

Influence of Silica Loading on the Mechanical Properties and Resistance to Oil and Thermal Aging of CR/NR Blends

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ABSTRACT: Blends of 75/25 chloroprene rubber(CR)/ natural rubber (NR) filled with various loadings of precipitated silica were prepared and their processability and mechanical properties as well as their resistance to thermal aging and oil were determined. The blend morphology was also studied using the atomic force microscopy technique. The results reveal that the mixing energy and the Mooney viscosity of the compound are increased continuously with increasing silica loading. It is also found that both scorch and optimum curing times are shortened while the total crosslink density is increased with increasing silica loading. The positive effect on cure could be explained by the chemical reaction between the allylic chlorine atom of CR and the silanol group on silica sur-

face. The tensile strength, modulus, and hardness of the blend vulcanizate are noticeably improved while the compression set at elevated temperature is impaired with increasing silica loading. The results also reveal that both thermal aging resistance and oil resistance of the blend vulcanizates, as represented by the relative properties, are enhanced with the addition of silica. The resistance enhancement is believed to arise from the combination of the dilution effect, the increased crosslink density and also the reduction of NR dispersed phase size. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3478–3483, 2007

Key words: silica; rubber; mechanical properties; blend; aging

INTRODUCTION

Rubber blends have now been widely used in the rubber industry. Proper selection of blend partners could result in a rubber blend with desirable properties. Blends of natural rubber (NR) and chloroprene rubber (CR) have recently been investigated.^{1–3} The NR/CR blends generally possess good mechanical properties because both NR and CR are strain-induced crystallizable. The addition of CR into NR helps to overcome the main shortcomings of NR, i.e., poor oil and aging resistance. Meanwhile, the presence of NR in CR improves elasticity and also low temperature flexibility.⁴ Recently, it has been reported that precipitated silica could form strong interaction with CR.⁵ In this system, the rubber-filler interaction takes place through hydrogen bonds between the negatively charged chlorine atom of CR and the positively charged hydrogen atom of the silanol groups on silica surface. In addition, at sufficiently high temperature, the chemical reaction between allylic chlorine atoms and the silanol groups could occur giving rise to an increased crosslink density of CR. However,

for NR, the roles of silica on reinforcement and curing system are different. As silica is a highly polar filler, the filler–filler interaction is quite strong giving rise to high tendency for filler agglomeration in the NR matrix and, thus, the difficulty in processing.⁶ In addition, the presence of silica has negative effects on cure and elasticity of NR because the silanol groups on silica surface could adsorb the cure activator necessary for sulfur vulcanization.⁷ Recently, it has been reported that the addition of CR into silica-filled NR and silica-filled EPDM could improve filler dispersion and, thus, the mechanical properties of the vulcanizates.^{8–9} As silica plays different roles in CR and NR, it is therefore interesting to investigate the effect of silica loading on the mechanical properties as well as the resistance to thermal aging and oil of CR/NR blends. In the present study, the blend ratio of 75/25 (CR/NR) was selected because preliminary study showed that this blend ratio gave satisfactory oil and aging resistance.

EXPERIMENTAL

Materials

All materials were used as received. NR (STR 5L) was manufactured in Thailand by Union Rubber

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TABLE I
Compound Formulation of 75/25 CR/NR Blend Used in This Study

Ingredient	Loading (phr)				
	75	75	75	75	75
Polychloroprene (CR)	75	75	75	75	75
Natural rubber (NR)	25	25	25	25	25
Zinc oxide	5	5	5	5	5
Magnesium oxide	4	4	4	4	4
Stearic acid	1	1	1	1	1
Silica	0	10	20	30	40
Santocure-TBBS ^a	1	1	1	1	1
ETU 22S ^b	0.3	0.3	0.3	0.3	0.3
Sulphur	2	2	2	2	2

