

Influence of Precipitated Silica on Dynamic Mechanical Properties and Resistance to Oil and Thermal Aging in CPE/NR Blends

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ABSTRACT: Blends of 80/20 CPE/NR filled with various silica loadings were prepared, and their properties were determined. It was found that cure properties are influenced significantly by the addition of precipitated silica. Scorch time and cure time decrease with increasing silica loading, which could be explained by the thermal history attributed to the shear heating in the blending stage. An increase in crosslink density as a function of silica loading is believed to be caused by a migration of curatives to the NR phase. In terms of phase morphology, with increasing silica loading, the NR dispersed phase size decreases due to the increase in compound viscosity and, thus, the shear stress available for efficient blending. An increase in silica loading also en-

hances resistance to oil due to the decrease in the NR dispersed phase size associated with the dilution effect, but gives no significant impact on thermal aging resistance. According to the change in damping peak height associated with the shift in T_g of the CPE phase, silica appears to preferentially migrate to the CPE phase due to the strong interaction between CPE and silanol groups of the silica surfaces. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2218–2224, 2005

Key words: oil resistance; aging; chlorinated polyethylene; natural rubber; blends

INTRODUCTION

It is generally known that chlorinated polyethylene (CPE) is produced by the introduction of chlorine atoms onto the polyethylene backbone to reduce the crystallization ability of polyethylene, so that enhancement in flexibility and resistance to hydrocarbon oil, heat, and weathering is achieved. According to published work, CPE has been blended with many polymers, including polyvinyl chloride (PVC),^{1–4} styrene-acrylonitrile (SAN),^{5,6} and polyurethane (PU).^{7,8} Compared to natural rubber (NR), CPE is relatively expensive, and therefore blending CPE with NR is one of the methods used to reduce the production cost of the final products requiring CPE properties. However, the amount of NR added is limited to the degree of resistance to oil and heat. In our previous work,⁹ it has been reported that CPE up to 50% by weight could be substituted by NR, giving similar tensile properties to neat CPE. The main limitation of the blends prepared from the previous work is the lack of recyclability due

to the use of a peroxide curing system, that is, both the NR and CPE phases are covulcanized. In addition, in our recent study,¹⁰ the peroxide curing is replaced by sulfur curing, so that only the NR dispersed phase in the CPE/NR blends is vulcanized. The result reveals that only 20% by weight of CPE could be replaced by NR to give blends with oil and thermal resistance close to neat CPE. Consequently, our present study aims to extend our previous work by investigating the effect of precipitated silica on oil and thermal aging resistance, as well as rheological and dynamic properties.

EXPERIMENTAL

Materials

Details of compounding ingredients and rubber formula used are given in Table I.

Mixing and vulcanization procedures

According to previous work,¹⁰ the CPE/NR blend ratio by weight of 80/20 was chosen because of its comparable oil and thermal aging resistance to those of neat CPE. Blending was carried out in a laboratory-

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TABLE I
Materials and Compounding Formulation Used in the Present Study

Material	Grade/Supplier	Amount (phr)
Chlorinated polyethylene (CPE)	Tyrin 702P/DuPont Dow Elastomer Co., Ltd., USA	80.0
Natural rubber (NR)	STR5/Thailand	20.0
Stearic acid	Commercial grade/Petch Thai Chemical Co., Ltd., Thailand	2.0
Magnesium oxide (MgO)	Starmag # 150/Konoshima Chemical Co., Ltd., Japan	5.0
Precipitated silica	HiSil 233/PPG-Siam Silica Co., Ltd., Thailand	varied
N- Isopropyl- N'- Phenyl- p-Phenylenediamine (IPPD)	Santoflex IPPD/Flexsys Co., Ltd., Belgium	4.0
Sulfur	Commercial grade/Chemmin Co. Ltd.	0.5
TBBS ^a (Vulkacit NZ)	Santocure TBBS/Flexsys Co., Ltd., Belgium	1.0

^a=N-t-butyl-2-benzothiazolesulfenamide

size two roll mill mixer (LabTech model LRM150, Thailand) at set temperatures of 145 and 140°C for front and back rolls, respectively. CPE was initially melted for 1 min and NR was then charged. After blending for 1 min, precipitated silica was added, and the mixing process was carried on for 3 min. Thereafter, curatives were charged and allowed to be mixed with the blends for 5 min to ensure homogeneous mixing. The blends were, finally, compression molded into 1-mm thick sheets under a pressure of 15 MPa at 155°C. Cure time used was determined from the Rubber Process Analyzer (RPA 2000, Alpha Technologies, USA).

