Mechanism of Silica Reinforcement in CPE/NR Blends by the Use of Rheological Approaches

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ABSTRACT: Blends of elastomeric chlorinated polyethylene (CPE) and natural rubber (NR) at blend composition ratio of 80/20 CPE/NR with various precipitated silica loadings were prepared. By the use of rheological approaches, a mechanism of silica reinforcement was proposed. Results obtained reveal that the viscoelastic behavior of blends is influenced remarkably by loadings of silica. A cure promotion phenomenon is found as silica is loaded due probably to the strong silica-CPE interaction and/or a reduction in curative absorption on silica surfaces. A strong Payne effect is observed, which is increased by a rise in silica loading, implying a formation of pseudocrosslink via a physical interaction, which could be disrupted at high strain of deformation. The proposed mechanism of silica reinforcement based on the formation of pseudocrosslink is validated by the deactivation of silanol groups on silica surfaces using silane-coupling agents. The bis-(3-triethoxysilylpropyl) tetrasulfane (Si-69) is found to be more effective in suppressing the pseudocrosslink than 3-thiocyanatopropyl triethoxy silane (Si-264), which is thought to be the result of its larger amount of alkoxy groups at a given silane loading. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2638–2645, 2008

Key words: reinforcement; silica; rheology; elastomers; blends

INTRODUCTION

Reinforcement of polymers by fillers is known to be one of important matter for producing rubber final products. Silica has been used as an important non-black filler for rubber to obtain highly reinforced vulcanized products. Compared with carbon black having similar specific surface area, silica contributes to a smaller magnitude of reinforcement because of its large amount of silanol groups (Si—OH) on the surfaces making silica capable of absorbing curatives on its surfaces and thus retarding curve in most rubbers. In addition, the presence of silanol group leads to strong filler–filler interaction giving rise to a high tendency for filler agglomeration in the rubber matrix and, hence, the difficulty in processing.

Chlorinated polyethylene (CPE) is widely known for its high resistances to hydrocarbon oil, heat, and weathering, which are mainly attributed to the saturated structure and the presence of chlorine atoms on the molecular backbone. CPE has generally been blended with various polymers including polyvinyl chloride (PVC),[1–4] styrene-acrylonitrile (SAN),[5,6] and polyurethane (PU)[7,8] to achieve desired properties. Referred to our previous work,[9–11] it has been reported that a certain amount of CPE could be substituted by NR, giving similar tensile properties to neat CPE, depending on curing systems used for vulcanizing NR phase in blends. In addition, in terms of rheological properties of CPE/NR blends, it has been found that, without the vulcanization of NR phase in blends, the elastic modulus of blends depends strongly on test frequency, due mainly to the domination of viscous response. By contrast, after curing of NR phase in blends, the blends with NR as a matrix demonstrate the time-independent elastic modulus while those with CPE as a matrix still reveal the time-dependent elastic modulus to some extent depending on NR composition ratio.[12] Results of silica reinforcement in CPE/NR blends has been reported, which is believed to be caused by a strong interaction between chlorine atoms of CPE and silanol functional groups of silica associated with the filler–filler interaction via hydrogen bonds. In terms of viscoelastic response, it could be stated that such interactions promote the formation of transient tridimensional network (or the so-called pseudocrosslink) causing a dominantly elastic response in the blends.[13] Therefore, this work aims to further the investigation of silica-reinforced CPE/NR blends by focusing on the mechanism, which controls

TABLE I
Materials Used in This Study

Material	Manufacturer/supplier	Amount (phr)	Remarks
Chlorinated polyethylene (CPE; Tyrin 702P)	DuPont Dow Elastomer Co., Ltd., USA	80	Raw polymer
Natural rubber (NR; STR5)	Union Rubber Products Co., Ltd., Thailand	20	Raw polymer
Stearic acid (Commercial grade)	Petch Thai Chemical Co., Ltd., Thailand	2	Cure activator
Magnesium oxide (MgO; Starmag no.150)	Konoshima Chemical Co., Ltd., Japan	5	Acid receptor
Santoflex I-PPD[a]	Flexsys Co., Ltd., Belgium	4	Antioxidant
Precipitated silica (HiSil 233)	PPG-Siam Silica Co., Ltd., Thailand	Variable	Reinforcing filler
Santogard PVI[b]	Flexsys Co., Ltd., Belgium	1	Cure inhibitor
Si-69 silane coupling agent[c]	JJ Degussa Co., Ltd., (Thailand)	Variable	Coupling agent
Si-264 silane-coupling agent[d]	JJ Degussa Co., Ltd., (Thailand)	Variable	Coupling agent
Ordinary sulphur (Commercial grade)	Chemmin Co. Ltd., Thailand	2	Curing agent

