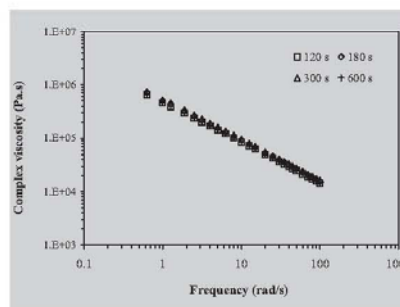
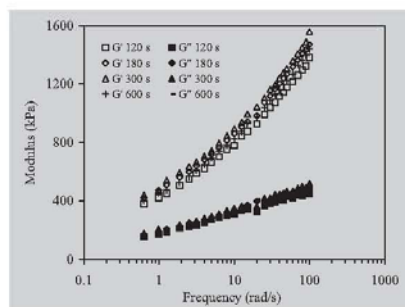
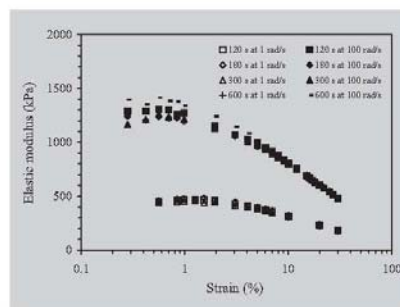
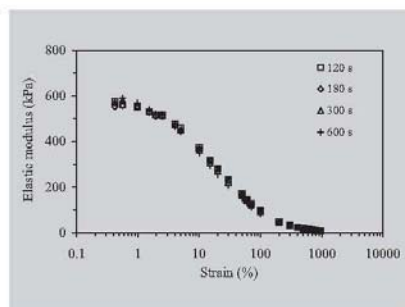


Figure 7 (left above): Elastic modulus, G' , as a function of % deformation strain at the test frequency of 3.14 rad/s (Payne effect) in filled uncured CPE/NR blends with the various mixing time.

Figure 8 (right above): Elastic modulus, G' , of filled uncured CPE/NR blends with various mixing time as a function of % deformation strain at low (1 rad/s) and high (100 rad/s) frequency.

Figure 9 (left below): Elastic modulus, G' , and loss modulus, G'' , of filled uncured CPE/NR blends with various mixing time as a function of frequency.

Figure 10 (right below): Complex viscosity, η^* , of filled uncured CPE/NR blends with various mixing time as a function of frequency.



3.2 VISCOELASTIC PROPERTIES OF UNVULCANISED BLENDS

Since the results presented in the section 3.1 reveal a role of mixing time in viscoelastic properties via the formation of silica transient network, it is logical to further consider whether such role is influenced by chemical crosslink via sulphidic linkages. As a consequence, in this section, the blends without curing agents were prepared, and their viscoelastic properties were determined. By this means, the effect of chemical crosslinks on viscoelastic behaviour could be neglected.

Strain sweep test

The effect of strain deformation on G' of uncured CPE/NR blends is demonstrated in Fig. 7. Similar to the cured blends, at a given strain, all uncured blends show no significant difference in G' with a strong Payne effect. Alternatively, the mixing time does not play a strong role in the formation of silica transient network whereas the strong interaction between chlorine atoms and silanol groups is responsible for the Payne effect as discussed previously in the section of cured blends.

Fig. 8 reveals that the strain in LVE region for both low and high frequencies is up to 1 %, and therefore, the 1 % strain is selected for the frequency sweep test. Evidently, the LVE region of uncured blends is narrower than that of cured blends (see also Fig. 2) that means the transient

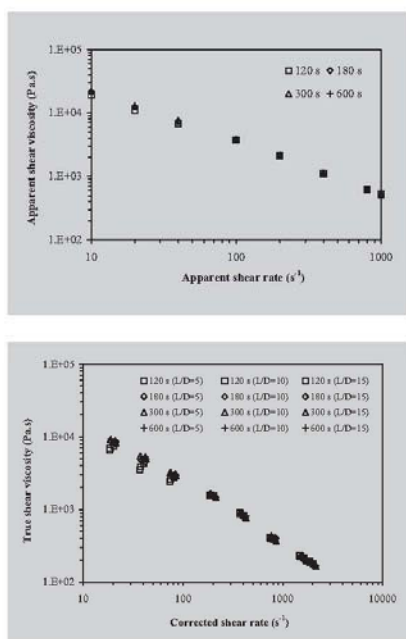
network of silica is weaker for the uncured blends.

