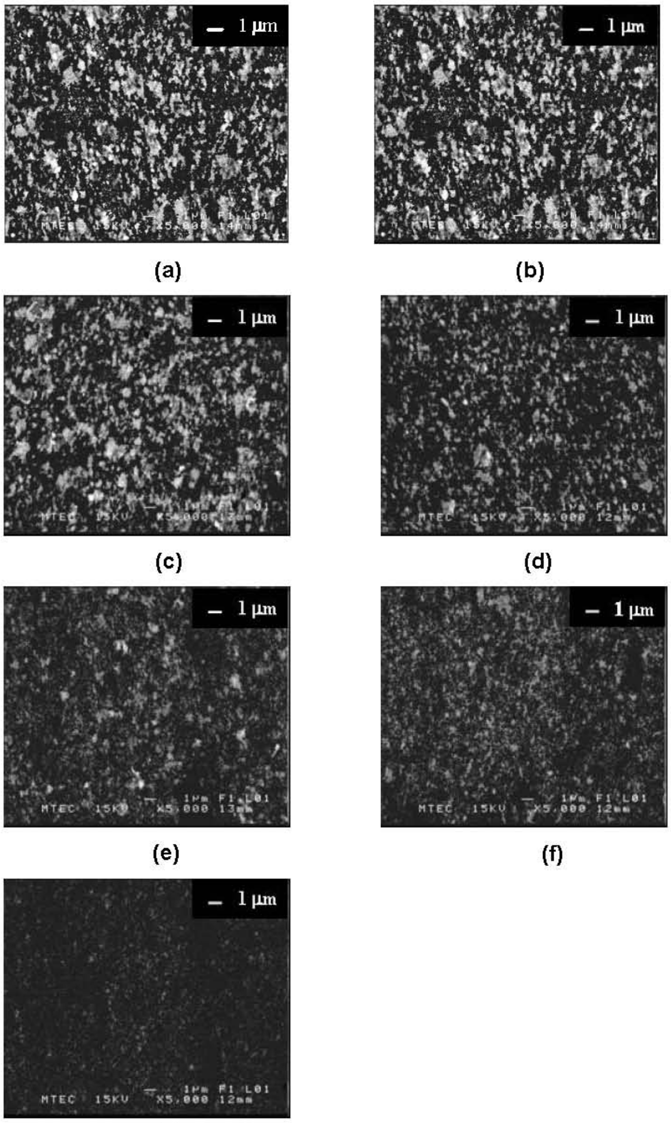
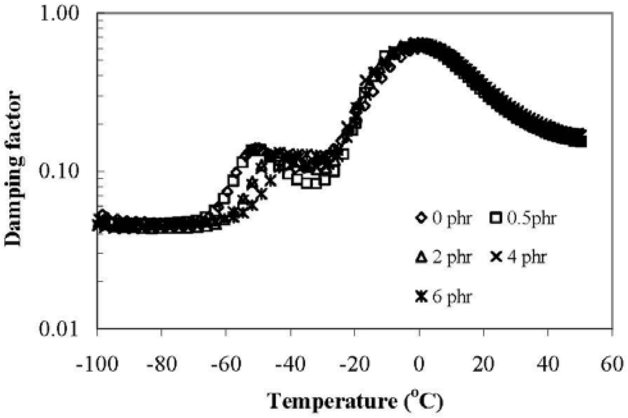
Figure 3



(a) (b) (c) (d) (e) (f) (g)

Figure 4



Damping factor
1.00
0.10
0.01
-100
-80
-60
-40
-20
0
20
40
60
Temperature (°C)
◇ 0 phr
□ 0.5phr
△ 2 phr
× 4 phr
✱ 6 phr