Morphological study

Phase morphology observation of the sample surfaces was accomplished using a JEOL JSM-6301F scanning electron microscope (SEM) with 20 kV accelerating voltage. To improve the phase contrast, the sample was stained by osmium tetroxide (OsO₄) and sputtered with gold before viewing.

Measurements of oil resistance and thermal aging properties

As mentioned in previous work,^{9,11–13} the relative tensile strength is successfully used as an indicator for determining resistance to oil and thermal aging. The higher the relative tensile strength, the higher the resistance.

For the oil resistance test, the test specimens were immersed in a bottle containing hydraulic oil (Tellus 100, Shell Co. Ltd., Thailand) at room temperature for 70 h. Thereafter, the specimens were removed from the oil and quickly dipped in acetone and blotted lightly with filter paper to eliminate the excess oil on the specimen surfaces. Finally, tensile properties of the specimens were measured. Changes in tensile properties after thermal aging were used to determine the oil resistance.

For the determination of thermal aging properties, the specimens were placed in an oven equipped with an air circulating system at the test temperature of 100°C for 24 h, according to ASTM D573. The aged specimens were then measured for tensile properties. Similar to the measurement of oil resistance, the changes in tensile strength after thermal aging were used to determine thermal aging resistance.

Measurement of dynamic mechanical properties

Dynamic mechanical properties were measured using a dynamic mechanical thermal analyzer (Gabo, Eplexor 25N) with tension mode of deformation at the test frequency of 10 Hz and dynamic strain amplitude of 0.1%. The temperatures of measurement were used in the ranges of –100 to 40°C, with a heating rate of 2°C/min.

RESULTS AND DISCUSSION

Influence of silica loading on cure properties

Silica is known to influence the crosslink reaction during vulcanization. In general cases, silica retards sulfur curing due to the presence of silanol groups on the silica surfaces.¹⁴ However, Figure 1 demonstrates the decreases in both scorch time (t_{s2}) and cure time (t_c) with increasing silica loading. The results could be explained by a thermal history. Since the shear heating during mixing increases with increasing silica loading caused by the increase in compound viscosity, the compounds with high loadings of silica would be subjected to a high thermal history, leading to the reduction in t_{s2} and t_c .

Regarding the crosslink density in blends, Figure 2 shows the torque difference between maximum and minimum torques determined from cure curves of cured 80/20 CPE/NR blends with various silica loading. Apparently, the torque difference increases with increasing silica loading, suggesting the increase in

total crosslink density. The explanation is proposed as follows: Due to the high polarity of both CPE and curatives, particularly the TBBS accelerator, a strong interaction forms between CPE and curatives, leading to a preferential distribution of curatives in the CPE phase. As precipitated silica is added, the silanol groups on the silica surfaces competitively interact with CPE, and therefore the curatives migrate more readily to the NR phase, resulting in a cure promotion in the NR phase and thus an increase in crosslink density as a function of silica loading.

Phase morphology

Most polymer blends are thermodynamically immiscible and, consequently, the phase morphology is usually observed as multi-phase. It is well known that the size of the dispersed phase can significantly influence the physical and mechanical properties of the immiscible blend. During blending, several factors are important in determining the final particle size of the dispersed phase of polymer blends, such as blend composition, interfacial tension, time of mixing, shear stress, and viscosity ratio.^{15–20}

In this section, the effect of silica loading on the phase morphology of cured 80/20 CPE/NR blends with cured NR as a dispersed phase in the CPE matrix is investigated. Results, as illustrated in Figure 3, show that the phase size of the NR dispersed is obviously reduced with increasing silica loading, which could be explained by the marked increase in matrix viscosity and thus the shear stress transferred to the NR dispersed phase.

