

Rheological Properties of Recycled Chlorinated Polyethylene/Natural Rubber Blends Vulcanized by Sulfur

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ABSTRACT: Blends of elastomeric chlorinated polyethylene (CPE) and natural rubber (NR) with a blend composition ratio of 80/20 were prepared and recycled. Viscoelastic properties of the blends as a function of the recycling cycle were monitored. The results obtained revealed that, with an increase in the number of recycling cycles, a noticeable change in the viscoelastic properties of blends could be observed; that is, a decrease in the elastic contribution associated with a noticeable shift in the glass-transition temperature of the NR phase of the blends was observed, implying a molecular change in the NR phase via a thermal chain-scission mechanism. The influence of magnesium oxide (MgO) as an acid acceptor for CPE on

the viscoelasticity of the blends was also investigated. Through a reduction of the amount of MgO, the molecular change was found to be more pronounced in NR than in CPE phases in a manner similar to the increase in the recycling cycles. An explanation of the changes in the viscoelastic properties of the blends with various MgO loadings and recycling cycles is proposed in terms of thermal degradation via a molecular chain-scission mechanism taking place mainly in the NR phase. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1051–1056, 2009

Key words: blends; degradation; recycling; rheology; viscoelastic properties

INTRODUCTION

In the mid 1970s, industrial societies suddenly became aware that the oil reserves upon which the polymer industry is at present based are limited. This was reinforced by a rapid escalation in the price of crude oil and its derivatives, which resulted in a call from ecologists and environmentalists to reverse the trend toward the throw-away society.^{1,2} One of the various problems that mankind faces is the problem of waste disposal management. Because polymeric materials do not decompose easily, disposal of waste polymers is a serious environmental problem. There are generally four methods of waste recycling: energy recovery (incineration), feedstock recycling (pyrolysis, hydrogenation, and gasification), chemical recycling (depolymerization), and material recycling.^{3–6}

Chlorinated polyethylene (CPE) possesses high resistance to hydrocarbon oil, heat, and weathering, which is attributed to the chlorine atoms added to the polyethylene backbone. According to published

work, CPE has been blended with many polymers, including poly(vinyl chloride),^{7–11} styrene-acrylonitrile,^{12,13} and polyurethane.^{14,15}

According to our previous work,^{16,17} up to 50 wt % of CPE can be replaced with natural rubber (NR); this gives a phase morphology with the NR phase dispersed in the CPE matrix, leading to good oil and thermal aging resistances of the blends similar to those of neat CPE. However, because a peroxide curing system is used in that work, both NR and CPE phases are vulcanized, and this means a lack of recyclability. Consequently, a sulfur curing system is used in 80/20 CPE/NR blends instead of peroxide. In this way, the NR phase in the blends can selectively be vulcanized,^{18–22} and so recycling of such blends should, in theory, be possible. Therefore, this study was aimed to extend our work by focusing mainly on the recycling of CPE/NR blends with and without magnesium oxide (MgO) as an acid acceptor of CPE. The rheological properties of CPE/NR blends were investigated.

EXPERIMENTAL

Materials

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

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TABLE I
Materials Used in the Study

Material	Manufacturer/supplier	Functionality	Amount (phr)
CPE (Tyrin 702P)	DuPont Dow Elastomer Co., Ltd., United States	Raw polymer	80
NR (STR20)	Thai Union Rubber Co., Ltd., Trang, Thailand	Raw polymer	20
Stearic acid (commercial grade)	Polychem Co., Ltd., Bangkok, Thailand	Cure activator	2
MgO (Starmag150)	Petch Thai Chemicals Co., Bangkok, Thailand	Cure activator and acid acceptor	Variable ^a
Sulfur (commercial grade)	Siam Chemicals Co., Ltd., Bangkok, Thailand	Curing agent	2
Santocure TBBS ^b	Flexsys Co., Ltd., United States	Cure accelerator	1
Santoflex IPPD ^c	Flexsys Co., Ltd., United States	Antioxidant	4
Santogard PVI ^d	Flexsys Co., Ltd., United States	Prevulcanization inhibitor	1

^a Amounts of stabilizer (MgO): 0, 1, 2.5, 4, and 5 phr.

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

^c *N*-Isopropyl-*N'*-phenyl-*p*-phenylenediamine.

^d *N*-(Cyclohexylthio)phthalimide.