Figure 5

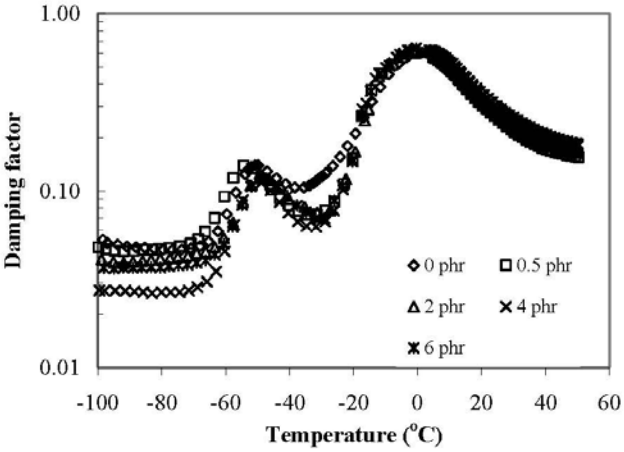
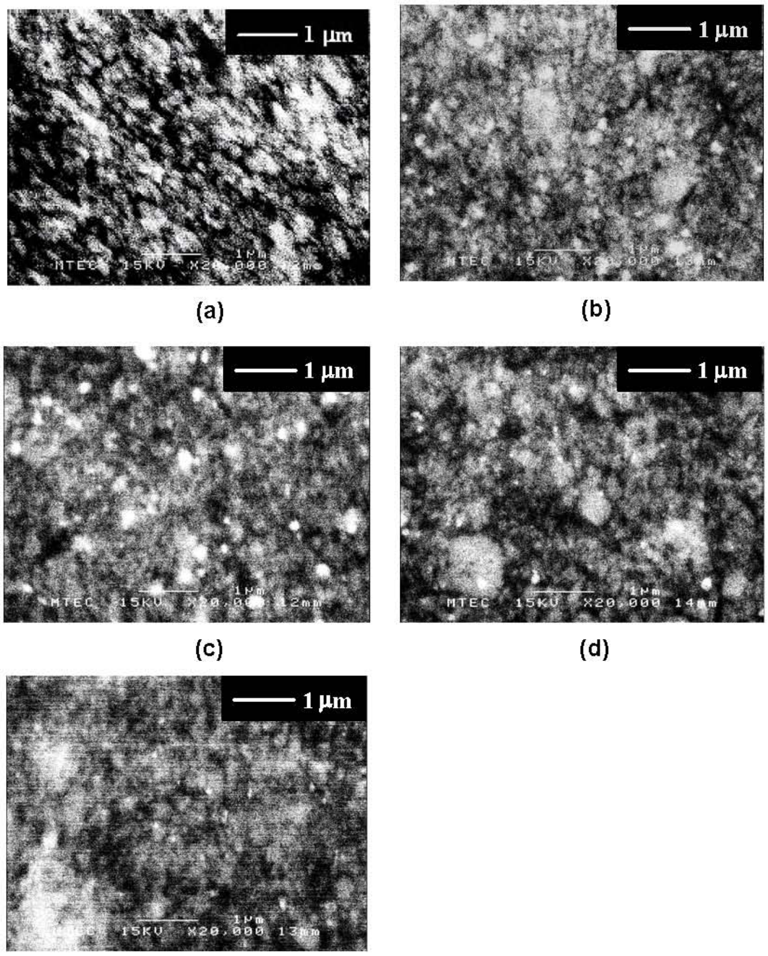

1.00
0.10
0.01
Damping factor
-100
-80
-60
-40
-20
0
20
40
60
Temperature (°C)
◇ 0 phr
□ 0.5 phr
△ 2 phr
× 4 phr
✱ 6 phr

Figure 6

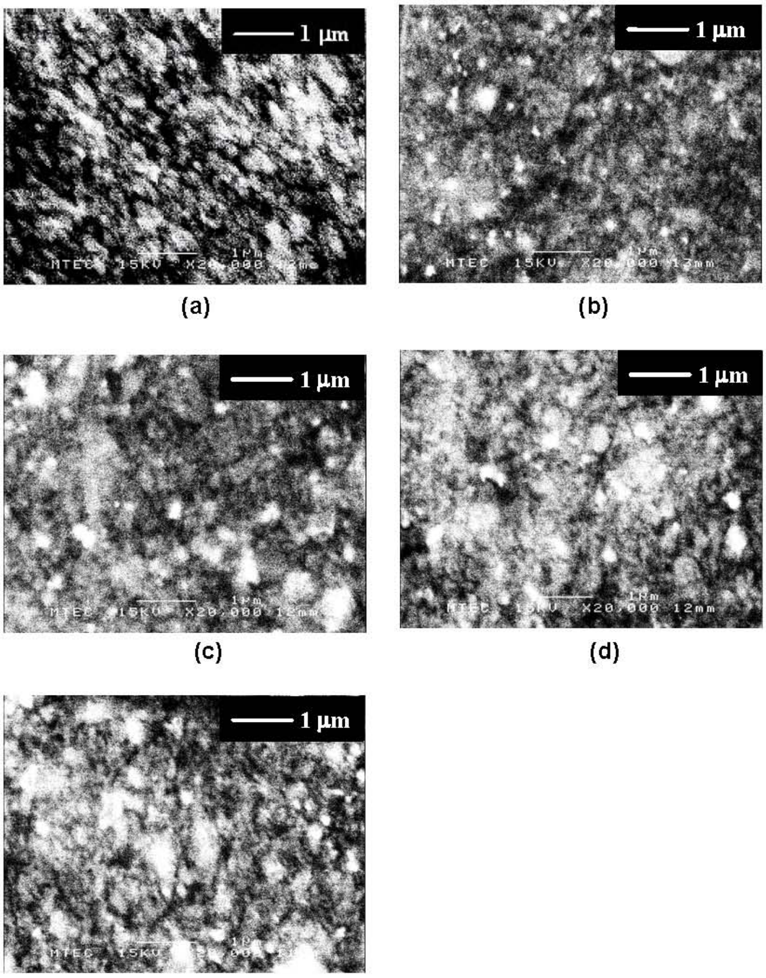


(a) (b)

