

# Mechanical Properties, Oil Resistance, and Thermal Aging Properties in Chlorinated Polyethylene/Natural Rubber Blends

CHAKRIT SIRISINHA,<sup>1</sup> PONGDHORN SAE-OUI,<sup>2</sup> JANTAGARN GUAYSOMBOON<sup>1</sup>

<sup>1</sup> Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Rd., Bangkok 10400, Thailand

<sup>2</sup> The National Metal and Materials Technology Center (MTEC), Rama 6 Rd., Bangkok 10400, Thailand

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**ABSTRACT:** The use of natural rubber (NR) for partly substituting elastomeric chlorinated polyethylene (CPE) was determined. Mechanical and thermal aging properties as well as oil resistance of the blends were also investigated. The amount of NR in blends significantly affected the properties of the blends. The blends with NR content up to 50 wt % possessed similar tensile strength to that of pure CPE even after oil immersion or thermal aging. Modulus and hardness of the blends appeared to decrease progressively with increasing NR content. These properties also decreased in blends after thermal aging. After oil immersion, hardness decreased significantly for the blends with high NR content, whereas no change in modulus was observed. The dynamic mechanical properties were determined by dynamic mechanical thermal analysis. NR and CPE showed damping peaks at about  $-40$  and  $4$  °C, respectively; these values correlate with the glass-transition temperatures ( $T_g$ ) of NR and CPE, respectively. The shift in the  $T_g$  values was observed after blending, suggesting an interfacial interaction between the two phases probably caused by the co-vulcanization in CPE/NR blends. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 22–28, 2002; DOI 10.1002/app.10171

**Key words:** blends; oil resistance; thermal properties; mechanical properties; natural rubber

## INTRODUCTION

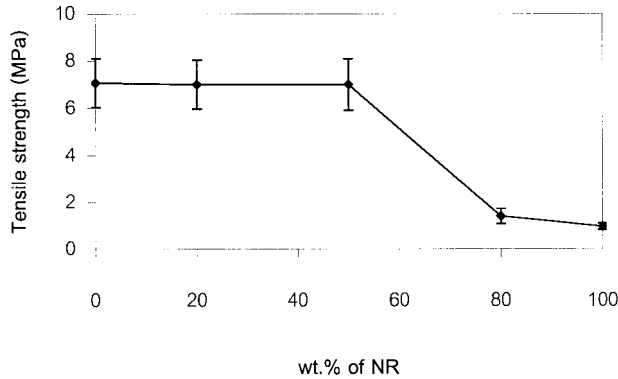
Blending of polymers is a popular technique to enhance properties such as mechanical and dynamic properties, thermal aging properties, processability, and oil resistance. Mechanical properties of polymer blends are generally controlled by many factors, including the nature of the polymer, blend composition,<sup>1–3</sup> blending conditions,<sup>4–6</sup> and interfacial adhesion.<sup>7–14</sup> Additionally, in the case of filled blends, the uneven distribution of filler in each phase of the blends is reported to significantly affect the me-

chanical properties of blends.<sup>15–17</sup> Fillers tend to preferentially reside in the phase with relatively low viscosity and similar polarity. The addition of some additives, such as processing oil, slipping agents, and/or compatibilizer also influences filler distribution in each phase of the blends and thus the blend mechanical properties.<sup>18,19</sup>

Chlorinated polyethylene elastomer (CPE) has been produced by introduction of chlorine atoms onto the polyethylene backbone to reduce its ability to crystallize. In addition, enhancement in resistance to hydrocarbon oil, heat, and weathering is also obtained. To obtain desired properties of the final products, CPE has been blended with many polymers, including poly(vinyl chloride) (PVC),<sup>7,9,11,20</sup> styrene-acrylonitrile

Correspondence to: C. Sirisinha (Sccsr@mahidol.ac.th).

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**Figure 1** Tensile strength of blends with various wt % NR.

(SAN),<sup>21,22</sup> and polyurethane (PU).<sup>23,24</sup> Compared with natural rubber (NR), CPE is more expensive and therefore blending of CPE/NR is one method to reduce the production cost of the final products requiring CPE properties. The present study aims to investigate mechanical and thermal aging properties as well as oil resistance of CPE/NR blends.