[a] N-Isopropyl-N'-phenyl-p-phenylenediamine.
[b] N-(cyclohexylthio)phthalimide.
[c] bis-(3-triethoxysilylpropyl)tetrasulfane (TESPT).
[d] 3-Thiocyanatopropyl triethoxy silane.

reinforcement of such blend systems highly filled with precipitated silica via rheological approaches. Silane-coupling agents, a bifunctional compound with two functionally active end groups, that is, the readily hydrolysable alkoxy group and the organofunctional group, were used to deactivate the silanol groups due to their strong interaction between alkoxy and silanol groups.[14] It is anticipated that if the silica reinforcement of CPE/NR blends is caused mainly by the silica-CPE and/or silica-silica interactions (i.e., pseudocrosslink), the deactivation of silanol groups by silane should lower the magnitude of reinforcement. Two types of silanes, that is, bis-(3-triethoxysilylpropyl) tetrasulfane (Si-69) and 3-thiocyanatopropyl triethoxy silane (Si-264), were used to study and compare their influences on deactivating the silanol groups and thus suppressing the silica reinforcement.

EXPERIMENTAL

Materials

Details of materials used and blend formulation are shown in Table I.

Mixing procedure

Referred to our previous work,[10] the CPE/NR blend composition ratio of 80/20 was used for the study as this blend ratio provides a comparable properties to neat CPE with a relatively low product cost. Blending of CPE and NR was performed with the use of two-roll mill (Labtech model LRM 150, Thailand) at set temperatures of 140 and 135°C for the front and back rolls, respectively. CPE was first molten for a minute, followed by the addition of masticated NR. After a minute of blending, the precipitated silica and silane-coupling agent (if any) were charged to the blend and allowed 5 min for filler dispersion and distribution. Then, the rest of compounding ingredients including cure activators, antioxidant, cure inhibitor, and curatives were incorporated to the blends, and mixing was continued for 5 min.

Measurement of cure and rheological properties

Cure behavior of blends was monitored with the use of Rubber Process Analyzer (RPA2000, Alpha Technologies, USA) at 155°C under a deformation strain of 15%. Scorch time (t_{s2}) defined as the time to reach a 2 dN m torque rise above the minimum torque and optimum cure time (t_{c90}) defined as the time to reach 90% cure were determined from cure curves.

Rheological properties of blends were measured using an oscillatory parallel-plate rheometer (Physica MCR500, Germany) under nitrogen atmosphere. A strain sweep test was conducted for determining Payne effect while the frequency sweep test was performed for monitoring the frequency-dependent properties of blends.

RESULTS AND DISCUSSION

Untreated silica

In this section, a precipitated silica is used as-received with no silane surface treatment. Generally, the presence of silanol groups on precipitated silica surfaces are known to retard curing in sulphur-cured vulcanisates, which is attributed to the absorption of curatives and cure activators on silica surfaces.[14] Surprisingly, the cure behavior of CPE/NR blends reveals that both scorch time (t_{s2}) and cure time (t_{c90}) decrease with increasing silica loading, as shown in Figures 1 and 2. The reduction in t_{s2} and t_{c90} might be the results of thermal history via shear heating, which is more pronounced in the blends with high silica loadings. As illustrated in Figure 3, the blends with high silica loadings possess relatively high
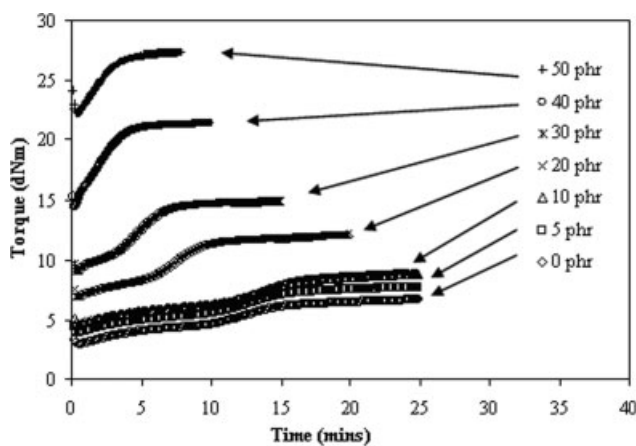
Figure 1 Cure curves of silica-filled CPE/NR blends with various silica loadings.

Figure 3 Complex viscosity of CPE/NR blends with various silica loadings at 170°C.

complex viscosities, which are caused by a hydrodynamic effect associated with a strong interaction between silica surfaces and CPE matrix.

In the case of crosslink density affected by the addition of precipitated silica, Figure 4 shows that the torque difference, as an indicator for crosslink density, increases with increasing silica up to 40 phr. This indicates the increase in crosslink density. Above 40 phr of silica, the decrease in crosslink density is observed. There are, in theory, two main factors controlling torque difference in silica-filled CPE/NR blends, namely, chemical interaction and physical interaction.