(c) (d)

(e)

Figure 7



(a) (b)

(c) (d)

(e)

เรื่องที่ 4

P. Prasopnatra, P. Sae-oui, **C. Sirisinha,** Rheological properties in recycled CPE/NR blends vulcanised by sulphur, *Journal of Applied Polymer Science* (accept with minor correction)

27-Jun-2008

Dear Dr. Sirisinha:

Thank you for resubmitting your manuscript (# APP-2007-11-3404.R1) entitled "RHEOLOGICAL PROPERTIES IN RECYCLED CPE/NR BLENDS VULCANISED BY SULPHUR" to the Journal of Applied Polymer Science. Your manuscript has been reviewed and the comments of the reviewer(s) are included at the bottom of this letter.

The reviewer(s) have recommended publication, but also suggest some minor revisions to your manuscript. Therefore, I invite you to respond to the reviewer(s)' comments and revise your manuscript.

You can upload your revised manuscript and submit it through your Author Center. Log into http://mc.manuscriptcentral.com/app and enter your Author Center, where you will find your manuscript title listed under "Manuscripts with Decisions." Click on the Create a Revision link in the Action column to begin the revised submission process. Please submit your revision by 24-Dec-2008.

When submitting your revised manuscript, please respond to each of the comments made by the reviewer(s) in the space provided. You should use this space to document any changes you make to the original manuscript. Please review the attached document listing the file requirements for your revision.

IMPORTANT: We have your original files. When submitting (uploading) your revised manuscript, please delete the file(s) that you wish to replace and then upload the revised file(s).

Once again, thank you for resubmitting your manuscript to the Journal of Applied Polymer Science. I look forward to receiving your revision.

Sincerely,

Dr. Ed Elce
Associate Editor, Journal of Applied Polymer Science
eelce@sumitomobakelite.com

RHEOLOGICAL PROPERTIES IN RECYCLED CPE/NR BLENDS VULCANISED BY SULPHUR

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ABSTRACT

Blends of elastomeric chlorinated polyethylene (CPE) and natural rubber (NR) with blend composition ratio of 80/20 were prepared and recycled. Viscoelastic properties of the blends as a function of recycling cycles were monitored. Results obtained reveal that, with increasing recycling cycles, a noticeable change in viscoelastic properties could be observed, i.e., a decrease in elastic modulus (G') associated with a noticeable shift in T_g of NR phase of blends are observed, implying a molecular change in NR phase via thermal chain-scission mechanism. An influence of magnesium oxide (MgO) as an acid acceptor for CPE on viscoelasticity of blends is investigated. By reducing the amount of MgO, the major change is unexpectedly found in NR rather than CPE phases with similar manner to the increase in recycling cycles. It is proposed that changes in viscoelastic properties of blends by varying MgO loading and recycling cycle are attributed mainly to similar molecular mechanism of thermal degradation, i.e., molecular chain scission in NR phase.

Keywords: Rheology; Blends; Degradation; Viscoelastic properties; Recycling

1. Introduction

In the mid 1970s, the 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 various problems which mankind faces is the problem of waste disposal management. Since 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, gasification), chemical (depolymerisation) and material recycling [3-6].

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, [7-11] styrene-acrylonitrile, [12,13] and polyurethane[14,15].

From our previous work [16,17], up to 50 %wt CPE could be replaced by natural rubber (NR), and still gives phase morphology with NR phase dispersed in CPE matrix, leading to good oil and thermal ageing resistances of the blends similar to those of neat CPE. However, since a peroxide curing system is used in those work, both NR and CPE phases are vulcanised which ends up with lack of recyclability. Consequently, a sulphur curing system is utilised in 80/20 CPE/NR blends instead of peroxide. By this means, the NR phase in the blends could selectively be vulcanised [18-22], and therefore a recycling of such blends should, in theory, be possible. Therefore, the present study aims to extend our series of work by focusing mainly on recycling of CPE/NR blends with and without magnesium oxide (MgO) as an acid acceptor of CPE. Rheological properties of CPE/NR blends will be investigated.

2. Experimental

2.1 Materials

Details of materials used and blend formulations are shown in Table 1.