Mixing procedure

In the initial step, NR was masticated at 40°C with a laboratory-size two-roll mill mixer (model LRM150, LabTech, Samuthprakam, Thailand) to achieve a Mooney viscosity (ML1+4 at 100°C) of approximately 60. For the blending process, CPE was melted on a front roll for 1 min at the set temperatures of 145 and 140°C for the front and back rolls, respectively. Afterward, the masticated NR was charged and further mixed for 4 min. Compounding ingredients were then added and mixed for 5 min before discharging. Finally, the blend was compression-molded into 1-mm-thick sheets under a clamping pressure of 15 MPa at 155°C to achieve a stage of cure of 99% as determined with a rubber process analyzer (RPA2000, Alpha Technologies, Akron, OH), and it was designated a virgin blend.

For a recycling procedure, the virgin blend was cut into small pieces and reprocessed on a two-roll mill under processing conditions similar to those used for the virgin blend. The discharged blend was called the first recycled blend. By repetition of the recycling cycles, the second, third, fourth, and fifth recycled blends resulted.

Measurement of the viscoelastic properties

The rheological study in this work was carried out under oscillatory shear flow with the use of a parallel-plate rheometer (model MCR 500, Physica, Germany). A 25-mm rotor with a grooved surface was used to prevent slippage between the polymer melt and rotor surface. A disc specimen approximately 25 mm in diameter and 1 mm thick was prepared from compression-molded sheets. All tests were performed at the test temperature of 170°C. With the strain sweep test, the linear viscoelastic region of the materials at the frequencies of 1 and 100 rad/s was

determined to be subsequently used in the frequency sweep test. In the frequency sweep test, the swept frequency in the range of 1–100 rad/s was applied to the test sample. The results for the elastic modulus (G'), loss modulus, complex viscosity, damping factor ($\tan \delta$), and creep compliance were recorded.

For the determination of the viscoelasticity as a function of temperature, a dynamic mechanical thermal analyzer (Gabo Explexor, Ahlden, Germany) with a tension mode of deformation was used at a test frequency and dynamic strain amplitude of 10 Hz and 0.1%, respectively. The temperature was swept from –100 to 40°C at a heating rate of 2°C/min.

RESULTS AND DISCUSSION

Effect of the recycling cycles

To gain information on the linear viscoelasticity of recycled CPE/NR blends, a strain sweep test was performed, and the results are illustrated in Figure 1. Clearly, a linear viscoelastic region exists at an approximately 0.5–15% strain amplitude, regardless of the recycling cycles. However, G' at a low strain appears to be affected strongly by the recycling cycles. Obviously, there are three main groups of G' results: (1) virgin and first recycled blends, (2) second and third recycled blends, and (3) fourth and fifth recycled blends. A discrepancy in G' of the virgin and first recycled blends appears to be insignificant and negligible. This is possibly due to the counterbalancing effect of CPE stiffening and NR softening effects via thermal degradation. With further recycling, the thermal degradation of the NR phase is more pronounced than that of the CPE phase, leading to a decrease in G' . A reduction in G' implies a decrease in the elastic behavior of the

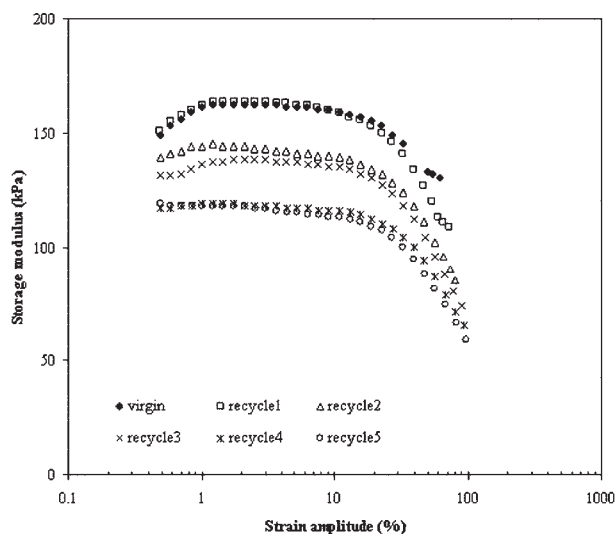


Figure 1 G' as a function of the strain amplitude at 1 rad/s for CPE/NR blends with various recycling cycles.

