

Rheological Properties, Oil, and Thermal Resistance in Sulfur-Cured CPE/NR Blends

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ABSTRACT: The use of natural rubber (NR) for partly substituting elastomeric chlorinated polyethylene (CPE) was carried out. Sulfur curing was used to vulcanize NR phase in the blends. Mechanical, rheological, and thermal aging properties as well as oil resistance of the blends were investigated. The amount of NR in blends significantly affects properties of the blends. With NR content in blends up to 20 wt %, tensile properties are similar to those of the pure CPE, even after either oil immersion or thermal aging. Rheological properties of CPE/NR blends determined from the rubber process analyzer (RPA 2000) and parallel-plate rheometer

are controlled strongly by the blend composition. The viscoelastic behavior of pure CPE and the blends with CPE as a major component is governed by the viscous response, which could be seen from the high damping factor, particularly at high strain, the short linear viscoelastic range, and the high degree of pseudoplasticity. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1129–1135, 2004

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

INTRODUCTION

To achieve enhancement in properties such as mechanical and dynamic properties, thermal aging properties, processability, and oil resistance, the popular technique usually carried out is by blending two or more polymers together. Generally, there are factors considerably affecting properties in polymer blends, e.g., nature of the polymer, blend composition,^{1–3} blending conditions,^{4–6} and interfacial adhesion.^{7–14} Additionally, in the case of filled blends the uneven distribution of filler in each phase of the blends is reported to affect significantly the mechanical properties of blends.^{15–17}

Chlorinated polyethylene (CPE) possesses high resistances to hydrocarbon oil, heat, and weathering, attributed to the chlorine atoms added to the polyethylene backbone. According to published work, CPE has been blended with many polymers, including polyvinyl chloride,^{7,9,11,18} styrene-acrylonitrile,^{19,20} and polyurethane.^{21,22} Compared to natural rubber (NR), CPE is more expensive and therefore blending CPE with NR is one method to reduce the production cost of final products requiring CPE properties. How-

ever, the amount of NR added is limited to the degree of resistance to oil and heat. In our previous work,²³ it was found that CPE up to 50% by weight could be substituted by NR, giving similar tensile properties to pure CPE. The main limitation of the blends prepared in the previous work is the lack of recyclability due to the use of a peroxide curing system, i.e., both NR and CPE phases are vulcanized. Therefore, the present study aims to prepare CPE/NR blends vulcanized by a sulfur-curing system, which would vulcanize only the NR phase in the blends. Mechanical, thermal aging, and rheological properties as well as oil resistance of CPE/NR blends are investigated.

EXPERIMENTAL

Materials

Details and amounts of materials used are shown in Table I.

Mixing procedure

The CPE/NR blend ratios of 100/0, 20/80, 50/50, 80/20, and 0/100 were used for the study. Blending was carried out in a laboratory-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

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TABLE I
Materials Used in the Present Study

Material	Manufacturer/supplier	Amount (phr)
Chlorinated polyethylene (CPE; Tyrin 3615P)	DuPont Dow Elastomer Co., Ltd., USA	— ^a
Natural rubber (NR; STR5)	Thailand	— ^a
Stearic acid (Commercial grade)	Polychem Co. Ltd., Thailand	2
Magnesium oxide (MgO, Commercial grade)	Boonthavorn Co. Ltd., Thailand	5
Sulfur	Siam Chemicals Co. Ltd., Thailand	2
TBBS ^b (Vulkacit NZ)	Bayer Co. Ltd. USA	1

^a Amounts of elastomers depending on blend ratio of CPE/NR: 100/0, 80/20, 50/50, 20/80, 0/100.

^b *N-t*-butyl-2-benzothiazolesulfenamide.

then charged. After blending for 4 min, curatives were added to the blends and the mixing process was carried on for 5 min before discharging. 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).

Measurement of tensile properties

Tensile test specimens were punched out from the compression-molded sheets using punching die. Tensile properties were measured using 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.

Measurements of oil resistance and thermal aging properties

The specimens to be tested 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 in order 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 rheological properties

Dynamic mechanical and rheological properties of blends were measured using the rubber process analyzer (RPA 2000, Alpha Technologies) and a parallel-plate rheometer (Physica MCR 500) at the test temperature of 170°C.

Blend morphology examination

Scanning electron microscopy (SEM) was performed by a Jeol scanning electron microscope, model JSM 5410. The sample was stained by Osmium tetroxide (OsO₄) and sputtered with gold before viewing.