## EXPERIMENTAL

### Materials

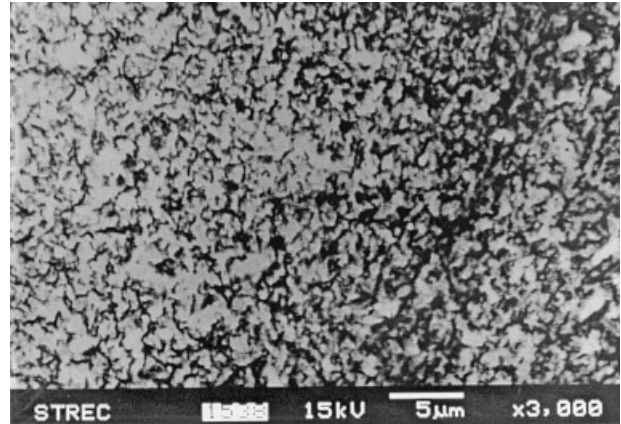
Chlorinated polyethylene (CPE; 3615P, DuPont Dow Elastomer Company, Ltd., USA) with chlorine content of 36%, and natural rubber (NR; STR 5 Thailand, ML1+4 @ 100 °C = 7 2) were used in the present study. Dicumyl peroxide (DCP; Percumyl D; Chemmin Company, Ltd., Thailand) was used as a curing agent.

### Mixing Procedure

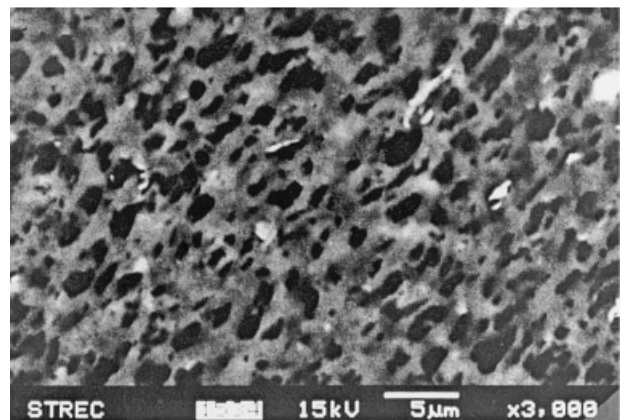
The CPE/NR blend ratios of 100/0, 20/80, 50/50, 80/20, and 0/100 were used for the study. Blend-

**Table I** Tensile Properties of Blends with Various wt % of NR

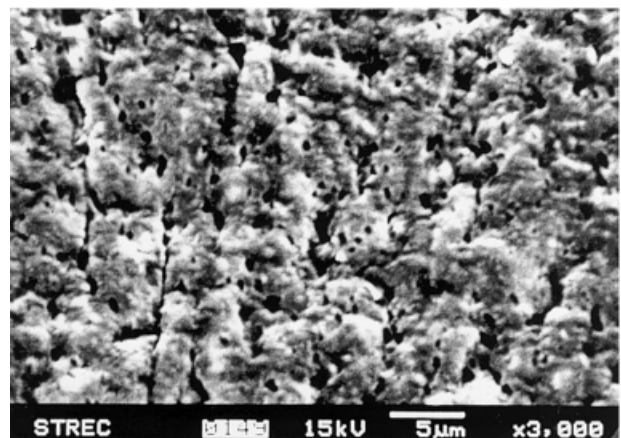
NR Content (wt %)	Tensile Strength (MPa)	Modulus at 100% Strain (MPa)	Elongation at Break (%)
0	7.07 ± 1.03	1.65 ± 0.27	691 ± 105
20	7.00 ± 1.04	1.23 ± 0.08	610 ± 63
50	7.07 ± 1.09	0.93 ± 0.06	523 ± 89
80	1.40 ± 0.32	0.72 ± 0.04	257 ± 81
100	0.95 ± 0.14	0.52 ± 0.16	227 ± 47



(a)