^a *N*-tert-butyl-2-benzothiazole sulfenamide

^b Ethylene thiourea

Products Corp. Polychloroprene (Neoprene W; ML1 + 4@100°C = 44) was supplied by DuPont Dow Elastomers. Precipitated silica (HiSil 255s, specific surface area = 175 m²/g) was manufactured by Tokuyama Siam Silica. *N*-tert-butyl-benzothiazole sulfenamide (Santocure-TBBS) was obtained from Reliance Technochem (Flexsys). Ethylene thiourea (ETU 22S) and magnesium oxide (MgO) were manufactured in Japan by Kawakushi and Konoshima Chemicals, respectively. Stearic acid, zinc oxide (ZnO), and sulfur (S₈) were obtained from Chemmin Corp., Thailand.

Preparation and testing of rubber compounds

The compounding ingredients, as given in Table I, were mixed in a laboratory-sized internal mixer (Haake Rheomix 3000p). The mixing conditions were set as follows; fill factor = 0.7, initial chamber temperature = 60°C, rotor speed = 40 rpm, and mixing time = 12 min. The compounds were thereafter sheeted out on a two-roll mill (Collin W100T). Mooney viscosity (MS1 + 4@100°C) was measured by using the Mooney viscometer (TechPro visc-TECH+). The cure characteristics, i.e., scorch time (t_s2), optimum curing time (t_c90) as well as minimum torque (M_L) and maximum torque (M_H) were determined using a moving die rheometer (TechPro MD+) at 155°C. As it is reported earlier that the torque difference ($M_H - M_L$) is directly proportional to the degree of crosslinking, it is therefore employed to indirectly represent the crosslink density of the vulcanizates herein.¹⁰

Testing of rubber vulcanizates

The tensile properties of the vulcanizates such as tensile strength, elongation at break, and 100% modulus (M_{100}) were determined using a universal testing machine (Instron 4301 series) following ISO 37. The hardness was determined according to ISO 868

using a Wallace Shore A durometer. The compression set at elevated temperature was evaluated based on ISO 815 (method B) at 70°C for 22 h. The thermal aging properties of the rubber vulcanizates were studied by placing the specimens in an aging oven at 100°C for 72 h prior to the determination of hardness and tensile properties. Oil resistance was measured according to ISO 1817 by immersing the specimens in nonpolar hydraulic oil (Shell-Tellus 100) for 7 days at room temperature (23°C). After the immersion, the specimens were blotted off with filtered paper and rinsed with acetone prior to the determination of tensile properties. Both aging and oil resistance of the vulcanizate is represented in terms of the relative properties, i.e., the ratio of the properties after aging (or oil immersion) to those before aging (or oil immersion). In this study, the blend morphology was examined using an atomic force microscope (AFM, Multimode Nanoscope IIIA). The AFM micrographs were taken on the newly exposed surface cut from the microtome under subambient condition.

RESULTS AND DISCUSSION

The influence of silica loading on mixing behavior is illustrated in Figure 1. Obviously, the mixing energy increases continuously with increasing silica loading. This is easily understandable because silica is a non-deformable solid and, thus, increasing silica loading gives rise to the reduction of deformable rubber portion in the compound, widely known as the dilution effect. This could significantly restrict the flow of rubber compound resulting in an increase in viscosity (as can be seen from Figure 2) and, thus, the mixing energy. Figure 3 shows the effect of silica loading on scorch time (t_s2) and optimum curing time (t_c90) of the rubber blends. Although silica shows retarding effect on sulfur vulcanization for most elastomers including NR, the results herein clearly show that, for 75/25 CR/NR blends, silica has a positive effect on cure, i.e., both scorch time and optimum curing time are found to decrease continuously with increasing silica loading. In addition, the state

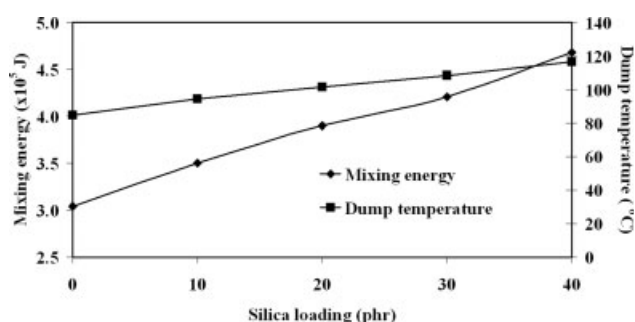


Figure 1 Effect of silica loading on mixing behaviors.