Frequency sweep test

Influence of mixing time on G' as a function of frequency of uncured blends is presented in Fig. 9. Apparently, G' of all uncured blends increases with increasing frequency due to the insufficient time available for molecular relaxation. Also, at a given frequency, there are only slight discrepancies in G' of blends with various mixing time, unlike the G' results of cured blends. The proposed explanation is that there is no curing stage in uncured blends, and therefore the thermal history inducing thermal degradation is much lower than that in cured blends. Furthermore, compared to the vulcanised blends (see Fig. 4), the uncured blends yield lower G' , which is due to the larger amount of viscous component via the absence of sulphur vulcanisation of NR phase in blends, leading to the lack of the molecular network.

In the case of the loss modulus, G'' , as illustrated in Fig. 9, G' of all compounds is clearly markedly higher than G'' at a given frequency. A crossover point of G' and G'' appears to be far lower than 1 rad/s, suggesting that the spring or elastic responses are prominent in these uncured blends, regardless the mixing time, which is due mainly to the presence of silica transient network.

Regarding the processability, the results of complex viscosity is illustrated in Fig. 10 showing



a pseudoplastic behaviour of all blends. At a given test frequency, complex viscosity, η^* , of blends is independent of mixing time, suggesting that the change in mixing time does not affect the processability of these uncured blends.

From the overall oscillatory results of both cured and uncured blends, it can be summarised that the mixing time affects viscoelastic properties in cured blends to some extent mainly via the formation of silica transient network, but does not significantly influence those in uncured blends. The vulcanisation of NR phase in blends appears to promote the silica transient network effect on viscoelastic behaviour of blends.

Steady shear properties of uncured filled blends

Apart from the oscillatory flow, the steady shear flow of uncured blends has been determined with the use of rate-controlled capillary rheometer. The logarithmic plots of apparent shear viscosity, η_a , as an indicator for processability against apparent shear rate, $\dot{\gamma}_a$, of uncured blends with various mixing time are illustrated in Fig. 11. A pseudoplastic behaviour could be observed in all blends. Additionally, the η_a of all uncured blends falls on the single correlation. In other words, the difference in mixing time does not give any significant difference in processability under steady shear flow.

By applying the Bagley correction to eliminate the elastic behaviour, the results are tabulated as shown in Table 3. It is evident that the

Mixing time [s]	Shear rate [s ⁻¹]	Elastic pressure [MPa]	R ²
120	10	3.60	0.9575
	20	4.45	0.9351
	40	4.61	0.9581
	100	4.65	0.9943
	200	5.76	0.9996
	400	7.66	0.9985
	800	9.22	0.9999
	1000	9.91	1.0000
	10	3.01	0.9926
	20	3.60	0.9904
180	40	3.77	0.9952
	100	4.35	0.9996
	200	5.85	0.9994
	400	7.77	0.9931
	800	9.09	0.9997
	1000	9.79	0.9999
	10	2.67	0.9936
	20	2.55	0.9925
	40	2.83	0.9956
	100	3.91	0.9989
300	200	5.57	1.0000
	400	7.27	0.9949
	800	8.64	0.9991
	1000	9.23	0.9999
	10	2.45	0.9979
	20	2.94	0.9959
	40	3.34	0.9967
	100	4.06	1.0000
	200	5.35	0.9999
	400	6.78	0.9975
600	800	8.22	0.9999
	1000	8.87	0.9999

Figure 11 (left above): Capillary flow curves of uncured CPE/NR blends with the various mixing time ($L/D = 15$).

Figure 12 (left below): Capillary flow curves after corrections of filled uncured CPE/NR blends with various mixing time and die geometry.

Table 3: Results determined from the Bagley correction.

entrance or elastic pressure increases with increasing shear rate for all blends, which is due undoubtedly to the insufficient time for molecular relaxation at high shear rate. Besides, at a given shear rate, the elastic behaviour of the blends is similar, indicating the insensitivity of elastic pressure to mixing time, which is in a good agreement with the result of G' , as illustrated earlier in Fig. 9.

Fig. 12 reveals the corrected results (i.e., η_{true} as a function of $\dot{\gamma}_{cor}$) of uncured blends with different mixing time and die geometry. Clearly, all blends exhibit a pseudoplastic behaviour similar to those before correction. In addition, at a given shear rate, the results of η_{true} are slightly lower than those of $\dot{\gamma}_{cor}$ (see also Fig. 11). The explanation is based on the elimination of elastic effect during steady shear flow. As mentioned previously, the formation of silica transient network gives a strong elastic response which could be excluded by the application of Bagley correction.