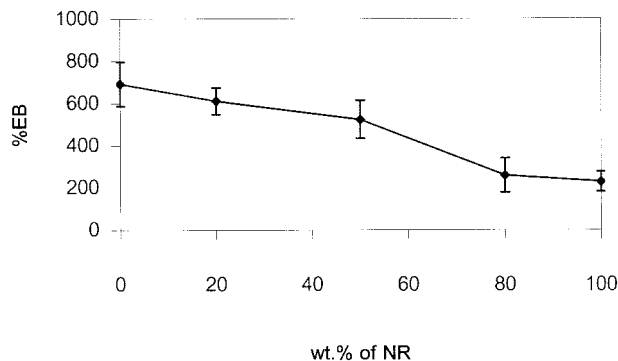
(b)



(c)

**Figure 2** Scanning electron micrographs of blends with various wt % NR: (a) 20 %; (b) 50 %; (c) 80 %.

ing was carried out in a laboratory-size internal mixer (Haake Rheomix 90) with a fill factor of 0.6, at a set temperature of 140 °C and a rotor speed of 40 rev min<sup>-1</sup>. NR was initially masticated for 1



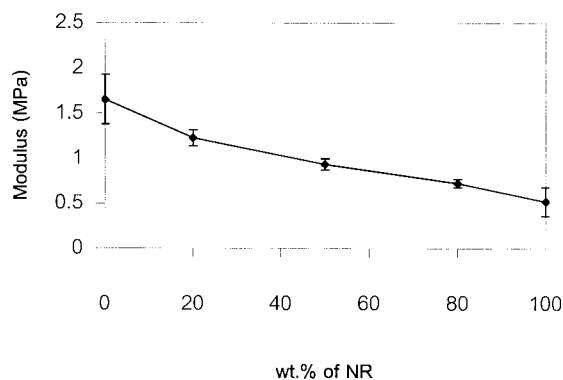
**Figure 3** Elongation at break of blends with various wt % NR.

min, and CPE was then charged. After blending for 3 min, 1 phr of DCP was added to the blends, and the mixing process was carried on for 1 min before discharging. The blends were thereafter sheeted on the cooled 2-roll mill and, finally, compression molded into 2-mm-thick sheets under a pressure of 15 MPa at 155 °C for 32 min (which gives ~96 % cure calculated from the half-life of DCP).

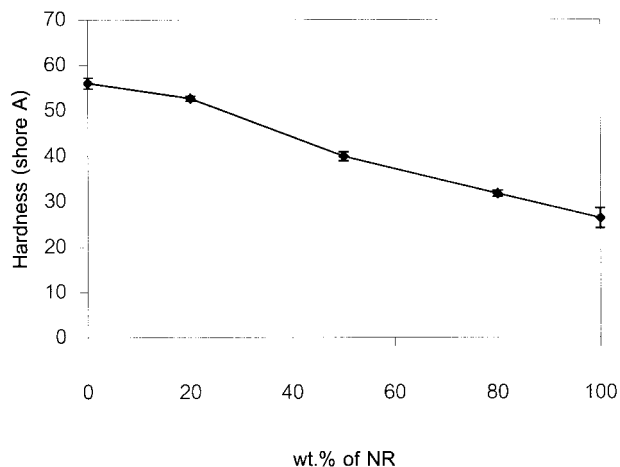
#### Measurements of Tensile Properties and Hardness

Tensile test specimens were punched out from the compression-molded sheets with a punching die according to Die C- ASTM D412-92. Tensile properties were measured with an Instron 4301 tensile tester with a crosshead speed of 500 mm/min and a full-scale load cell of 1 kN in accordance with ASTM D638.

Hardness of 6-mm-thick samples was measured according to ASTM D2240-9 with a Zwick durometer (model D-7900) and Shore A scale at room temperature.



