.2005.01.008
7. N. Sombatompop, C. Kantala and E. Wimolmala: Polymers and Polymer Composites Vol. 14 No. 4 (2006) p. 331-347.
8. N. Rattanasoma, T. Saowapark and C. Deeprasertkul: Polymer Testing Vol. 26 (2007) p. 369-377.
doi:10.1016/j.polymertesting.2006.12.003