Mechanical properties

As mentioned previously, in CPE/NR blends, only the NR phase would be cured by sulfur vulcanization. The

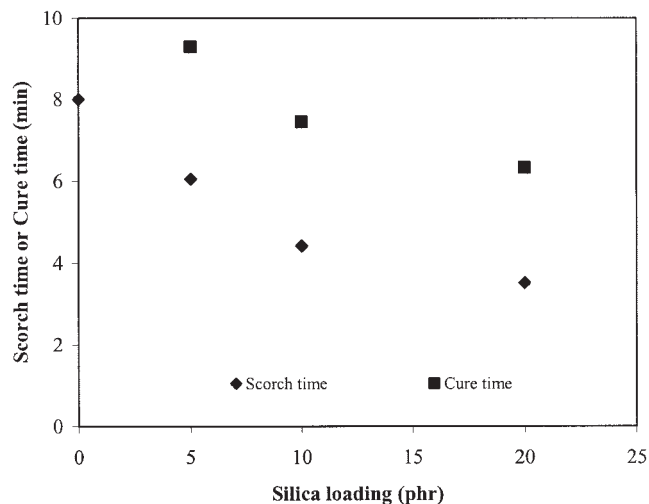


Figure 1 Scorch time (t_{s2}) and cure time (t_c) of 80/20 CPE/NR blend as a function of silica loading.

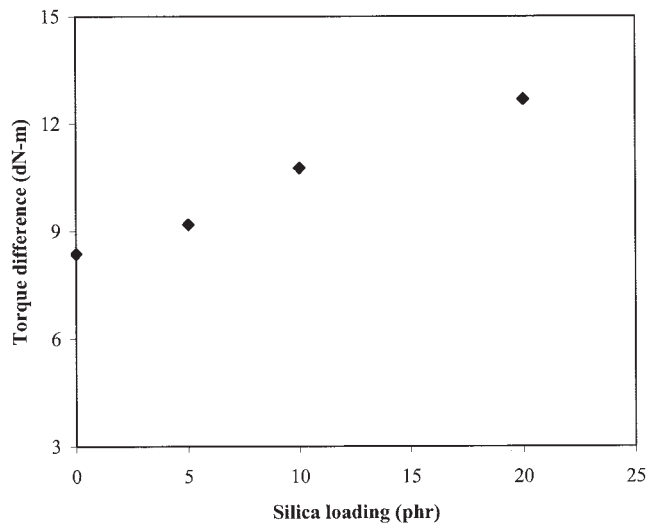


Figure 2 Relationship between crosslink density (in terms of torque difference) and silica loading.

unvulcanized CPE phase would give relatively poor strength, which is expected to be increased by the use of silica as a reinforcing filler caused by a strong interaction between the silica surfaces and the CPE. Figure 4 presents the influence of precipitated silica loading on the tensile strength of cured CPE/NR blends. Clearly, the unfilled blend possesses the lowest tensile strength. The tensile strength progressively increases with increasing silica loading. There are three main proposed explanations, namely, reinforcing effect, crosslink density effect, and phase morphology effect. As for the reinforcing effect, it is known that a good reinforcing effect in elastomers can be achieved by a good filler–elastomer interaction.²¹ In the present system, chlorine atoms on CPE molecules and silanol groups on silica surfaces would give a strong interaction between the CPE and silica, and thus a good reinforcing effect. As for the crosslink density effect, the increase in silica loading yields a higher crosslink density (as illustrated previously in Fig. 2) and thus a higher strength. Regarding the phase morphology effect, it has been acknowledged that the smaller the phase size, the higher the tensile properties in the blend.^{11,12} From the phase morphological results discussed previously, the higher silica loading results in a smaller phase size of the blends.