RESULTS AND DISCUSSION

It has widely been known that the sulfur crosslinking system is only applicable to rubber with double bonds. In the present study, only the NR phase is targeted to be vulcanized while the CPE phase is left unvulcanized, so that the blends with NR as a dispersed phase in CPE matrix could be recycled. As a result, the sulfur crosslinking system was chosen for this purpose. Figure 1 shows the cure curve of pure CPE filled with curatives based on the sulfur-curing system. It is clear that there is no torque rise after a long cure time of 10 min, indicating that pure CPE could not be vulcanized by the curatives used in the present study.

It is widely known that, with sulfur curing, zinc oxide (ZnO) is generally used as a cure activator, by reacting with stearic acid to yield the soluble zinc that

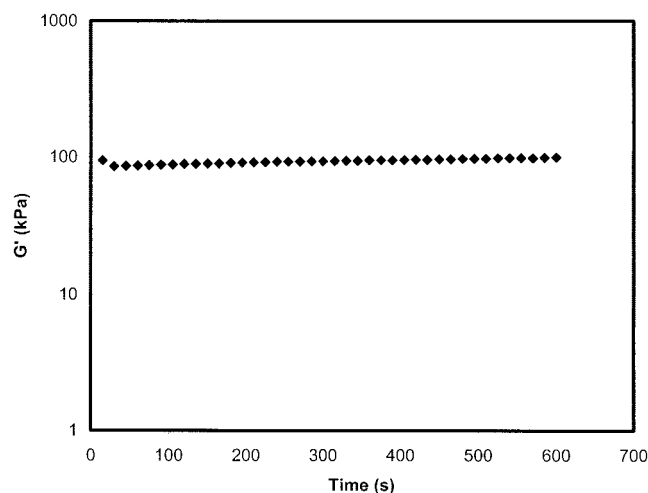
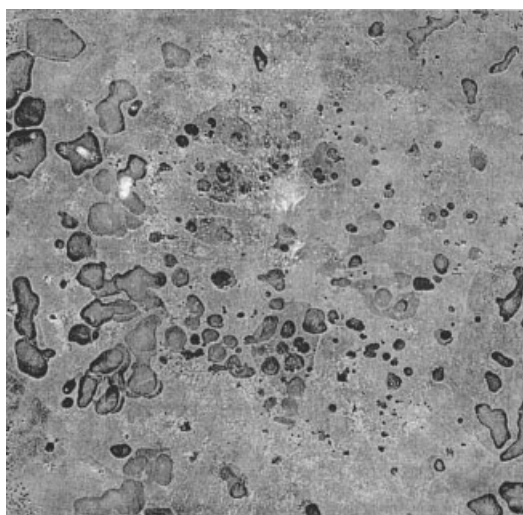


Figure 1 Cure curve of pure CPE measured from a parallel-plate rheometer under oscillating deformation at a vulcanization temperature of 170°C.

could efficiently activate the sulfur vulcanization. However, when the blends are compression molded, it appears that there are a large number of bubbles on the product surfaces, as shown in Figure 2(a). The bubbles are believed to be caused by the hydrochloric gas generated from CPE during compression molding.²⁴ Consequently, a suitable acid scavenger is required, and, in the present work, magnesium oxide (MgO) as a acid scavenger and cure activator is used instead of ZnO. Figure 2(b) shows a remarkable improvement in surface quality by the use of MgO.



(a)



(b)

Figure 2 Surface quality of the vulcanized 50/50 CPE/NR blends: (a) with ZnO; (b) with MgO.

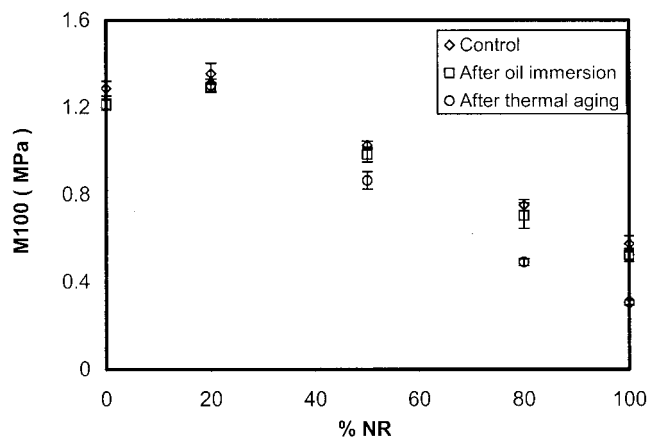


Figure 3 Modulus at 100% strain of blends with various wt % of NR.