In the case of chemical interaction, the main reactions taking places could be the dehydrochlorination and/or the sulphidic linkage formation in NR phase. The former process could occur among CPE molecules giving C—C linkages or between CPE molecules and silanol groups on silica surfaces giving Si—O—C chemical linkages. Apart from the dehy-
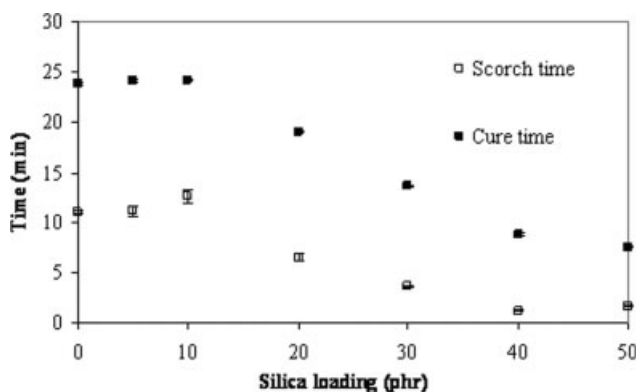
drochlorination process, the sulphidic linkages via sulphur vulcanization of NR phase could remarkably play a strong role on torque difference of cure curves. It is possible that the interaction between silanol groups and chlorine atoms of CPE might be much stronger than that between curatives and silica, leading to a reduction in absorption of curatives on silica surfaces. Therefore, the free curatives could increase cure efficiency of the systems, leading to a cure promotion phenomenon as illustrated schematically in Figure 5.

In the case of physical interaction, the torque difference could be caused by a formation of silica transient network due to strong silanol–chlorine and silanol–silanol interactions, which is sometimes known as pseudocrosslink as shown in Figure 6. In other words, the results of torque difference observed are due not only to the sulphidic linkages of NR phase, but also to the strong pseudocrosslinks. The proposed statement is supported by the results of time sweep test of neat CPE with various loading of silica as shown in Figure 7. It could be seen that a signifi-

Figure 2 Scorch time (t_{s2}) and cure time (t_{c90}) of CPE/NR blends with various silica loadings determined from cure curves (Fig. 1).
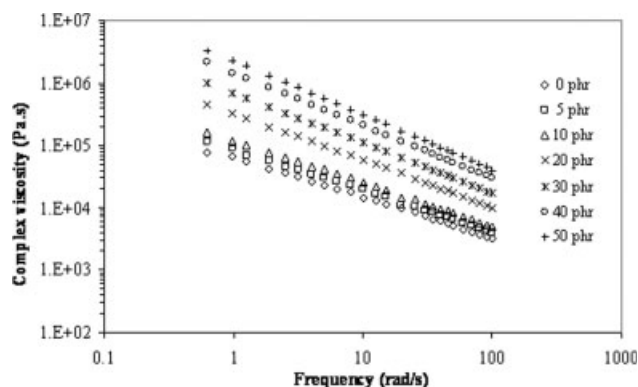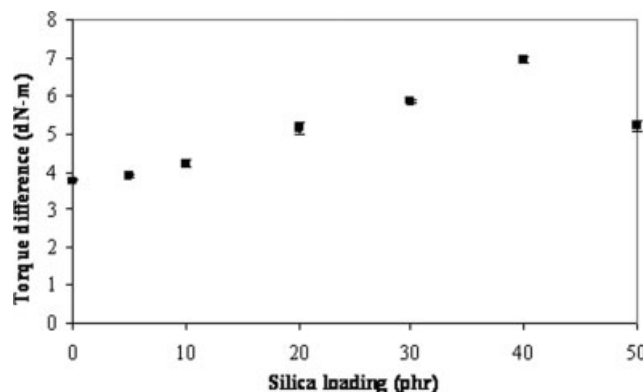

Figure 4 Crosslink density (in terms of torque difference) of CPE/NR blends with various silica loadings.