Oil resistance

According to previous work,^{9–13} the relative properties after oil immersion could be used as an indicator for determining the resistance to oil of cured CPE/NR blends. The results of relative tensile strength (Rel TS) as a function of silica loading is illustrated in Figure 5. It is evident that the relative tensile strength increases markedly with increasing silica loading. The result is

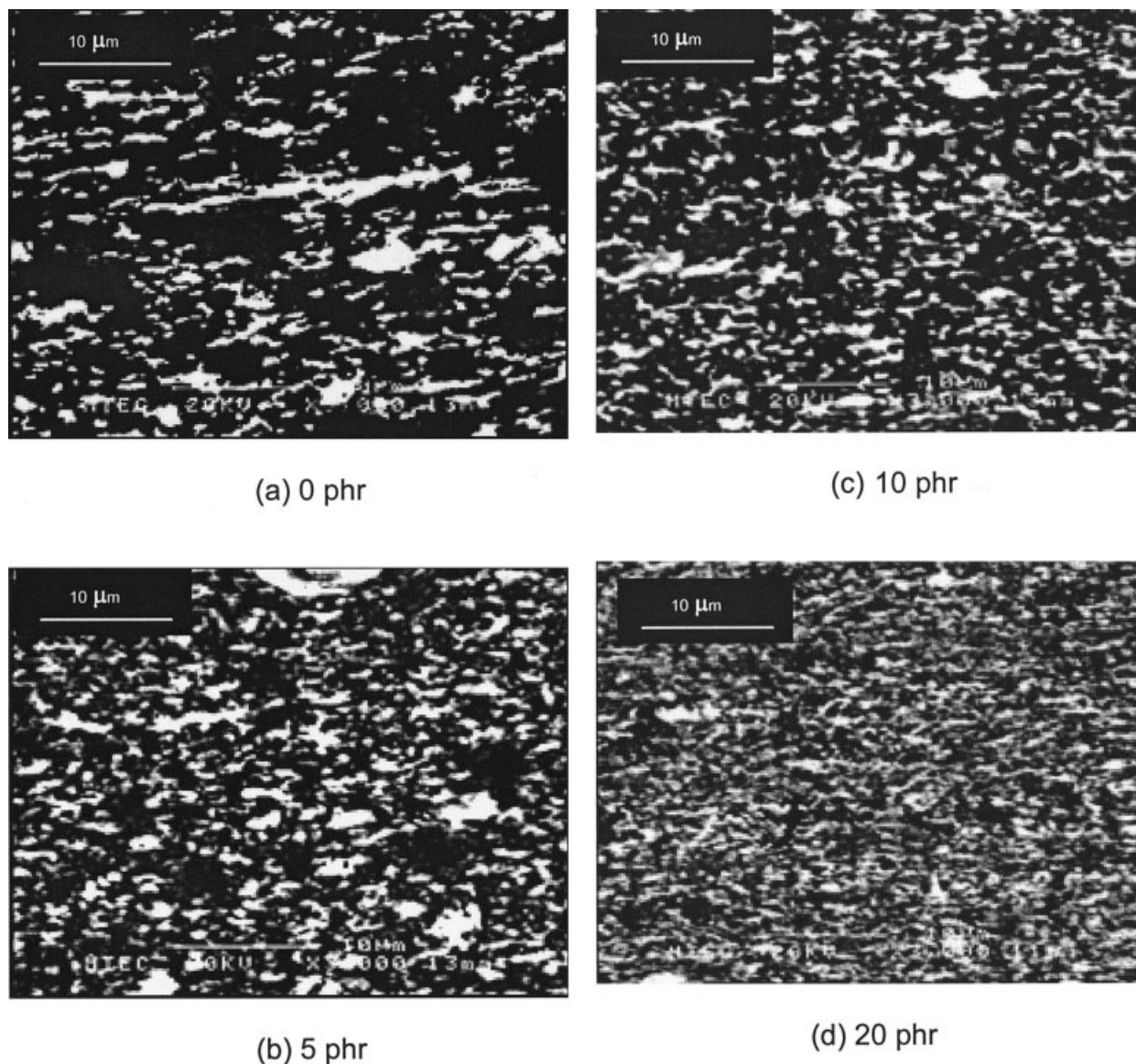


Figure 3 Scanning electron micrographs of 80/20 CPE/NR blends with different silica loadings: (a) 0 phr; (b) 5 phr; (c) 10 phr; (d) 20 phr.

in good agreement with the blend morphological results discussed previously. In other words, the phase morphology controls strongly the oil resistance of the blends. Referring to previous reports,^{11–13} the smaller the phase size of NR, the higher the oil resistance of NBR/NR and CPE/NR blends. In addition to the phase morphology, the dilution of polymers in blends by the non-swell precipitated silica could be responsible for the improvement in oil resistance as a function of silica loading.