blends. Compared to CPE, the NR phase possesses double bonds that are more prone to thermal oxidation, even in the presence of an amine-based antioxidant.²³ In contrast, CPE, having no unsaturation, could in theory be thermally degraded via both chain-scission and crosslink mechanisms. In the blend system studied, it seems that the latter is more likely to occur via a dehydrochlorination process.²⁴ To support the proposed explanation, a time sweep test at the high temperature of 170°C was performed on neat CPE and NR specimens, and the measured results are exhibited in Figure 2. Evidently, with increasing test duration, G' of neat CPE and NR increases and decreases, respectively, and this sup-

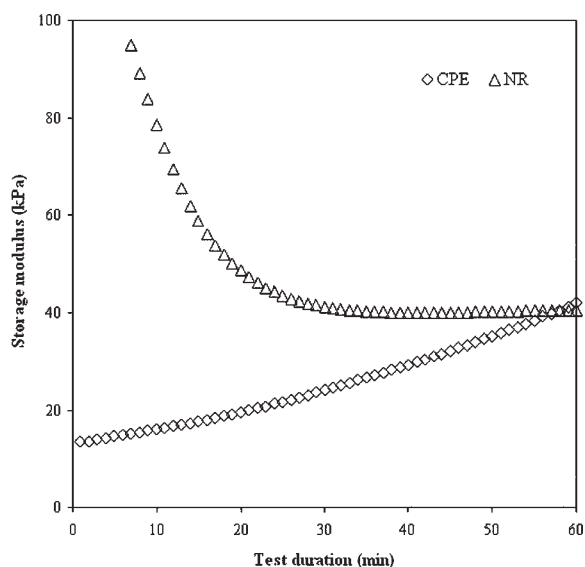


Figure 2 G' for neat CPE and NR as a function of the test duration at 170°C.

ports the proposed explanation of Figure 1: a reduction in G' with an increasing number of recycling cycles is caused by the occurrence of chain scission mainly in the NR phase and slightly in the CPE phase. This leads to a decrease in the elastic contribution.

The $\tan \delta$ results, as shown in Figure 3, agree very well with the G' results. The virgin and first recycled blends are classified as the group with the lowest $\tan \delta$ values, which imply the highest magnitude of elastic behavior via a high extent of molecular entanglement due to their good thermal stability. At a high strain of deformation, the upswing of $\tan \delta$ of such blends is relatively small, and this supports the high degree of molecular entanglement, as discussed earlier. In contrast, the group subjected to a highly thermal history, that is, the fourth and fifth recycled blends, reveals the highest $\tan \delta$ value because of the highest degree of thermal degradation via a molecular chain-scission mechanism occurring mainly in the NR phase.

A dependence of G' on the frequency is exhibited in Figure 4. A starting test frequency lower than 1 rad/s was not applicable in this work because the long test duration required for collecting data would then affect the thermal degradation of the blends. In other words, at a very low test frequency, the frequency effect would suffer interference by the occurrence of thermal degradation during the test duration. Noticeably, all the blends show increases in moduli with increasing frequency, and this is typical for viscoelastic materials. With reference to a spring-dashpot model, the higher the frequency is, the lower the dashpot response is because of the insufficient time for its response. Thus, the bulk response is dominated by a spring component rather

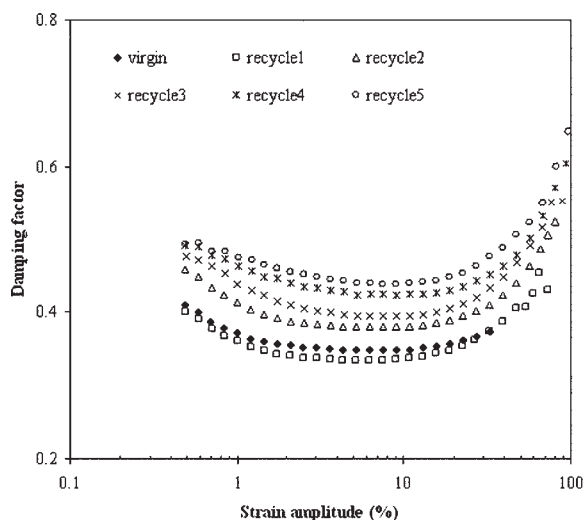


Figure 3 $\tan \delta$ as a function of the strain amplitude at 1 rad/s for CPE/NR blends with various recycling cycles.