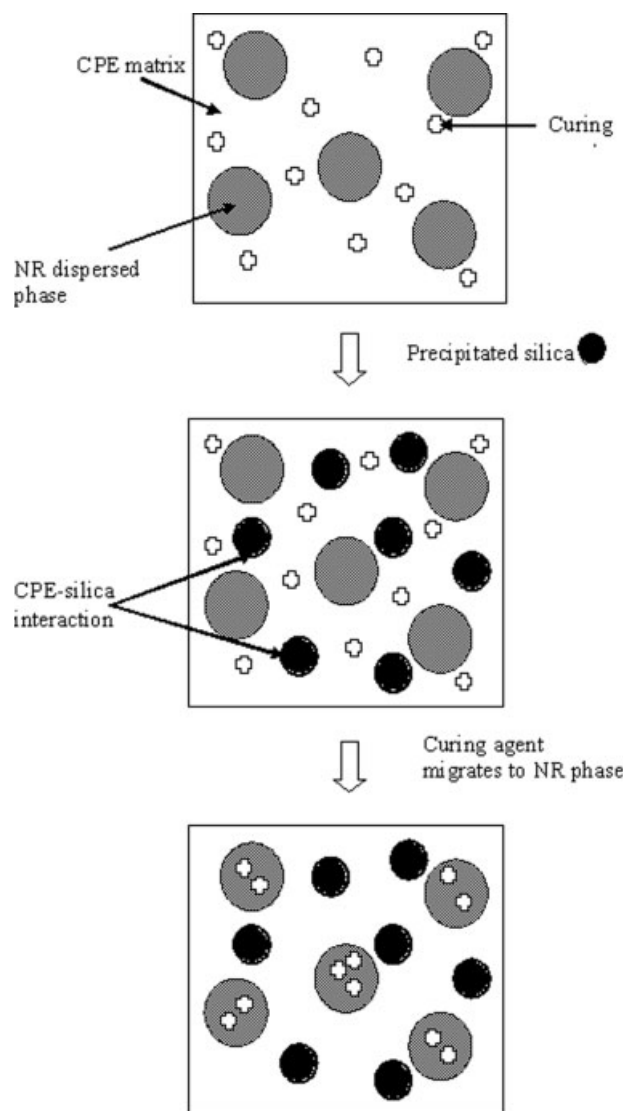**Figure 5** Schematic model of a curing agent migration to NR phase leading to a sulphur cure promotion of silica-filled blends.

Figure 6 Schematic model of a pseudocrosslink formation caused by CPE-silica and silica–silica interactions.

Figure 9 shows the results of strain sweep test, which is usually used for determining the Payne effect. Storage modulus (G') at low strain of the blends apparently increases with increasing silica loading, which is the combined consequences of hydrodynamic, filler–rubber and filler–filler network effects, associated with an incomplete silica dispersion, particularly at high silica loading. Additionally, the blends with high silica loading, that is, with the silica loading higher than 20 phr, show a strong Payne effect, that is, a remarkable decrease in G' with increasing strain of deformation. The effect of silica loading on magnitude of reinforcement could

cant increase in torque difference could still be observed in neat CPE filled with silica (i.e., no NR related).

Regarding the viscoelastic behavior, changes in storage modulus (G') and damping factor (tan δ) are monitored as functions of deformation strain and angular frequency at 170°C. Thus, one might expect that the results reported might be interfered by molecular degradation effect taking place during the test duration. As a result, the thermal stability test must first be performed, and its results are illustrated in Figure 8. It is evident that the storage torque of all filled blends is stable within a small range of 1–2 dN m. Alternatively, it could be stated that any change found in viscoelastic behavior is not significantly affected by the thermal degradation of blends.
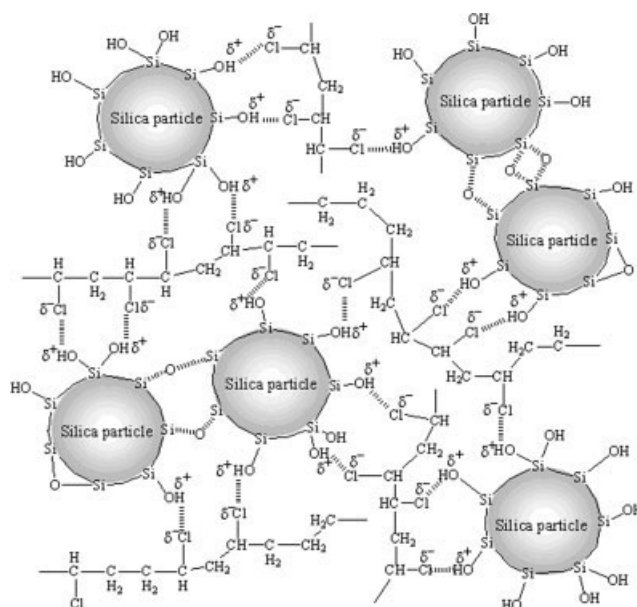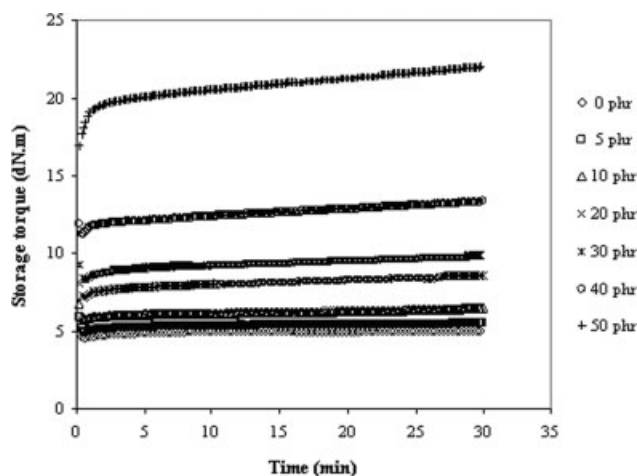

Figure 7 Time sweep test results at 155°C for 30 min of neat CPE with various loadings of precipitated silica.