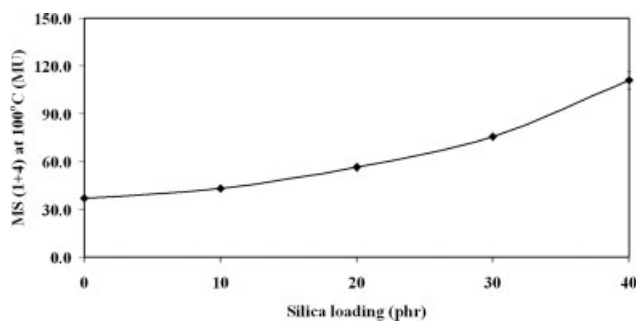


Figure 2 Effect of silica loading on Mooney viscosity of the blend compounds.

of cure represented by the torque difference ($M_H - M_L$) is also found to increase continuously with increasing silica loading as shown in Figure 4. Explanation is given by the chemical reaction between the allylic chlorine atoms of CR and the silanol groups on silica surface. Such reaction could lead to additional crosslinks in CR phase giving rise to the overall increased crosslink density of the rubber blends.⁵ Apart from such chemical reaction, the cure acceleration found with increasing silica loading is also thought to arise from the thermal history of the compounds. During mixing, the increase in silica loading could lead to a significant increase in compound viscosity and, thus, mixing temperature (see also Fig. 1). As the mixing carried out in the present study was a single step mixing, i.e., the curatives were added into the rubber 3 min prior to dumping from the internal mixer, the blends with high silica loading were therefore subjected to higher temperature during mixing than those with low silica loading. Both scorch time and optimum curing time are thus reduced with increasing silica loading.

The effect of silica loading on tensile properties, hardness, and compression set at elevated temperature of 75/25 CR/NR blend is illustrated in Table II. It could be observed that, without silica, the blend still possesses relatively high tensile strength (~ 24.6 MPa). This is possibly due to the fact that both CR and NR are able to crystallize upon stretching lead-

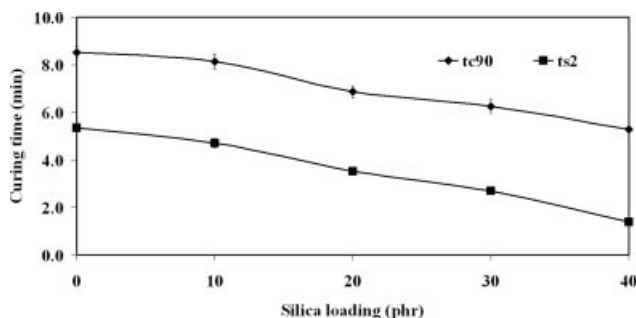


Figure 3 Influence of silica loading on cure characteristics (t_{s2} and t_{c90}).

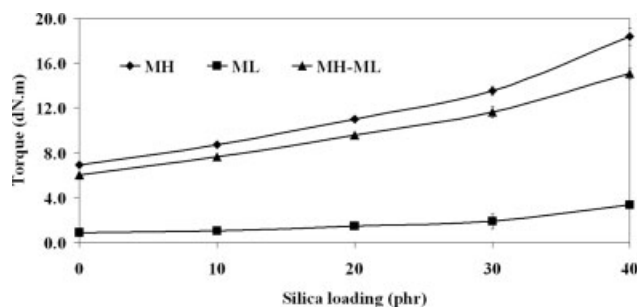


Figure 4 Influence of silica loading on minimum torque (M_L), maximum torque (M_H), and torque difference ($M_H - M_L$).