**Figure 4** Modulus at 100% strain of blends with various wt % NR.

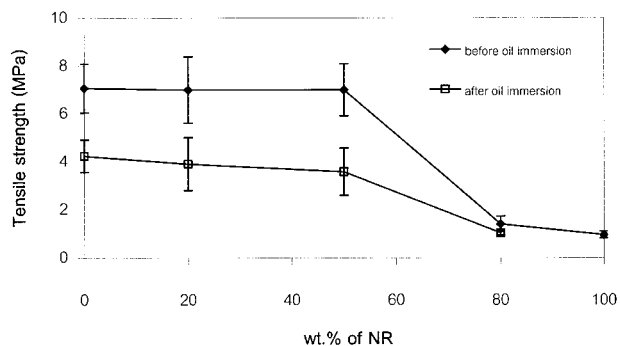


**Figure 5** Hardness of blends with various wt % NR.

#### Measurements of Oil Resistance and Thermal Aging Properties

The specimens to be tested were immersed in a bottle containing hydraulic oil (Tellus 100, Shell, Company Ltd., Thailand) at room temperature for 70 h. Thereafter, the specimens were removed from the oil, quickly dipped in acetone, and blotted lightly with filter paper to eliminate the excess oil on the specimen surfaces. Finally, tensile properties and hardness of the specimens were measured. Changes in tensile properties and hardness of specimens 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 and hardness. Similar to the measurement of oil resistance, the changes in tensile strength and hardness of specimens



**Figure 6** Change in tensile strength of blends with various NR contents after oil immersion.

after thermal aging were used to determine thermal aging resistance.

### Measurement of Dynamic Mechanical Properties

Dynamic mechanical properties of rubber vulcanizates were measured with a dynamic mechanical analyzer (DMA; Polymer Laboratories Mk II) under a bending mode of deformation, with a peak-to-peak displacement and frequency of 64  $\mu\text{m}$  and 1 Hz, respectively. Measurements were carried out in the temperature range  $-130$ – $50$   $^{\circ}\text{C}$  at a heating rate of 5  $^{\circ}\text{C}/\text{min}$ .

### Blend Morphology Examination

Scanning electron microscopy (SEM) was performed with a Jeol scanning electron microscope (model 5800LV). The sample was stained with osmium tetroxide ( $\text{OsO}_4$ ) and sputtered with gold before viewing.

## RESULTS AND DISCUSSION

### Mechanical Properties

The relationship between tensile strength of the blends and amount of NR in the blends are shown in Figure 1 and Table I. It is clear that tensile strength of pure NR is much lower than that of pure CPE because of the thermal degradation of NR during mixing at 140  $^{\circ}\text{C}$ . It must be noted that it is necessary to use the mixing temperature of 140  $^{\circ}\text{C}$  because CPE could not completely melt at a mixing temperature  $<140$   $^{\circ}\text{C}$ .

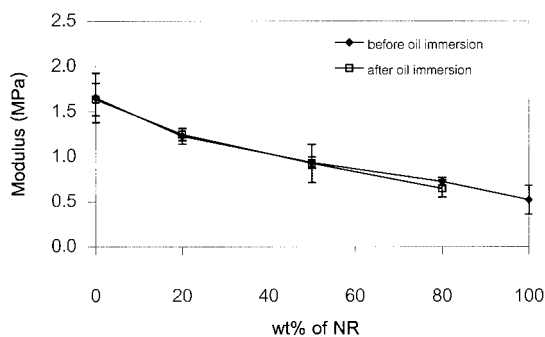
It is evident that the tensile strength of CPE/NR blends with NR content up to 50 % by weight is close to that of pure CPE, indicating that the CPE phase is responsible for the high tensile strength of the blends. Scanning electron

**Table II Tensile Properties of Blends with Various wt % of NR after Oil Immersion**

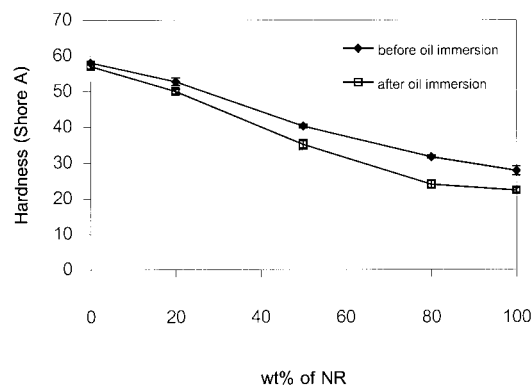
NR Content (wt %)	Tensile Strength (MPa)	Modulus at 100% Strain (MPa)	Elongation at Break (%)
0	$4.23 \pm 0.67$	$1.64 \pm 0.18$	$387 \pm 76$
20	$3.90 \pm 1.10$	$1.25 \pm 0.07$	$366 \pm 51$
50	$3.57 \pm 0.98$	$0.93 \pm 0.21$	$281 \pm 93$
80	$1.02 \pm 0.09$	$0.64 \pm 0.09$	$169 \pm 32$
100	N/A	N/A	N/A