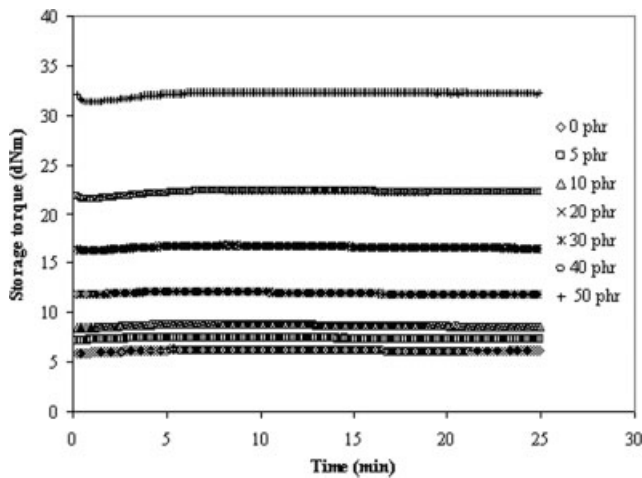**Figure 8** Time sweep test results at 170°C for 25 min of CPE/NR blends with the various loadings of silica.

Figure 10 Relative elastic modulus (relative G') at 1 and 100% strain with test frequency of 3.14 rad/s of CPE/NR cured blends with various silica loadings as a function of silica volume fraction.

theoretically be determined by the use of Guth-Gold equation [eq. (1)].

$$\text{Relative } G' = \frac{G'_{\text{filled}}}{G'_{\text{unfilled}}} = 1 + 2.5\phi + 14.1\phi^2 \qquad (1)$$

where G'_{unfilled} is the elastic modulus of unfilled compounds, G'_{filled} the elastic modulus of filled compounds, and ϕ the filler volume fraction.

Figure 10 shows a relative modulus calculated from Guth-Gold equation, which excludes the filler network and filler–rubber effects. It is evident that the experimental data at 1% strain in the linear viscoelastic (LVE) region are much higher than the calculated data, indicating the presence of filler network and/or filler–rubber interaction via a strong CPE-silica interaction between chlorine atoms and silanol groups. However, because the silica network and filler–rubber interaction are physically transient, both of network and interaction could be disrupted
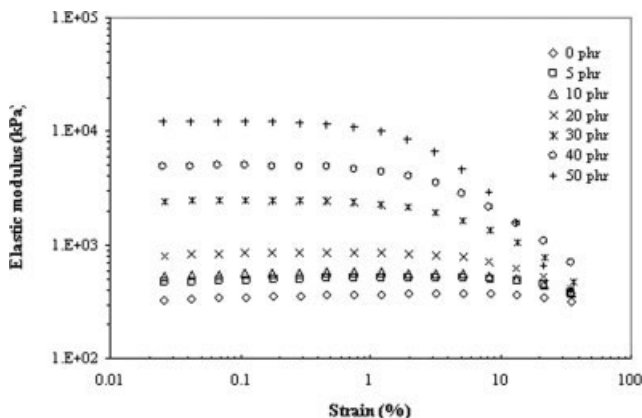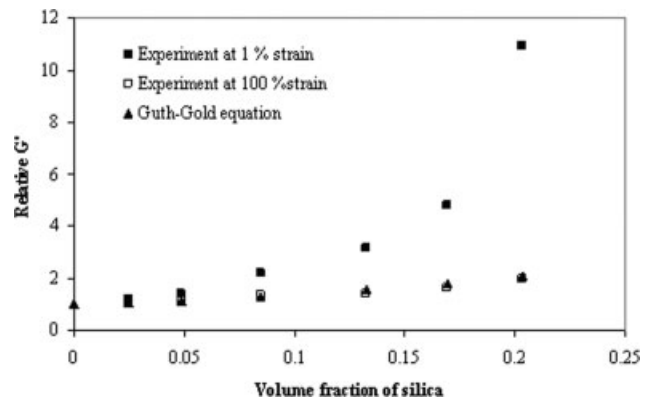
by the application of high strain to the test specimen as demonstrated by a reduction in G'. Therefore, the experimental G' falls down to the calculated G' based on the Guth-Gold equation at high strain of 100%. Moreover, the Guth-Gold results are a strong evidence that both silica network and silica-CPE interaction, that is, pseudocrosslink, are physical interaction, which could be disrupted at high strain.