Effect of blend composition

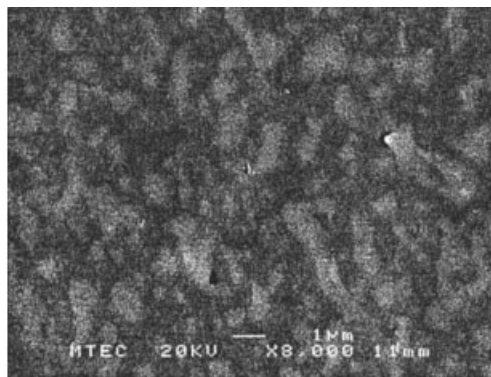
Oil and thermal resistance

Figure 3 shows the comparison of the tensile modulus at 100% strain (M100) of the blends as a function of NR content in the blends before and after oil immersion and thermal aging. For the blends before oil immersion or thermal aging, which are denoted as Control in the figure, it is evident that M100 of CPE/NR blends with NR content of 20% by weight is obviously similar to that of pure CPE, which means CPE phase is responsible for the high M100 of the blends. Scanning electron micrographs as shown in Figure 4 reveal two-phase blend morphology in which CPE is the continuous phase in the blends with NR contents of 20 wt %, which is in agreement with the modulus result. However, as NR content is higher than 20 wt %, M100 of the blends starts to linearly decrease, which can be explained by the dilution effect, i.e., a large amount of high-tensile modulus CPE is diluted by a large amount of low-modulus NR, and NR becomes the continuous phase, as shown in Figure 4. After oil immersion, M100 of all blends decreases to similar extent, regardless of the blend ratio. In the case of thermal aging, it appears that the M100 of blend after thermal aging decreases, particularly in blends with high NR content. In other words, for the blend system studied, the M100 is more sensitive to thermal aging than the oil immersion.

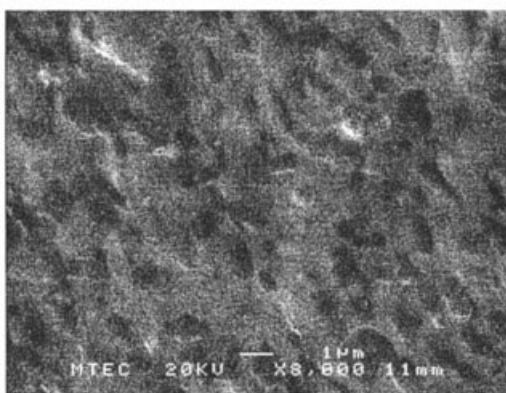
Results of tensile strength as shown in Figure 5 reveal a similar trend to those of M100, but more obvious, i.e., tensile strength of the blends with 20 wt % NR is close to that of pure CPE after oil immersion and thermal aging, indicating good oil and thermal resistance. With the NR content larger than 20 wt %, although the blends possess high tensile strength before oil immersion or thermal aging (denoted as Control in the figure), those blends reveal a significant decrease in tensile strength after either oil immersion

or thermal aging, implying low resistance to oil and thermal aging.

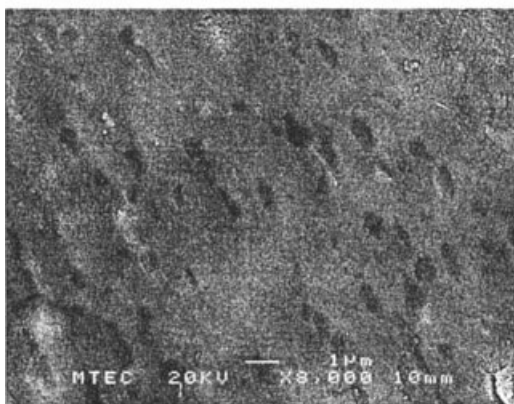
If the tensile results discussed in the present work are compared with those reported in the previous work,²³ in which CPE/NR blends were prepared and vulcanized with dicumyl peroxide (DCP), there are



(a)



(b)



(c)

Figure 4 Scanning electron micrographs of CPE/NR blends with various wt % of NR (CPE phase is shown as a dark phase): (a) 20%; (b) 50%; (c) 80%.