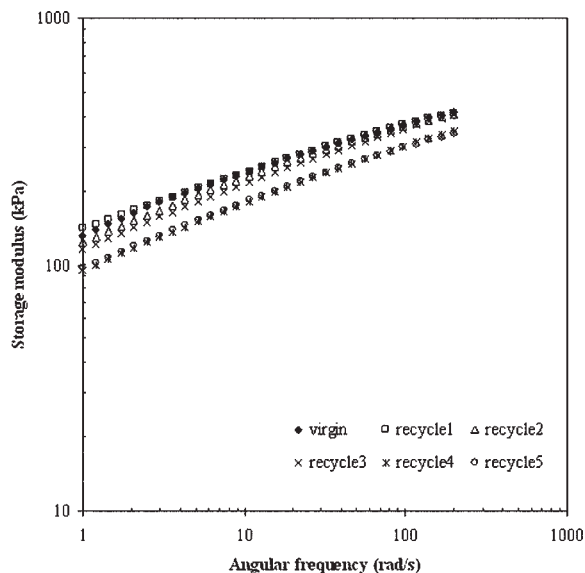


Figure 4 G' as a function of the angular frequency at 10% strain for CPE/NR blends with various recycling cycles.

than a dashpot component as the frequency increases. In terms of the molecular aspect, the dashpot response is related directly to the occurrence of molecular relaxation via molecular flow (or molecular slippage). At a high frequency, there is insufficient time available for molecular relaxation leading to an increase in the elastic contribution. In addition, the sensitivity of G' to the frequency slightly increases with an increasing number of recycling cycles. It has previously been reported that the decrease in the elastic behavior of CPE/NR blends results in an increase in the time-dependent behavior.^{19,21,25} Consequently, the results of frequency-dependent G' agree with the proposed explanation of a molecular chain-scission mechanism.

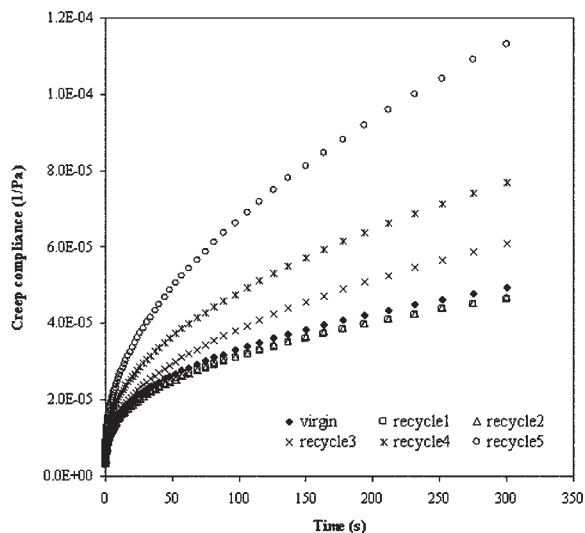


Figure 5 Creep compliance for CPE/NR blends with various recycling cycles.

To further explore changes in the viscoelastic properties affected by the thermal history, a creep test was conducted. Figure 5 exhibits the creep compliance as a function of time at a given shear stress. As expected, creep compliance increases with time for all blends. Also, the rate of the creep phenomenon is more evident in the blends with a high magnitude of thermal experience. According to the spring-dashpot model, creep is a result of a dashpot response at a very low test frequency, which means a molecular flow. Thus, the blends with a high number of recycling cycles would reveal high creep values attributable to a large number of highly chain-scissioned molecules caused by thermal degradation. Notably, the resultant trends for blends with different numbers of recycling cycles are more apparent in the case of the creep test versus the oscillatory test. Alternatively, it could be stated that the molecular structure of polymers determined via a rheological response is most sensitive at a very low test frequency.

Effect of MgO

As discussed in a previous section, it is believed that changes in the viscoelastic properties of 80/20 CPE/NR blends caused by thermal experience occur mainly in the NR phase rather than the CPE phase. This is because of a saturation structure of the CPE backbone. As a result, an attempt to alter the thermal stability of the CPE phase was carried out through the variation of the amount of MgO as a thermal stabilizer via hydrochloric acid acceptance.