Figure 11 shows G' of blends with various loadings of silica as a function of frequency. As expected, G' at any given frequency increases with silica loading due to the reinforcing effect as discussed previously. Also, it is clear that G' of all blends increases with increasing frequency, which is caused by the insufficient time for molecular relaxation. Notably, the slope of G' plots is relatively shallow for the blends with high silica loading. The result can be explained by the presence of filler network and filler–rubber interaction via a strong CPE-silica interaction (i.e., the interaction between chlorine atoms
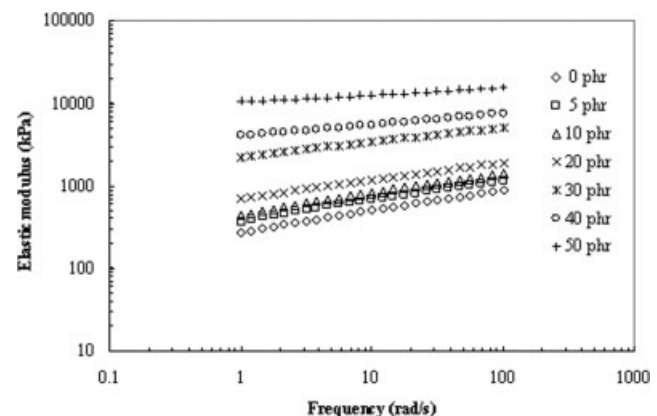

Figure 9 Payne effect of cured CPE/NR blends with various silica loadings.

Figure 11 Elastic modulus (G') of vulcanized CPE/NR blends with various silica loadings as a function of frequency.
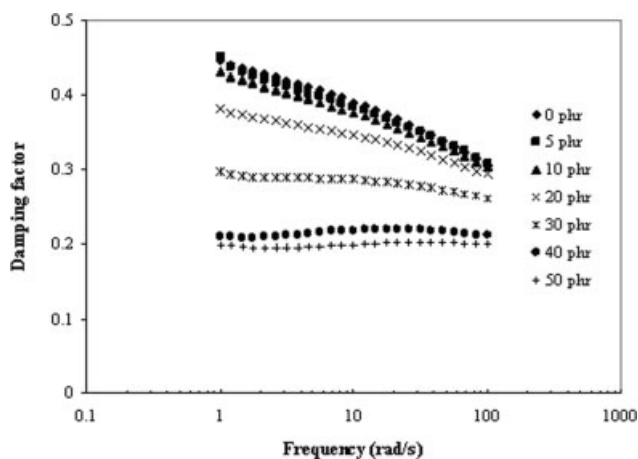
Figure 12 Damping factor (tan δ) of vulcanized CPE/NR blends with various silica loadings as a function of frequency.

Figure 14 Optimum cure time of filled CPE/NR blends with Si-69 and Si-264 silanes.

and silanol groups). Such network and interaction act as pseudocrosslink and, therefore, with increasing silica loading, the amount of pseudocrosslink increases, and thus the elastic response with time-independent behavior (i.e., an elastic spring component is dominant over the dashpot one). The G' results are in good agreement with damping factor results as illustrated in Figure 12. The damping factor decreases and is less frequency-dependent with increasing silica loadings, implying an increase in elastic response of the system via a formation of pseudocrosslink.

bic. Chemical structures of the silanes used are shown in Figure 13.

Figure 14 illustrates the optimum cure time as a function of silane loading in silica-filled blends with Si-69 and Si-264 silanes. It is evident that the optimum cure time significantly increases with increasing silane loading. The results could be explained by

Silane-treated precipitated silica

From section Untreated silica, it is proposed that the reinforcing mechanism of CPE/NR blends with precipitated silica takes place via silanol groups on silica surfaces. Thus, this section aims to validate such proposed mechanism by intentionally deactivating the silanol groups with two different organo-silane-coupling agents, namely, bis-(3-triethoxysilyl-propyl)tetrasulfane (Si-69,TESPT) and 3-thiocyanato-propyl triethoxy silane (Si-264). It is widely known that the silanes are used to modify surfaces on silica surfaces by making silica surfaces more hydropho-
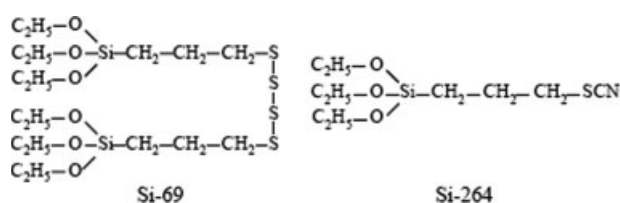