ing to high tensile strength of the gum blend. It could also be observed that the tensile strength is increased gradually with increasing silica loading until it reaches a maximum at ~ 30 phr. Further increase in silica loading could lead to significant drop in tensile strength. Similar results are also found in other published work.¹¹ The initial increase in tensile strength with increasing silica loading could be explained by the reinforcing effect of the fine silica and also by the increased crosslink density of the blend vulcanizate. The detrimental effect on tensile strength found at high silica loading could be explained by the dilution effect.¹² At high silica loading, there would not be enough rubber matrix to hold the silica particles together leading to poorer tensile strength. The 100% modulus (M_{100}), on the other hand, is found to increase continuously with increasing silica loading. Explanation is simply given by the combination of the dilution effect and the increase in total crosslink density. As hardness is closely related to modulus of the vulcanizate, it is also found that hardness of the blend is increased continuously and linearly with increasing silica loading. Generally, when silica is added into rubber at sufficiently high loading, the distance between silica aggregates becomes close enough to induce strong interaction between aggregates giving rise to an additional network, namely filler–filler network. This filler–filler network should result in a sharp increase in hardness at high silica loading. However, the linear relationship between hardness and silica loading implies that the filler–filler networks hardly takes place in this blend and, therefore, plays very little effect on the hardness. Since the degree of filler–filler networks is inversely proportional to the degree of filler dispersion, it is therefore thought that the low degree of filler–filler network found in this work arises from the good dispersion obtained in this blend. This is understandable because silica and CR, which is the matrix in this blend, are both polar in nature and they interact with each other strongly through the hydrogen bond. Such strong rubber–fil-

TABLE II
Effect of Silica Loading on Tensile Properties, Hardness, and Compression Set at Elevated Temperature

Silica loading (phr)	Tensile properties				
	Tensile strength (MPa)	100% Modulus (MPa)	Elongation at break (%)	Hardness (Shore A)	Compression set (%)
0	24.6 ± 0.7	0.75 ± 0.05	902 ± 14	43.1 ± 0.3	33.6 ± 1.1
10	25.9 ± 0.6	0.88 ± 0.01	891 ± 7	47.5 ± 0.1	36.5 ± 1.8
20	26.1 ± 1.3	1.10 ± 0.03	823 ± 14	52.8 ± 0.2	36.6 ± 1.5
30	26.8 ± 0.8	1.40 ± 0.08	805 ± 16	58.0 ± 0.3	39.8 ± 0.2
40	23.4 ± 0.8	1.67 ± 0.04	750 ± 4	63.2 ± 0.7	47.5 ± 1.2

ler interaction could lead to improved filler dispersion because of an additional drag taking place during the mixing process. The results in Table II also reveal that the elongation at break (EB) decreases significantly with increasing silica loading. This is attributed to the combination of the dilution effect and the increased crosslink density.

The dependence of compression set at elevated temperature on silica loading is also illustrated in Table II. Although increasing silica loading would result in an increase in total crosslink density, the compression set is found to increase continuously with increasing silica loading. The results indicate that the main factor governing the compression set is the dilution effect. The higher the silica loading, the lower the elasticity of the rubber vulcanizate.