micrographs, as shown in Figure 2, reveal two-phase blend morphology where CPE is the continuous phase in the blends with NR contents up to 50 wt %. This result is in agreement with the tensile results and implies that it is possible to reduce the production cost of the elastomeric products with tensile strength similar to pure CPE by blending CPE with NR up to 50 % by weight. For example, the ultimate tensile strength and the elongation at break of CPE compounds required for wire and cable applications have been reported to be  $\sim 8$ – $9$  MPa and 500 %, respectively.<sup>25</sup> It can be seen that the blends with up to 50 wt % NR could give properties in the required range. However, with NR content  $>50$  wt %, tensile strength of the blend starts to decrease. This result can be explained by the dilution effect; that is, the high-tensile-strength CPE is diluted by a large amount of low-strength NR and NR becomes the continuous phase, as shown in Figure 2c.

Similarly, the elongation at break result shown in Figure 3 (and also Table I) reveals that as the amount of NR in blends increased up to 50 % by weight, the elongation at break slightly de-

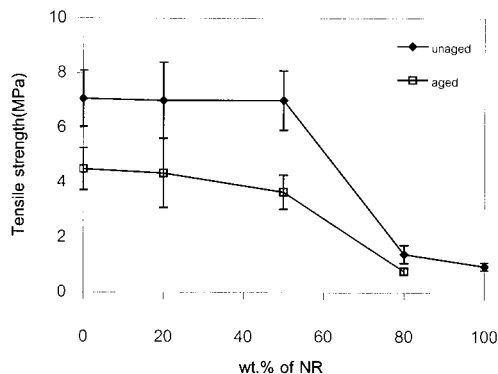


**Figure 7** Change in modulus at 100% strain of blends with various NR contents after oil immersion.



**Figure 8** Change in hardness of blends with various NR contents after oil immersion.





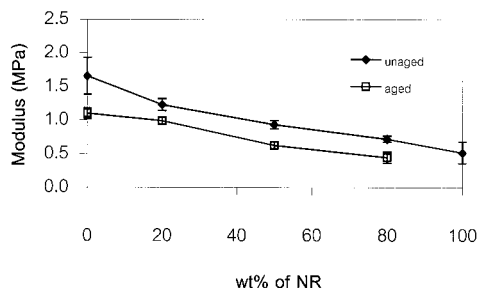
**Figure 9** Change in tensile strength of blends with various NR contents after thermal aging.

creases. For the blend with NR >50 % by weight (i.e., 20/80 blend), the elongation at break drops to the values close to that of pure NR. This result is in agreement with that of tensile strength and a similar explanation could therefore be applied.

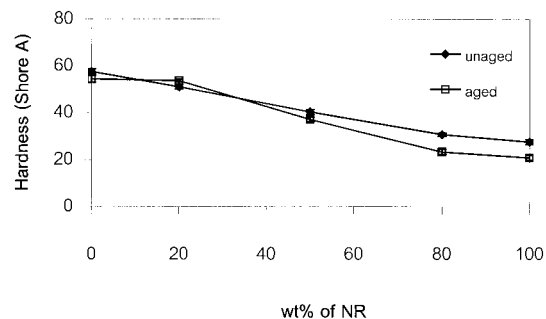
Unlike the results of tensile strength and elongation at break, the modulus at 100 % strain and hardness appears to decrease systematically with increasing amount of NR (Figures 4 and 5). The decrease in these properties is approximately in accordance with the interpolated values (i.e., additive line) and therefore could be explained by the dilution effect, which is caused by the addition of the low modulus and low hardness NR into the blends.

#### Oil Resistance and Thermal Aging Properties

According to our previous work,<sup>26</sup> the changes in properties after oil immersion could be used as an indicator of the resistance to oil, to minimize the mastication effect that might occur during blending and could interfere with the results of oil swelling tests. The results of oil resistance based on the changes in tensile properties after oil immersion are presented in Figures 6 and 7 (see also