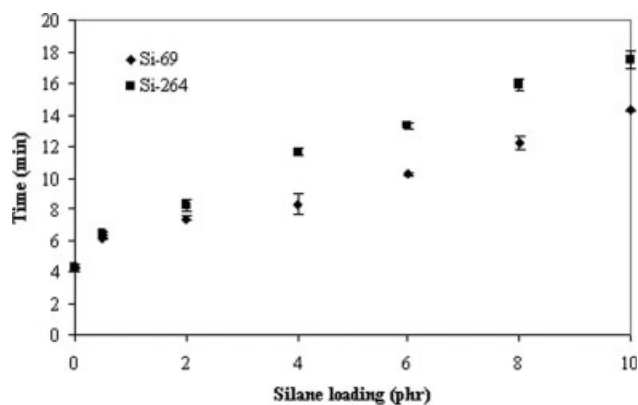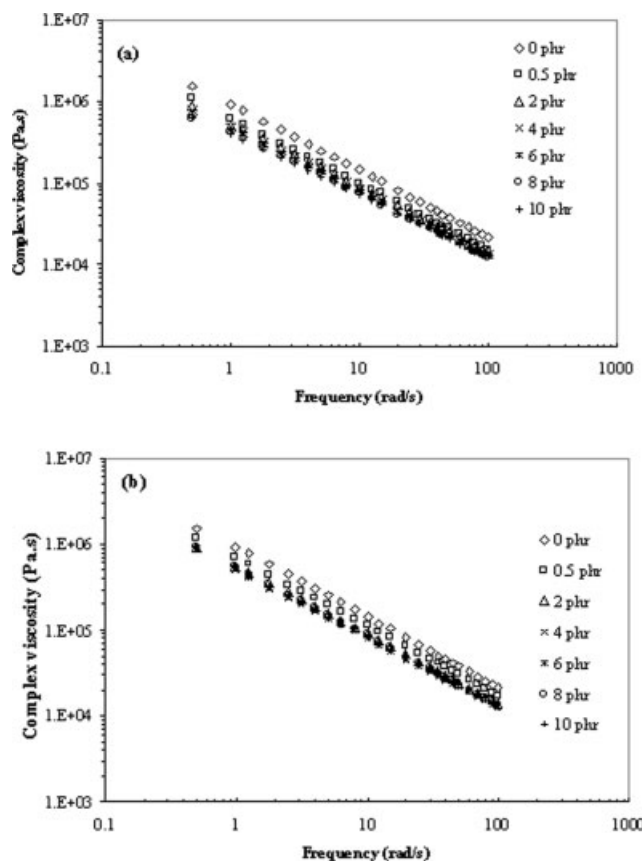**Figure 13** Chemical structures of Si-69 (TESPT) and (Si-264).

Figure 15 Complex viscosity of silica filled blend vulcanisates influenced by different silane loadings: Si-69 (a); Si-264 (b).
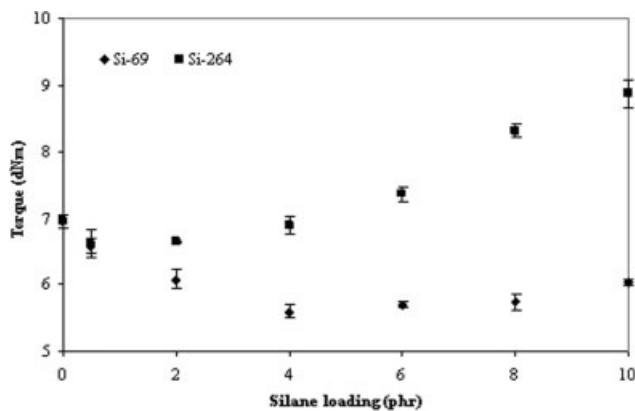
Figure 16 Crosslink density (in terms of torque difference) of silica-filled CPE/NR blends with the various silane loading.

the reduction of thermal history via a plasticizing effect provided by silanes as illustrated in Figure 15. Complex viscosity decreases with silane loading due mainly to a reduction in molecular restriction. Additionally, as discussed previously, the untreated silica could promote curing of NR phase via a strong interaction between silanol groups and chlorine atoms leading to a release of curatives to NR phase. Thus, as silanes are loaded to the blends, the amount

of silanol groups for interacting with chlorine atoms is reduced, which causes a reduction in cure efficiency and thus the increase in optimum cure time.