Figure 6 illustrates the influence of the MgO loading on G' under a strain sweep test of the fifth recycled blends. It is evident that, at any given strain

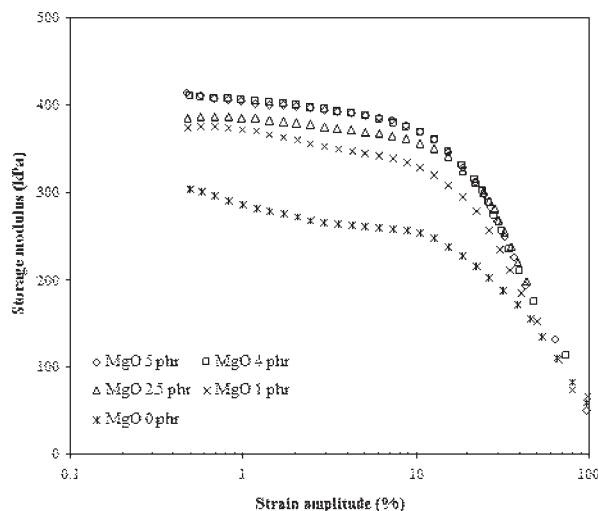


Figure 6 Influence of the MgO loading on G' as a function of the strain amplitude at 100 rad/s in the fifth recycled blends.

amplitude of deformation, G' of the blends decreases with the MgO loading decreasing. Notably, the blend without MgO reveals relatively low G' in comparison with blends with MgO, and this implies a relatively small magnitude of elastic behavior or poor thermal stability of this blend. Initially, it was anticipated that, by the alteration of the MgO loading, the occurrence of thermal degradation via dehydrochlorination would be observed. A dehydrochlorination process in a chlorinated polymer would generally yield a crosslink and thus a rise in the stiffness (or G' in this case), as illustrated previously in Figure 2. However, the overall results for the blends with various loadings of MgO reveal the opposite trend, that is, a decrease in G' . On the basis of the results obtained here, it is hypothesized that the decrease in G' might involve a molecular change of the NR phase rather the CPE phase.

To prove this hypothesis, a dynamic mechanical thermal analysis test was performed, and the glass-transition temperature (T_g) results for each phase of the blends are summarized in Table II. It is evident that the values of T_g , determined from the damping peaks of each phase, are affected by the MgO loading in a similar manner. By a reduction of the MgO loading, T_g of both the NR and CPE phases shifts to a lower temperature, but this is more pronounced in the NR phase. An explanation is proposed as follows: with a low loading of the acid acceptor (MgO), a large amount of hydrochloric acid released from the CPE dehydrochlorination reaction might cause acidity of the bulk, accelerating the molecular change of the NR phase via the molecular chain-scission mechanism. It is also noticeable that the trend of the NR T_g shift to a lower temperature is similar to that found in blends with various numbers of recycling cycles, as illustrated in Table III. As discussed previously, with an increase in the thermal history, the NR phase with its unsaturation structure is prone to be degraded, and this leads to its greater molecular mobility and thus a shift in T_g to a lower temperature. However, an explanation for the slight shift in T_g of the CPE phase is not known at present.

TABLE II
 T_g Values of CPE and NR Phases in the Fifth Recycled CPE/NR Blends

MgO loading (phr)	T_g (°C)	
	NR phase	CPE phase
0	-51.0	-0.8
1	-52.4	-0.5
2.5	-50.3	-2.6
4	-52.5	-0.6
5	-47.8	-1.1

TABLE III
 T_g Values of CPE and NR Phases in CPE/NR Blends with Various Recycling Cycles

Recycling cycle	T_g (°C)	
	NR phase	CPE phase
Virgin	-40.4	-0.8
First	-38.4	-0.8
Second	-53.3	-0.6
Third	-54.8	-0.5
Fourth	-53.2	-0.7
Fifth	-51.0	-0.8

CONCLUSIONS

Blends of CPE and NR with a blend composition ratio of 80/20 were prepared and recycled. Changes in the viscoelastic properties of the blends by recycling were monitored. The following conclusions could be drawn from the results:

1. With an increasing number of recycling cycles, a decrease in the blend elastic behavior associated with a significant shift in T_g of the NR phase was observed. The results imply a molecular change mainly in the NR phase via a thermal chain-scission mechanism.
2. By a reduction of the amount of MgO as an acid acceptor for CPE, the major change was found to be more pronounced in the NR phase than the CPE phase in a manner similar to the increase in the number of recycling cycles. It is therefore believed that changes in the viscoelastic properties of blends by variation of the MgO loading and recycling cycles are attributable to a similar thermal degradation mechanism, that is, a molecular chain-scission process taking place mainly in the NR phase.

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