Moreover, it is known that an elongational flow is important in many applications including fibre spinning and coating [31]. In the present work, the capillary results give some information on elongational flow via the use of entrance pressure [2], as illustrated in Fig. 13. It is evident that the elongational viscosity, η_e , of blends decreases with increasing elongational rate, $\dot{\epsilon}$, indicating a tension thinning behaviour, which might probably be caused by the disruption of silica

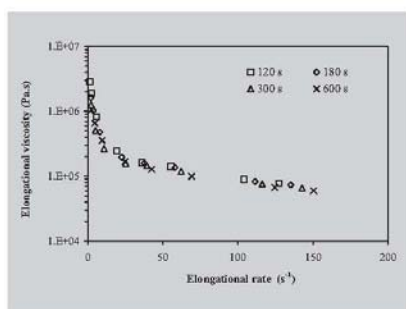


Figure 13 (left): Elongational viscosity as a function of elongational rate of uncured blends as determined from capillary results.

Figure 14 (middle): Plots of apparent shear viscosity measured by capillary rheometer (■) and complex viscosity determined from RPA 2000 (□) as a function of shear rate or frequency in filled uncured CPE/NR blends with various mixing time.

Figure 15 (right): Plots of true shear viscosity measured by capillary rheometer (■) and dynamic viscosity determined from RPA 2000 (□) as a function of shear rate or frequency in filled uncured CPE/NR blends with various mixing time.

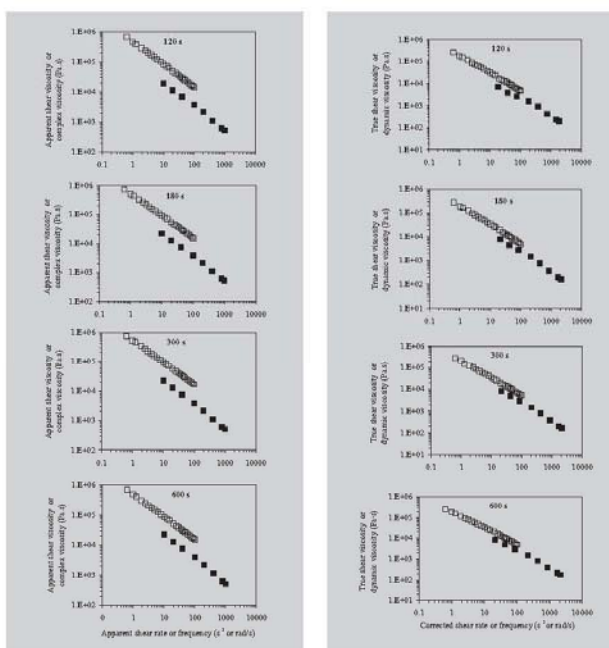
transient network. Additionally, results of all blends fall on a single correlation, implying that the time of mixing used in this study does not influence significantly the elongational behaviour.

Fig. 13 exhibits a comparison of $\eta^*(\omega)$ and $\eta_a(\dot{\gamma}_a)$ of the blends with different mixing time determined from oscillatory and steady shear tests, respectively. It is obvious that all blends do not obey the Cox-Merz concept, i.e., $\eta^*(\omega)$ is greater than $\eta_a(\dot{\gamma}_a)$. The explanation is based on the fact that the strain imposed to the blends in the oscillatory flow with in the LVE region is much smaller than that in the capillary flow. Consequently, the presence of silica transient network would promote elastic response and thus the $\eta^*(\omega)$. Similar observation has been reported in CPE/NR blends with different blend ratio and silica loading [12, 13].

To correlate the oscillatory to steady shear data more effectively, the dynamic viscosity, η' , and true shear viscosity, η_{true} , are plotted, as illustrated in Fig. 15. Apparently, the discrepancy of steady and oscillatory shear results is markedly reduced, which suggests that the Cox-Merz concept is valid to some extent in filled systems when the elastic component is eliminated. The result is in good accordance with previous work reported elsewhere [13].