Thermal aging resistance

It is initially expected that the reduction in phase size of the blends via the addition of precipitated silica would improve thermal resistance.^{12,13} The thermal

aging resistance in terms of relative tensile strength influenced by silica loading is illustrated in Figure 6. It is unexpectedly evident that the thermal aging resistance does not change significantly with an increase in silica loading. The result implies that despite the obvious decrease in phase size, the silica loading does not control the thermal aging resistance in CPE/NR blends. The explanation is not known at present.

Dynamic mechanical properties

The effect of precipitated silica loading in 80/20 CPE/NR blends on the dynamic mechanical properties has been determined as a function of temperature, as presented in Figures 7 and 8. It is evident that there are two glass transition temperatures (T_g) indicating

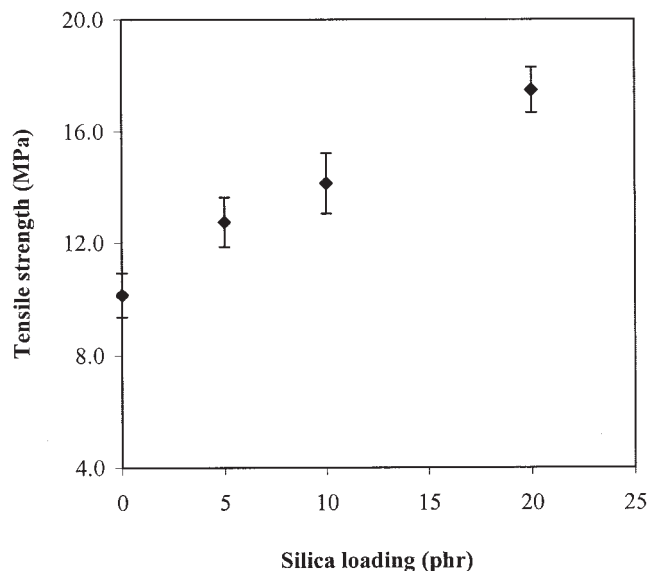


Figure 4 Relationship between tensile strength and amount of silica loading in 80/20 CPE/NR blends.

the two-phase morphology, which agrees well with the phase morphological results discussed previously. Figure 7 demonstrates storage modulus (E') of unfilled and silica-filled CPE/NR blends. It appears that E' at a temperature higher than the glass transition of the CPE phase in blends increases with increasing silica loading, which could be explained by the hydrodynamic effect associated with the strong interaction between silanol groups on the silica surfaces and the chlorine atoms of CPE. The damping factor ($\tan \delta$) over a temperature range of -100 to 40°C and glass transition temperatures (T_g) of CPE and NR phases determined from the damping peaks of blends with various silica loadings are given in Figure 8. Clearly,

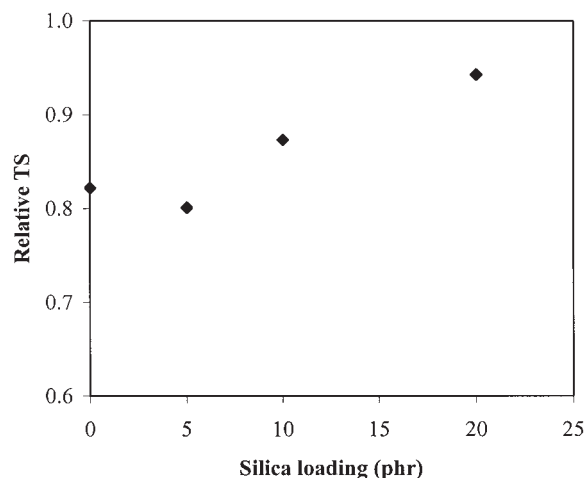


Figure 5 Relationships among tensile strength (TS) after oil immersion, relative tensile strength (relative TS), and silica loading in 80/20 CPE/NR blends.