**Figure 10** Change in modulus at 100% strain of blends with various NR contents after thermal aging.



**Figure 11** Change in hardness of blends with various NR contents after thermal aging.

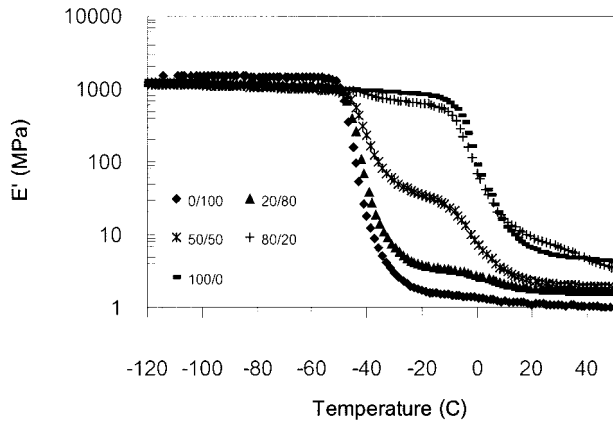
Table II). It is obvious from Figure 6 that tensile strength of all compounds decreases after oil immersion. It is interesting that the strength of the blends with NR up to 50 % by weight is similar to that of pure CPE with high resistance to oil. Notably, the tensile result of pure NR compound after oil immersion could not be determined because of the highly nonuniform swelling of samples, which led to a nonuniform change in sample geometry.

Unexpectedly, as seen in Figure 7, the modulus at 100% strain of all compounds does not significantly change after oil immersion. In other words, the modulus at 100% strain is not sensitive to oil immersion. A change in hardness of the blends after oil immersion is revealed in Figure 8. The magnitude of the decrease in hardness increases with increasing NR content.

Thermal aging properties of the compounds studied are shown in Figures 9–11 and Table III. Generally, properties of all compounds decrease after aging. The magnitude of the decrease in tensile strength depends on blend ratio. It is known that CPE exhibits good resistance to thermal aging compared with NR. Thus, by blending CPE with NR, it was initially expected that the blends would show a sharp decrease in properties

**Table III** Tensile Properties of Blends with Various wt % of NR after Thermal Aging

NR Content (wt %)	Tensile Strength (MPa)	Modulus at 100% Strain (MPa)	Elongation at Break (%)
0	4.49 ± 0.77	1.10 ± 0.08	604 ± 48
20	4.34 ± 1.25	0.99 ± 0.05	499 ± 86
50	3.65 ± 0.62	0.63 ± 0.05	446 ± 60
80	0.78 ± 0.11	0.45 ± 0.08	198 ± 34
100	N/A	N/A	N/A



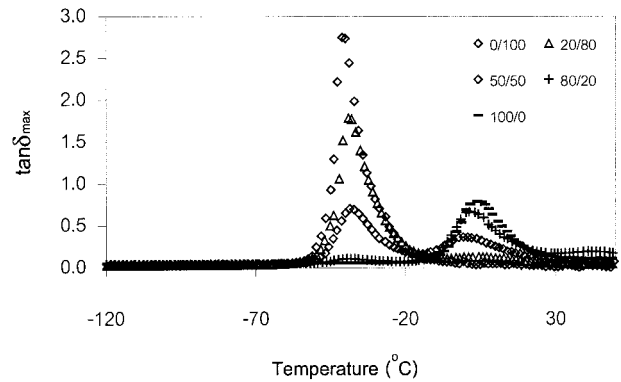
**Figure 12** Plot of storage modulus against temperature of blends with various CPE/NR blend ratios.

after aging, because of the dilution effect. Surprisingly, the results obtained, shown in Figure 9, reveal that the tensile strength of 80/20 and 50/50 CPE/NR blends is more or less similar to that of pure CPE, which is in agreement with the results of oil resistance and blend morphology discussed previously. A significant decrease in tensile strength is observed with the 20/80 CPE/NR blend.

The modulus of all compounds is relatively sensitive to thermal aging, compared with oil change, as shown in Figure 10. A significant decrease in modulus after aging is observed. Also, the modulus of all specimens decreases progressively with increasing NR content in blends; this result is attributed to the dilution effect. The hardness results after thermal aging, shown in Figure 11, are in the same trend as that after oil immersion, shown in Figure 8; that is, the decrease in hardness becomes obvious with blends having an amount of NR >50 wt %.