4 CONCLUSIONS

From all obtained rheological results of 80/20 CPE/NR blends with various mixing time, the following conclusions could be drawn: The formation of silica transient network associated with the strong interaction between silanol group on silica surfaces and chlorine atoms of CPE plays role in viscoelastic properties of blends to some



extent, especially in the case of cured blends. Mixing time significantly influences viscoelastic properties of vulcanised blends which is due probably to the high extent of thermal degradation, but does not affect significantly in uncured blends. The validity of a correlation between oscillatory and steady shear results via the Cox-Merz concept is mainly controlled by the presence of silica transient network effect rather than the mixing time effect, and the superimposition of oscillatory and steady shear results is possible when the elastic component is eliminated from the apparent results.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the Thailand Research Fund (TRF) for funding this research.

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เรื่องที่ 2

P. Phewphong, P. Sae-oui, **C. Sirisinha**, Mechanism of silica reinforcement in CPE/NR blends by the use of rheological approaches, *Journal of Applied Polymer Science*, **107**, 2638-2645, 2007.

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

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Received 18 June 2007; accepted 20 September 2007

DOI 10.1002/app.27444

Published online 13 November 2007 in Wiley InterScience (www.interscience.wiley.com).

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 cure 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

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Contract grant sponsor: Thailand Research Fund.

Journal of Applied Polymer Science, Vol. 107, 2638–2645 (2008)
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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 organo-functional 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_{90}) 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_{90}) decrease with increasing silica loading, as shown in Figures 1 and 2. The reduction in t_{s2} and t_{90} 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

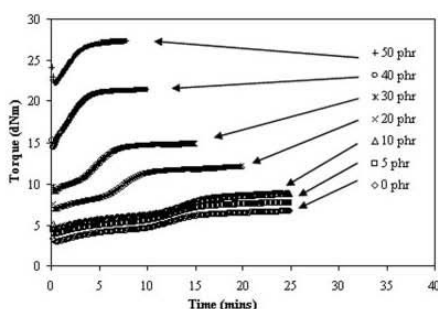


Figure 1. Cure curves of silica-filled CPE/NR blends with various silica loadings.

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 place 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-

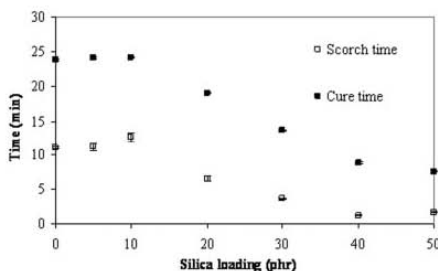


Figure 2. Scorch time (t_{22}) and cure time (t_{90}) of CPE/NR blends with various silica loadings determined from cure curves (Fig. 1).

Journal of Applied Polymer Science DOI 10.1002/app

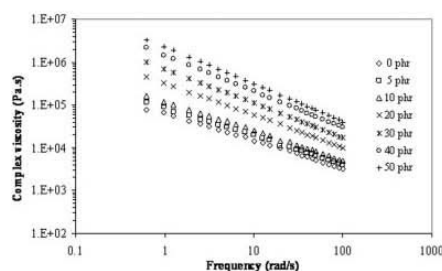


Figure 3. Complex viscosity of CPE/NR blends with various silica loadings at 170°C.

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-

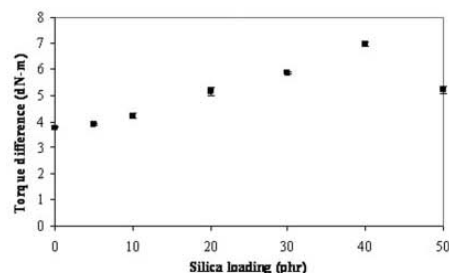


Figure 4. Crosslink density (in terms of torque difference) of CPE/NR blends with various silica loadings.

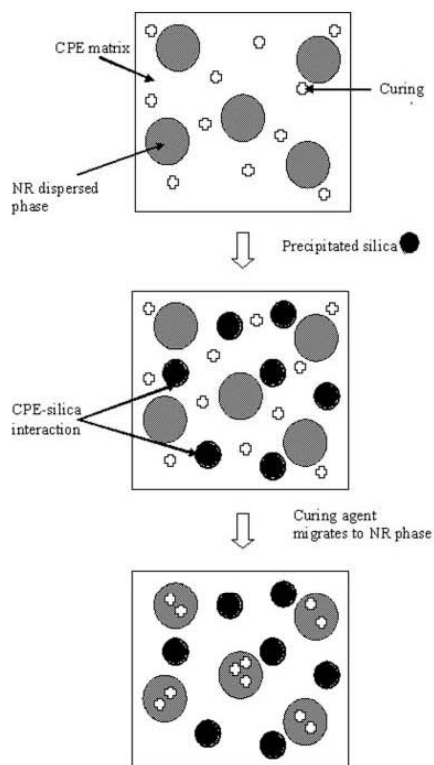


Figure 5 Schematic model of a curing agent migration to NR phase leading to a sulphur cure promotion of silica-filled blends.