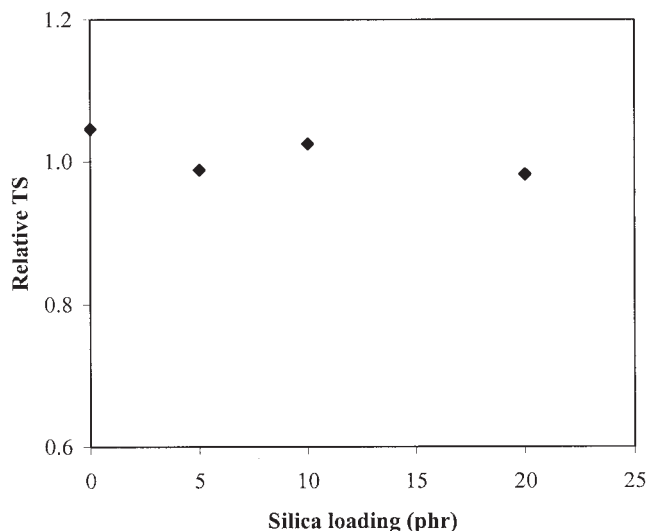


Figure 6 Relationships between silica loading and relative tensile strength (relative TS) after thermal aging in 80/20 CPE/NR blends.

the T_g of the NR phase rarely changes, while the T_g of the CPE phase slightly shifts to higher temperature with increasing silica loading, which supports the proposed explanation of the strong interaction between silica and CPE as discussed previously.

Figure 9 shows $\tan \delta_{\max}$ values of the CPE and NR phases in 80/20 CPE/NR blends with various amounts of silica. It can be observed that the unfilled blend reveals the highest $\tan \delta_{\max}$ in both phases, which could be explained by a large magnitude of molecular mobility. In the case of filled blends, the segmental motions of CPE are restricted by silica particles via the strong interaction between silanol groups and the chlorine atoms of CPE chains. This would

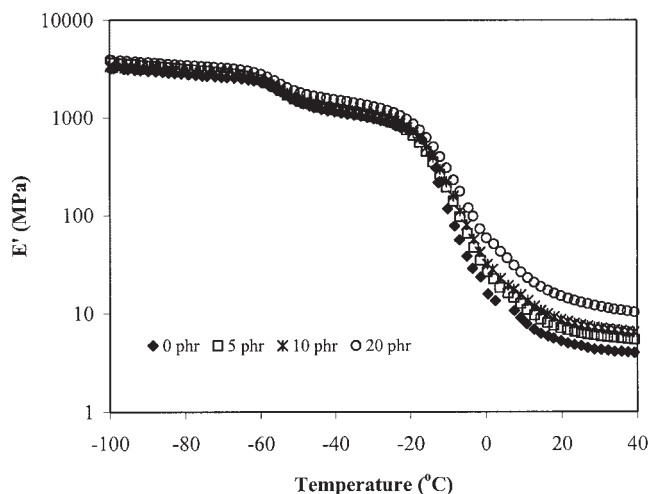


Figure 7 Storage modulus (E') as a function of temperature of 80/20 CPE/NR vulcanizate blends with various silica loadings.

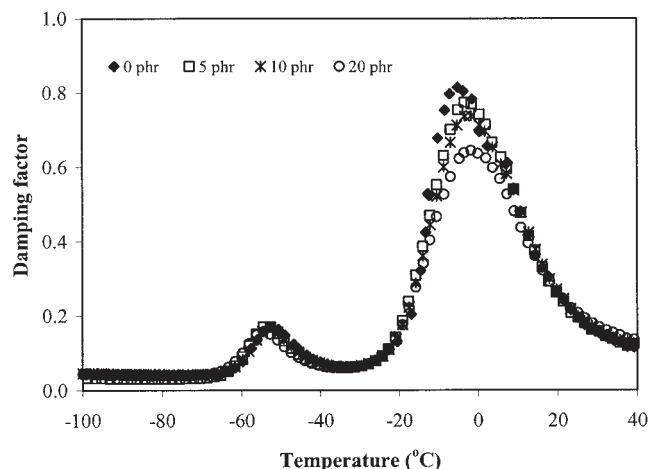


Figure 8 Tan δ as a function of temperature of 80/20 CPE/NR vulcanizate blends with various silica loadings.