### Dynamic Mechanical Properties

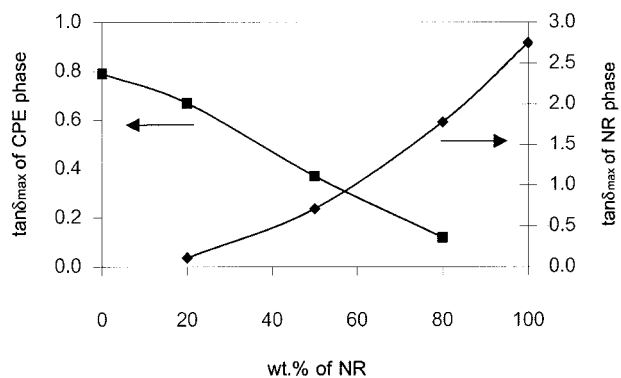
The storage modulus as a function of temperature for each CPE/NR blend ratio is shown in Figure 12. The glass-transition temperatures ( $T_g$ ) of pure NR (i.e., 0/100 blend) and pure CPE (i.e., 100/0 blend) are approximately  $-40$  and  $4$  °C, respectively. For pure CPE and the 80/20 CPE/NR blend, the main drop in storage modulus takes place at a higher temperature than for compounds with blend ratios of 50/50, 20/80, and 0/100. This result indicates that the final products produced from compounds with the CPE/NR blend ratios of 100/0 and 80/20 can maintain their high modulus under broader service temperature conditions, compared with other blend ratios. In



**Figure 13** Plot of  $\tan \delta_{\max}$  against temperature of blends with various CPE/NR blend ratios.

addition, it can be seen that the trend of storage modulus at room temperature ( $\sim 30$  °C) is in agreement with that of tensile modulus obtained from tensile tests shown earlier in Figure 7.

The damping properties of the blends are shown in Figure 13. Two damping peaks are observed in all blends, supporting a two-phase morphology. Peak height depends on the amount of each phase in blends. Plot of the  $\tan \delta_{\max}$  peak height against the amount of NR in the blends is shown in Figure 14. The height of  $\tan \delta_{\max}$  of NR phase increases progressively with the amount of NR in blends, whereas that of CPE decreases, which can be attributed to the dilution effect. The  $T_g$  shifts (as determined from the temperature at damping peak) as a function of amount of NR are shown in Table IV. Compared with the  $T_g$  of pure components, the  $T_g$  of each component in blends shifts slightly toward each other. The shift in  $T_g$  values implies an interfacial interaction between phases taking place. A possible explanation is proposed as follows. As DCP is added, DCP generates free radicals on the backbones of both



**Figure 14** Plot of  $\tan \delta_{\max}$  of each phase in blends as a function of wt % NR.

**Table IV** Glass Transition Temperatures of CPE and NR Phases in CPE/NR Blends

Blend Ratio	$T_g$ of CPE Phase (°C)	$T_g$ of NR Phase (°C)
100/0	3.8	—
80/20	1.9	-37.5
50/50	-0.1	-37.9
20/80	-0.5	-39.0
0/100	—	-41.1

CPE<sup>25,27,28</sup> and NR. The radicals generated on the backbones are not stable and therefore tend to recombine, resulting in the possibility of co-vulcanization that could increase the interaction between CPE and NR phases.

## CONCLUSIONS

The use of natural rubber (NR) for partly substituting elastomeric chlorinated polyethylene (CPE) was determined, and the mechanical and thermal aging properties, as well as oil resistance of the blends, were investigated. The amount of NR in blends significantly affects the properties of the blends. In blends of  $\leq 50$  wt % NR content, tensile strength is similar to that of the pure CPE, even after either oil immersion or thermal aging. In other words, CPE plays strong roles in tensile properties of the blends with NR content up to 50 wt %. Modulus and hardness of the blends decrease progressively with increasing NR content. These properties also decrease in blends after thermal aging. After oil immersion, hardness decreases significantly for the blends with high NR content, whereas no change in modulus was observed.

The dynamic mechanical properties of pure NR and CPE determined by DMTA reveal damping peaks at about  $-40$  and  $4$  °C, correlating with the  $T_g$  of NR and CPE, respectively. The shift in the  $T_g$  values was observed after blending, which indicates the interfacial interaction between phases probably caused by the co-vulcanization in blends. Damping peak height of each phase in blends depends strongly on the amount of each phase in blends.

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