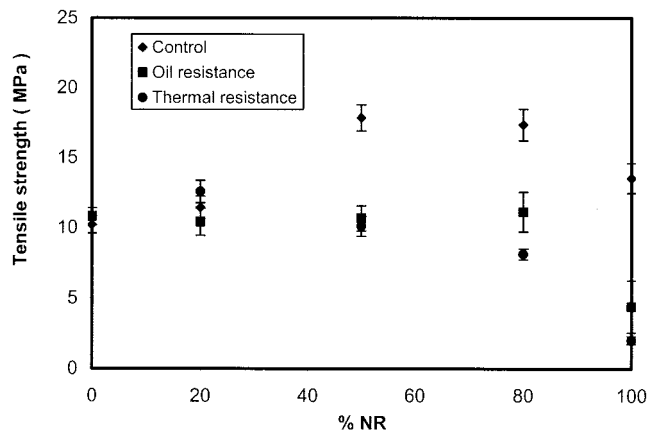


Figure 5 Tensile strength of blends with various wt % of NR.

two main points to be discussed. The first point is the difference in tensile strength and the second one is the maximum NR content in blends with no change in oil and thermal resistance compared to pure CPE. As for the first point, it is clear from Figure 6 that the tensile strength obtained in this work is higher than that obtained from the previous work, particularly in the case of the blends with high NR content. The difference in tensile strength could be explained by the lower possibility of thermal degradation in NR phase for the blend systems studied in the present study. For the blends prepared in the previous work,²³ DCP was used as a curing agent and therefore the radicals taking place during blending at high temperature promote the thermal oxidation, resulting in molecular chain-scission of NR phase. The MgO added in the present study as a CPE acid scavenger also improves tensile strength of the blends with low NR content. As for the second point, one could note that the maximum content of NR with oil and thermal resistance similar to those of pure CPE in the present study is 20

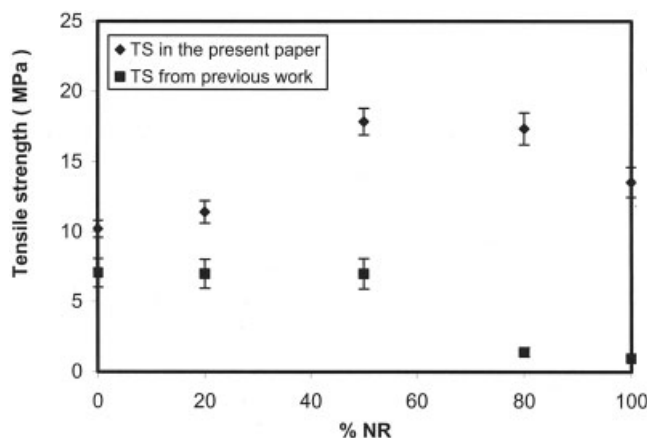


Figure 6 Comparison of tensile strength results of blends prepared from the present study and those from the previous work.²³

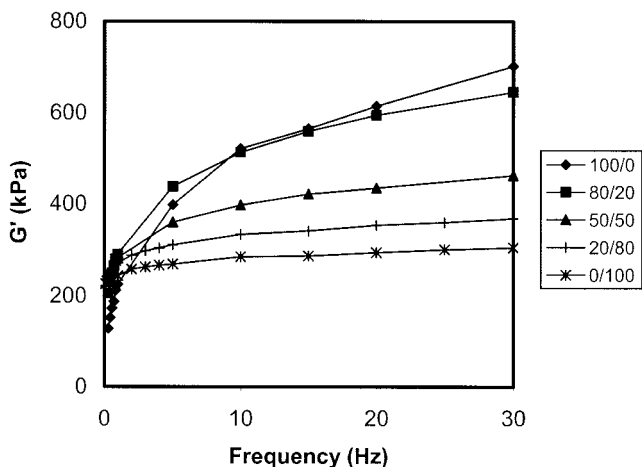


Figure 7 Storage modulus (G') as a function of frequency of blends with various CPE/NR blend ratios determined from RPA 2000(10% strain; 170°C).

wt %, which is much lower than the NR content of 50 wt % reported in the previous work. The proposed explanation is based on a difference in crosslinking systems. In the previous work, a peroxide cure has been used, which could vulcanize both CPE and NR phases, leading to good properties of blends with CPE matrix even with high NR content. By contrast, CPE matrix in blends in the present study is not vulcanized and therefore the blends with NR content higher than 20 wt % yield poor oil and thermal resistance.

Rheological properties

Figure 7 reveals the elastic modulus or storage modulus (G') as a function of frequency of blends with various composition ratios. It is clear that pure CPE possesses a much higher G' than pure NR especially at high frequency. This is due to the thermal oxidation of NR during blending at high temperature, leading to a molecular chain-scission and thus a reduction in elasticity. It is also evident that G' decreases with increasing NR content, which is attributed to a dilution effect. The G' result is in agreement with the tensile modulus result shown earlier in Figure 3.