result in the reduction of $\tan \delta_{\max}$. It is also evident that the decrease in damping peak is more pronounced in the CPE phase than the NR phase, supporting the explanation of strong interaction between CPE and the silanol group.^{22,23}

In addition to the strong interaction, the decrease in damping peak in filled compounds could yield the information of filler distribution in each phase of the polymer blends.^{23–25} In the present work, % reduction of $\tan \delta_{\max}$ is used to determine filler distribution in each phase of the blends as given in Eq. (1).

$$\% \text{ Reduction} = \frac{(\tan \delta_{\max})_{\text{gum}} - (\tan \delta_{\max})_{\text{filled}}}{(\tan \delta_{\max})_{\text{gum}}} \times 100 \quad (1)$$

The results obtained, as presented in Table II, exhibit that the value of $\tan \delta_{\max}$ of the CPE phase signifi-

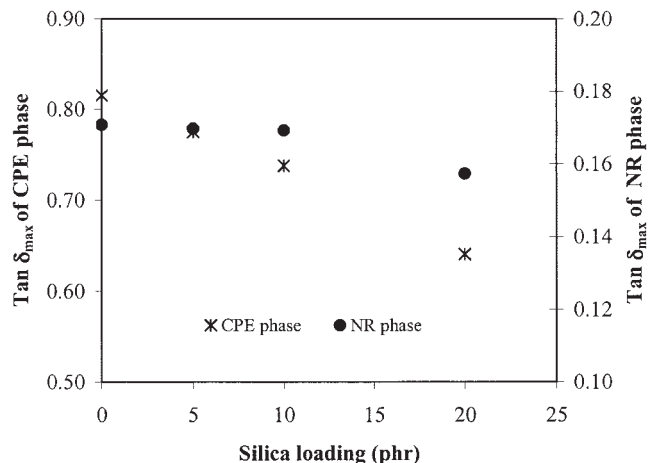


Figure 9 Damping factor peak height ($\tan \delta_{\max}$) of NR and CPE phases in 80/20 CPE/NR vulcanizate blends as a function of silica loadings.

TABLE II
% Reduction of $\tan \delta_{\max}$ of CPE and NR Phases from Silica Filled 80/20 CPE/NR Blends

Amount of silica loading (phr)	% reduction of $\tan \delta_{\max}$	
	NR phase	CPE phase
0	—	—
5	0.61	4.95
10	0.89	9.50
20	7.85	21.42

cantly decreases with increasing silica loading, which is due to the preferential migration of silica to the CPE phase. A strong interaction between silanol groups on the silica surfaces and the chlorine atoms of CPE would make silica reside preferentially in the CPE phase. Meanwhile, the NR phase shows a marginal change in $\tan \delta_{\max}$. However, as silica loading is increased to 20 phr, $\tan \delta_{\max}$ of the NR phase obviously decreases, due probably to the saturation of silica in the CPE phase and silica therefore starts to migrate to the NR phase. Similar observations in silica filled NR/ENR-25 blends have been reported elsewhere.²⁴

CONCLUSIONS

The phase morphology and resistance to oil and thermal aging of 80/20 CPE/NR blends filled with precipitated silica were investigated. The following conclusions could be drawn:

1. Scorch time and cure time of 80/20 CPE/NR blends decrease with increasing silica loading, which could be explained by the thermal history attributed to the shear heating during blending. An increase in crosslink density as a function of silica loading is believed to be caused by a migration of curatives to the NR phase.
2. The phase size of 80/20 CPE/NR blends decreases with increasing silica loading due to the increase in compound viscosity and thus the shear stress available for efficient blending.
3. An increase in silica loading enhances the resistance to oil due to the decrease in phase morphology associated with the dilution effect, but gives no significant effect on thermal aging resistance.
4. According to the change in damping peak height associated with the shift in T_g of the CPE phase, silica appears to preferentially migrate to the CPE phase due to the strong interaction between CPE and silanol groups of the silica surfaces.

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