Figure 5 represents the effect of silica loading on the relative tensile strength of the blend vulcanizate after being subjected to thermal aging and oil immersion. As can be seen, both aging and oil resistances of the blend vulcanizates tend to increase with increasing silica loading. Again, the explanation is given mainly by the dilution effect. It is widely known that, when the rubber vulcanizate is exposed to high temperature or oil, only the rubber portion is susceptible to degradation or swelling. Increasing silica loading means the degradable rubber portion is diluted giving rise to higher thermal aging and oil resistances. In addition to the dilution effect, the improved resistance to aging and oil is also thought to arise from the morphology of the blend. Since CR and NR are thermodynamically immiscible and, consequently, the phase morphology of this blend should be observed as multi-phase. Since this blend contains only 25% of NR, it could be expected that NR would be dispersed throughout the continuous CR phase. Without silica, the viscosity of the rubber and, thus, the mixing torque are relatively low resulting in a large dispersed NR phase as shown in Figure 6 (the bright area represents NR phase, whereas the dark area represents CR phase). Obviously, the addition of silica into the blend significantly reduces the size of the dispersed NR phase because the presence of silica brings about an

increase in compound viscosity and, thus, gives high shearing force during mixing. The higher the silica loading, the smaller the dispersed NR phase. The reduction of NR phase size is thought to contribute somehow to the better thermal aging and oil resistance of the rubber blend. Similar results also found in the system of CPE/NR and NBR/NR blends in which the oil resistance is found to increase with decreasing phase size of NR.¹³⁻¹⁵

The effect of silica loading on relative 100% modulus of the blend vulcanizate after being exposed to thermal aging and oil is represented in Figure 7. The results clearly show that, for aging test, the relative 100% modulus is greater than 1. The results indicate that the modulus of the blend vulcanizate is increased after being subjected to high temperature. The increase in 100% modulus is thought to arise from the post curing effect, which is commonly found in CR. The post curing of CR phase takes place due to the formation of intermolecular crosslinking and/or intramolecular cyclization between CR main chains.¹⁶ It is also found that the relative 100% modulus is increased continuously with increasing silica loading. The results imply that the degree of post curing is directly proportional to silica loading. The chemical reaction between the silanol group and the allylic chlorine atom in CR, which could take place at high temperature, could

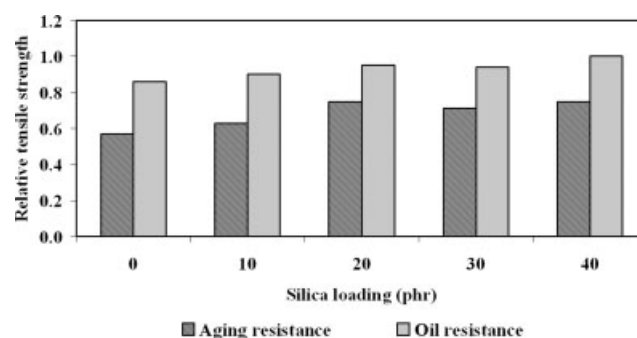


Figure 5 Relationship between silica loading and relative tensile strength of the blend vulcanizates after aging and oil immersion.