In the case of damping factor or $\tan \delta$ (i.e., the ratio of loss modulus to storage modulus) as a function of frequency shown in Figure 8, it could be seen that pure NR gives much lower damping factor than pure CPE, despite having a low storage modulus (G'). This indicates that the NR possesses a very low viscous response. In other words, the molecular mobility of NR is restricted strongly by the sulfur crosslink. The damping factor in blends increases with increasing CPE content, which is a result of the dilution effect. In addition, from Figure 8, it is evident that the damping factor of the blends with CPE/NR blend ratios of 100/0 and 20/80 tends to decrease with increasing frequency, indicating a behavior of viscous materials

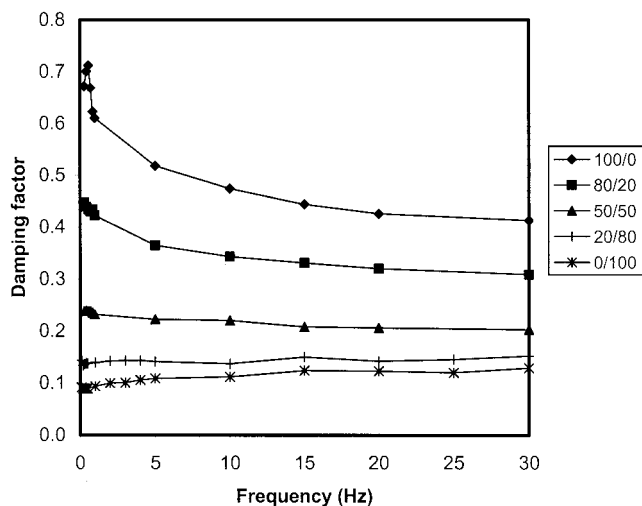


Figure 8 Damping factor ($\tan \delta$) as a function of frequency of blends with various CPE/NR blend ratios determined from RPA 2000 (10% strain; 170°C).

or, uncured CPE as a matrix in this case. The higher the frequency, the shorter the time available for molecular mobility, and thus the lower the damping factor. By contrast, in the blends with cured NR as a major component, i.e., blends with CPE/NR blend ratios of 20/80 and 0/100, the damping factor slightly increases with increasing frequency, which is a common behavior usually found in elastic materials. A relatively large amount of energy is required to produce free volume for molecular mobility, leading to a large value of loss modulus and thus damping factor. In other words, with 20/80 and 0/100 CPE/NR blend ratios, NR phase is believed to be a continuous phase. To support this result, the parallel-plate rheometer with an oscillating mode of deformation was utilized and the result obtained as shown in Figure 9 is clearly

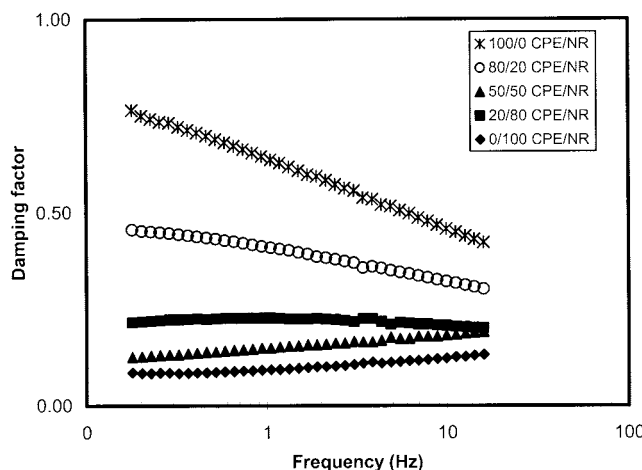


Figure 9 Damping factor ($\tan \delta$) as a function of frequency of blends with various CPE/NR blend ratios determined from a parallel-plate rheometer (2% strain; 170°C).

in accordance with the RPA result.