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 ($\tan \delta$) 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.

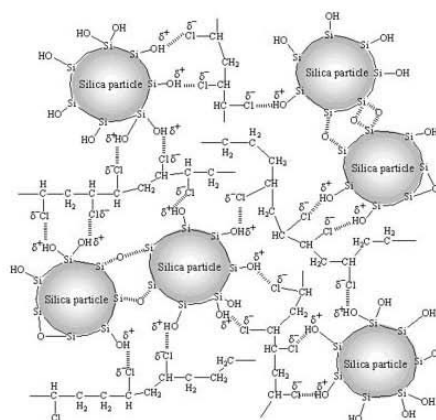


Figure 6 Schematic model of a pseudocrosslink formation caused by CPE-silica and silica-silica interactions.

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

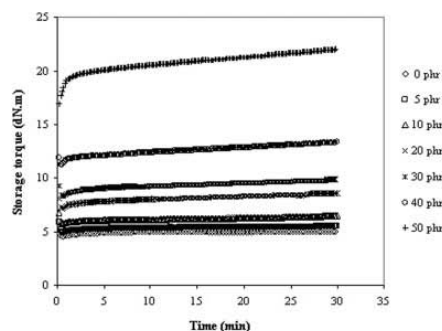


Figure 7 Time sweep test results at 155°C for 30 min of neat CPE with various loadings of precipitated silica.

Journal of Applied Polymer Science DOI 10.1002/app

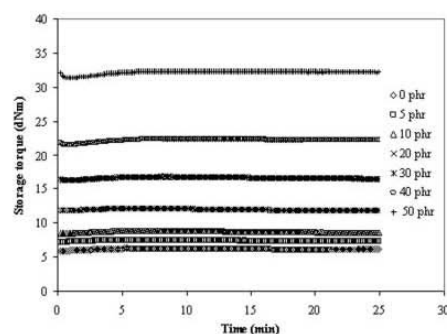


Figure 8. Time sweep test results at 170°C for 25 min of CPE/NR blends with the various loadings of silica.

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

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

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

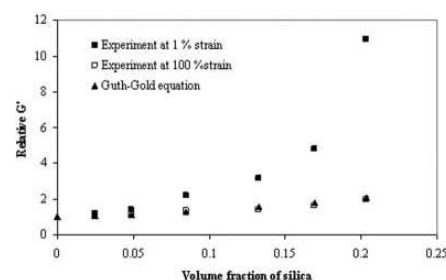


Figure 10. Relative elastic modulus (relative G') at 1 and 100% strain with test frequency of 3.14 rad/s of CPE/NR cured blends with various silica loadings as a function of silica volume fraction.

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

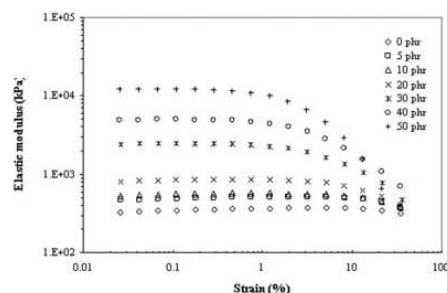


Figure 9. Payne effect of cured CPE/NR blends with various silica loadings.

Journal of Applied Polymer Science DOI 10.1002/app

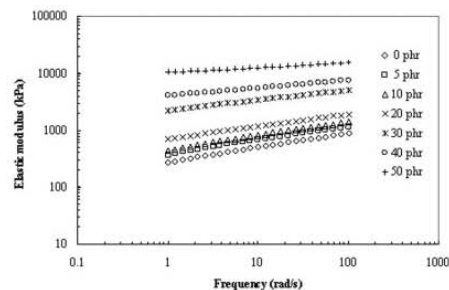


Figure 11. Elastic modulus (G') of vulcanized CPE/NR blends with various silica loadings as a function of frequency.