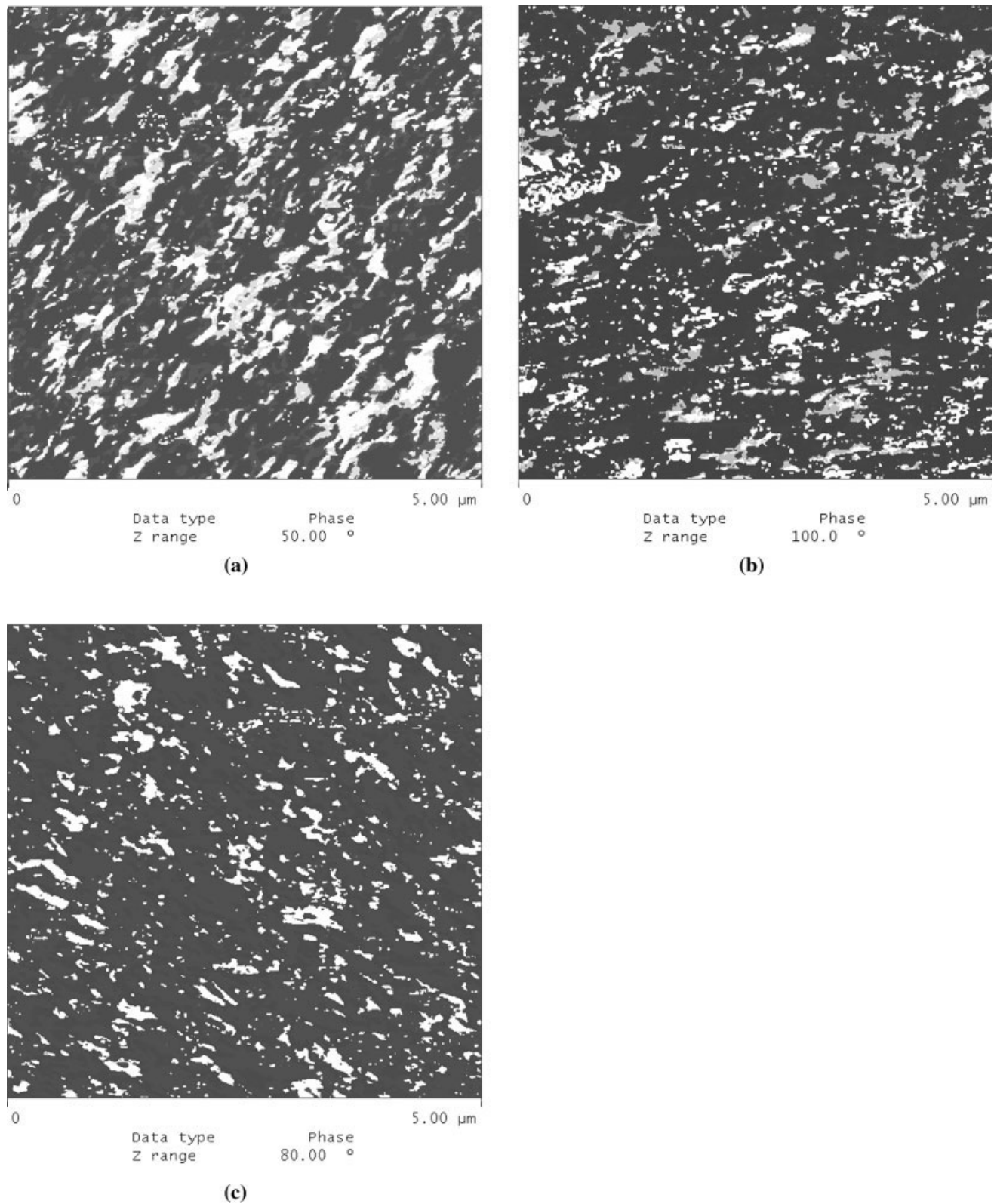


Figure 6 AFM micrograph of 75/25 CR/NR blends (a) without silica; (b) 20 phr of silica, and (c) 40 phr of silica.

be used to explain the results. Similar trend is also found for the relative 100% modulus after oil immersion test, i.e., the relative 100% modulus is gradually

increased with increasing silica loading. Again, the improvement in oil resistance with increasing silica loading arises from the combination of dilution

effect, enhanced crosslink density, and smaller dispersed NR phase. Similar results are also found for the relative hardness as shown in Figure 8. The same explanation is applied.

CONCLUSIONS

The results reveal that increasing silica loading gives positive effect on cure characteristics of the blend, i.e., both scorch time and optimum curing time markedly decrease with increasing silica loading. The overall crosslink density is also increased with increasing silica loading. The tensile strength is found to improve slightly with increasing silica loading up to 30 phr. This improvement is attributed to the combination of the reinforcing effect of fine silica particles and the overall increased crosslink density. As expected, the modulus of the blend vulcanizate increases progressively with increasing silica loading. The enhanced crosslink density and the dilution effect could be used to explain the results. Although increasing silica loading would lead to an increase in total crosslink density, the compression set, on the other hand, is impaired. Explanation is given by the dilution effect. As the presence of silica increases considerably the viscosity of the compound, the size of NR dispersed phase is found to decrease with increasing silica loading. The reduction of NR phase size could enhance the resistance to thermal aging and oil of the blend vulcanizates. Apart from the phase morphology, the improvement in thermal