Plots of damping factor against % strain of blends with various blend ratios are shown in Figure 10, revealing that the damping factor of all blends does not change with % strain at low strain and rises at high strain. This indicates the linear viscoelastic behavior at low strain. NR possesses the broadest linear viscoelastic (LVE) region while pure CPE has the narrowest, which could be explained by the chemical crosslink in NR. The broadness of the LVE region in blends is between that of pure CPE and pure NR, depending on the blend ratio. In addition, the damping factor of pure CPE is much higher than that of pure NR, attributed to the strong viscous response in pure CPE. One can see that even at a high % strain, the damping factor of pure NR is still less than 1, indicating the domination of the elastic response over the viscous response, which is caused by the sulfur crosslink in NR. In the case of pure CPE, a large amount of loss energy due to molecular slippage during flow results in a relatively high value of damping factor. The damping factor of the blends decreases with increasing NR content due to the dilution effect.

As for the complex viscosity as a function of frequency in blends, Figure 11 shows that the complex viscosity of all compounds decreases with increasing frequency, which is not uncommon, indicating the pseudoplastic behavior of the materials. It could also be seen that the complex viscosity plot of compounds with CPE as a major component reveals a shallower slope than those with NR as a major component. This means the blends with CPE as a matrix possess a higher power law index, or is more Newtonian-like, indicating a smaller degree of molecular restriction during flow. As one can expect, the sulfur crosslinking

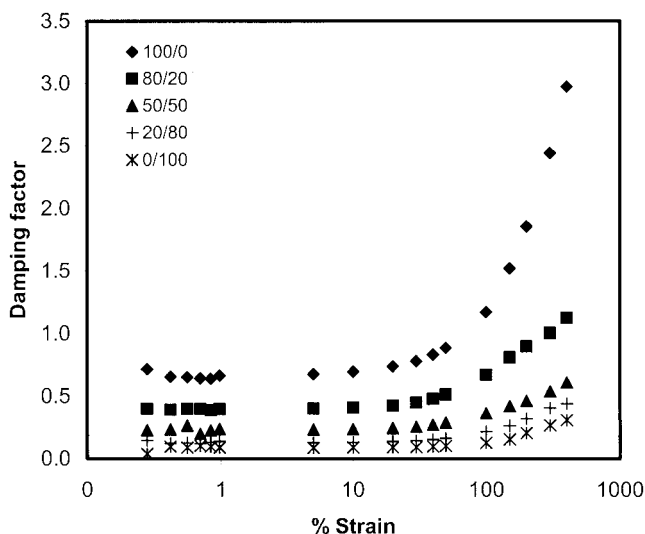


Figure 10 Damping factor ($\tan \delta$) as a function of % strain of blends with various CPE/NR blend ratios determined from RPA 2000 (1 Hz; 170°C).

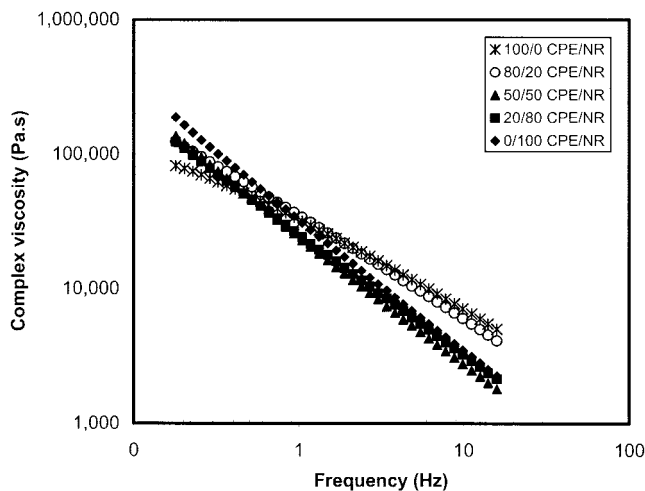


Figure 11 Complex viscosity as a function of frequency of blends with various CPE/NR blend ratios determined from a parallel-plate rheometer (2% strain; 170°C).

taking place in the NR phase is a major factor responsible for molecular restriction during flow and, therefore, the compounds with NR as a major component show a strong pseudoplasticity during flow as illustrated by the steep slope of the plots.

CONCLUSION

A blend between elastomeric chlorinated polyethylene (CPE) and natural rubber (NR) with a sulfur curing system (i.e., only NR phase was vulcanized) was prepared. Mechanical, rheological, 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. With NR content in blends of 20 wt %, tensile properties are similar to those of pure CPE, even after either oil immersion or thermal aging.

Rheological properties of CPE/NR blends determined from the rubber process analyzer and parallel-plate rheometer are controlled strongly by the blend composition. The viscoelastic behavior of pure CPE and the blends with CPE as a major component is governed by the viscous response, which could be seen from the high damping factor, particularly at high strain, the short linear viscoelastic range, and the high degree of pseudoplasticity.

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