The results of crosslink density via torque difference are illustrated in Figure 16. Surprisingly, the results reveal that the two silane-coupling agents affect cure characteristics of the compounds differently. By increasing silanes, Si-69 reduces crosslink density whereas Si-264 increases crosslink density. Also, a strong evidence of pseudocrosslink suppression by silanes is illustrated in Figure 17. The extent of Payne effect decreases remarkably with increasing silane loading. Clearly, to achieve a similar magnitude of pseudocrosslink suppression, a larger amount of silane is required for the Si-264. In other words, at any silane loading, Si-69 silane is more effective in deactivating the silanol group on silica surfaces than the Si-264 silane, which is due probably to the larger amount of alkoxy groups in its molecules, which would reduce the formation of pseudocrosslink more efficiently (see also Fig. 13). The additional evidences of suppression in the
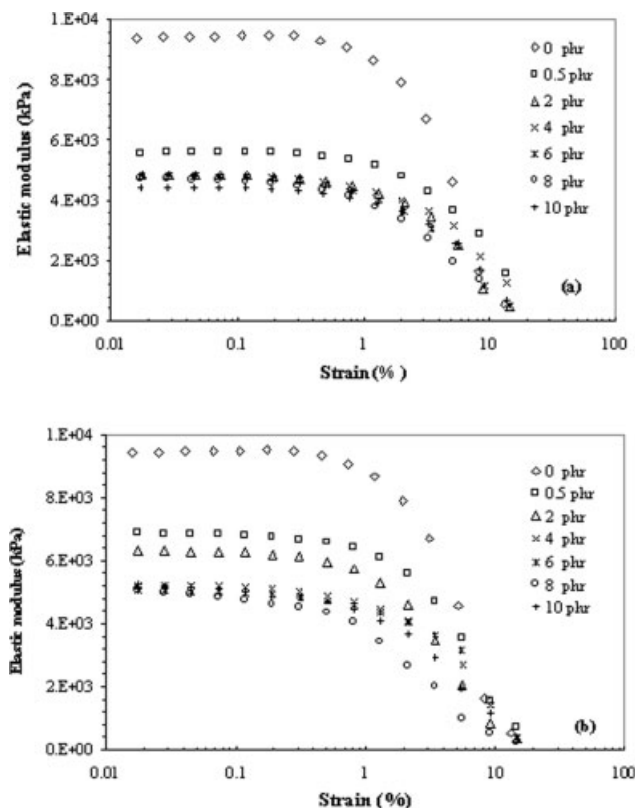

Figure 17 Payne effect of silica-filled blend vulcanisates with different silane loadings: Si-69 (a); Si-264 (b).
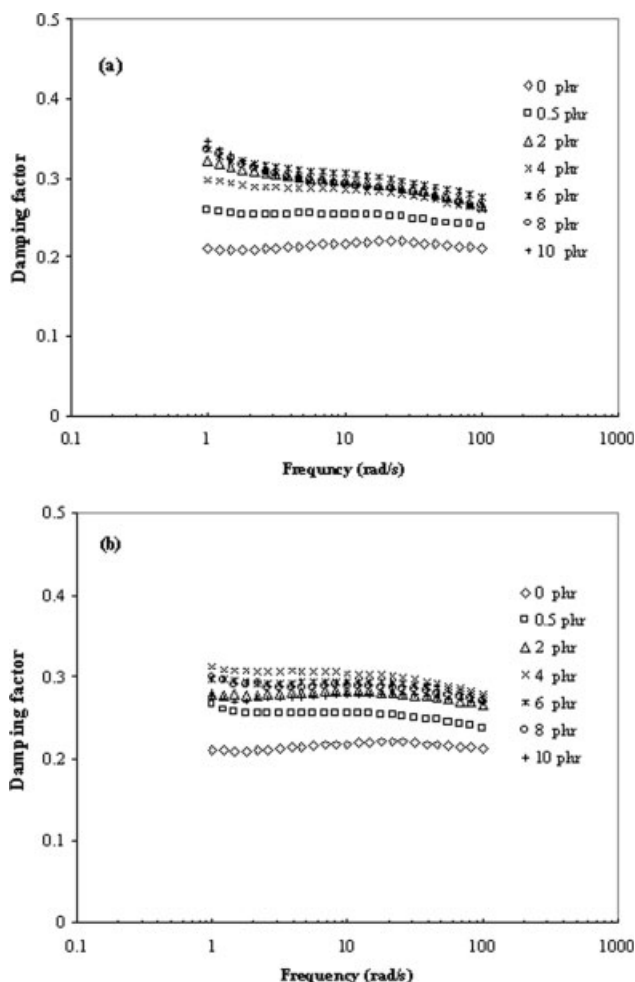

Figure 18 Damping factor of silica filled blends with different silane loading: Si-69 (a); Si-264 (b).

transient network formation are the results of damping factor as shown in Figure 18. It can be seen that by increasing silane loading, the damping factor increases, associated with the increased sensitivity of damping factor to frequency, particularly in the blends with Si-69, implying a decrease of elastic component in the system, that is, the reduced extent of pseudonetwork in the present blend systems.

CONCLUSIONS

This study examines a reinforcing effect of CPE/NR-cured blends filled with precipitated silica with the use of rheological properties. The addition of silica to the blends strongly affects the cure behavior of filled blends; a cure promotion phenomenon is found, as silica is loaded due to the strong silica-CPE interaction and a reduction in absorption of curatives on silica surfaces. A strong Payne effect is observed, which is increased by a rise in silica loading. This implies a formation of pseudocrosslink via a physical interaction, which could be disrupted at high strain of deformation. A mechanism of silica reinforcement via a formation of pseudocrosslink is validated by the suppression of Payne effect as silane-coupling agents are added. The Si-69 silane is more effective in suppressing the pseudocrosslink than Si-264.

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