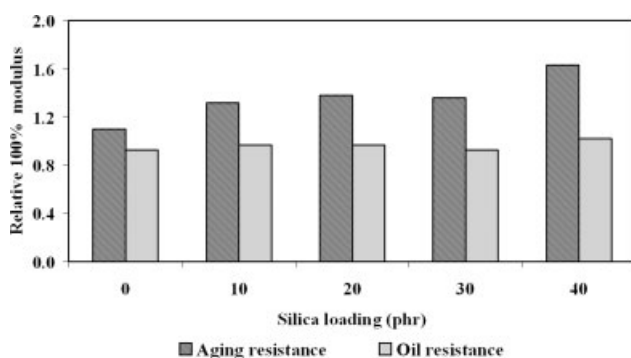


Figure 7 Relationship between silica loading and relative 100% modulus of the blend vulcanizates after aging and oil immersion.

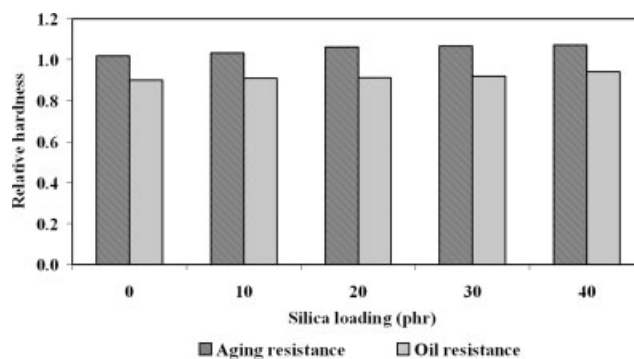


Figure 8 Relationship between silica loading and relative hardness of the blend vulcanizates after aging and oil immersion.

aging and oil resistances of the blend vulcanizate is also believed to arise from the dilution effect and the increased crosslink density in the presence of silica.

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References

- Ismail, H.; Leong, H.C. *Polym Test* 2001, 20, 509.
- Saad, A.L.G.; El-sabbagh, S. *J Appl Polym Sci* 2001, 79, 60.
- Helaly, F. M.; El-sabbagh, S.H. *J Elastomers Plastics* 2002, 34, 335.
- Hofmann, W. *Rubber Technology Handbook*; Hanser: Munich, 1989.
- Wang, G.; Li, M.; Chen, X. *J Appl Polym Sci* 1999, 72, 577.
- Wolff, S.; Wang, M. *J Rubber Chem Technol* 1992, 65, 329.
- Byers, J. T. *Rubber World* 1998, 218, 38.
- Choi, S. S. *J Appl Polym Sci* 2002, 83, 2609.
- Das, A.; Debnath, S. C.; De, D.; Basu, D. K. *J Appl Polym Sci* 2004, 93, 196.
- Sae-oui, P.; Sirisinha, C.; Thepsuwan, U.; Hatthapanit, K. *Eur Polym J* 2006, 42, 479.
- Sae-oui, P.; Rakdee, C.; Thanmathorn, P. *J Appl Polym Sci* 2002, 83, 2485.
- Blow, C. M. *Rubber Technology and Manufacture*; Butterworths: London, 1971.
- Pattanawanidchai, S.; Sae-oui, P.; Sirisinha, C. *J Appl Polym Sci* 2005, 96, 2218.
- Sirisinha, C.; Sae-oui, P.; Guaysomboon, J. *Polymer* 2004, 45, 4909.
- Sirisinha, C.; Sae-oui, P.; Guaysomboon, J. *J Appl Polym Sci* 2003, 90, 4038.
- Miyata, Y.; Atsumi, M. *Rubber Chem Technol* 1989, 62, 1.