2.2 Mixing procedure

In the initial step, NR was masticated at 40 °C using a laboratory-size two-roll mill mixer (LabTech model LRM150, Thailand) to achieve Mooney viscosity (ML1+4 at 100 °C) of approximately 60. For blending process, CPE was melted on a front roll for 1 minute at the set temperatures of 145 °C and 140°C for the front and back rolls, respectively. Afterward, the masticated NR was charged and further mixed for 4 minutes. Compounding ingredients were, thereafter, added and mixed for 5 minutes prior to discharging. Finally, the blend was compression moulded into 1-mm-thick sheets under clamping pressure of 15 MPa at 155°C to achieve stage-of-cure of 99% as determined from the Rubber Process Analyzer (RPA2000, Alpha Technologies, USA), and designated as a "Virgin" blend.

For a recycling procedure, the virgin blend was cut into small pieces, and re-processed on two-roll mill under similar processing conditions to the virgin blends as described earlier. The blend discharged was denoted as "1st recycled blend". By repeating the recycling cycles, the 2nd, 3rd, 4th and 5th recycled blends were resulted.

2.3 Measurement of viscoelastic properties

Rheological study in this wok was carried out under oscillatory shear flow with the use of a parallel plate rheometer (Physica model MCR 500, Germany). A 25-mm rotor with grooved surface was used to prevent slippage between polymer melt and rotor surface. A disc specimen with approximately 25 mm in diameter and 1 mm in thickness was prepared from compression moulded sheets. All tests were performed at the test temperature of 170 °C. With the strain sweep test, a linear viscoelastic (LVE) region of materials at the frequency 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 to 100 rad/s was applied to the test sample. The results of elastic modulus (G'), loss modulus (G"), complex viscosity (η^*), damping factor (tanδ) and creep compliance were recorded.

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

3. Results and discussion

3.1 Effect of recycling cycles

In order to gain information on linear viscoelasticity of recycled CPE/NR blends, a strain sweep test is performed, and results obtained are illustrated in Figure 1. Clearly, a linear viscoelastic (LVE) region is apparently to be approximately 0.5 – 15% strain amplitude, regardless the recycling cycles. However, storage modulus (G') at low strain appears to be affected strongly by recycling cycles. Obviously, there are 3 main groups of G' results, i.e., (i) virgin and 1st recycled blends; (ii) 2nd and 3rd recycled blends; and (iii) 4th and 5th recycled blends. A reduction in G' implies a decrease in molecular elasticity of blends. Compared to CPE, NR phase possesses double bonds which are more prone to thermal oxidation, even with the presence of amine-based antioxidant [23]. By contrast, CPE contains no unsaturation and therefore is relatively difficult to be degraded via chain-scission process. Furthermore, the thermal degradation mechanism of CPE is more likely to be a dehydrochlorination process, which would lead to a rise in G' instead of a decrease in G' as illustrated in Figure 1 [24]. In order to support the proposed explanation, the time sweep test at high temperature of 170 °C was performed on neat CPE and NR, and results measured are exhibited in Figure 2.

Evidently, with increasing test duration, G' of neat CPE and NR increases and decreases, respectively, supporting the proposed explanation of Figure 1 that a reduction in G' with increasing recycling cycle is caused mainly by the occurrence of chain-scission in NR phase. This would lead to a decrease in molecular entanglement and thus elasticity (G'). In other words, the thermal degradation of CPE/NR blends is believed to be governed mainly by NR phase.

Damping factor (tanδ)results as shown in Figure 3 agree very well with the G′ results. The virgin and 1st recycled blends are classified as the group with the lowest tanδ implying the highest magnitude of elasticity via a high extent of molecular entanglement due to their good thermal stability. At high strain of deformation, the swing up of tanδ of such blends is relatively small, supporting the high degree of molecular entanglement as discussed earlier. By contrast, the group subjected to highly thermal history, i.e., 4th and 5th recycled blends, reveals the highest damping factor due to the highest degree of thermal degradation via molecular chain-scission of NR phase.

A dependence of G' on frequency is exhibited in Figure 4. It must be noted that the starting test frequency lower than 1 rad/s was not applicable in this work due to the fact that a long test duration required for collecting data would then affect thermal degradation of blends. In other words, at very low test frequency, the frequency effect will be interfered by the occurrence of thermal degradation during the test duration. Noticeably, all blends show increases in moduli with increasing frequency which are typical characteristics of viscoelastic materials. Referred to a spring-dashpot model, the higher the frequency, the lower the dashpot response due to the insufficient time for its response. Thus, the bulk response is dominated by a spring component rather than dashpot component as frequency increases. In terms of molecular aspect, the dashpot response is related directly to the occurrence of molecular relaxation via molecular flow (or molecular slippage). At high frequency, there is insufficient time available for molecular relaxation leading to an increase in elasticity. In addition, the sensitivity of G' to frequency slightly increases with increasing recycling cycles. It has previously been reported that the decrease in elastic behaviour of CPE/NR blends results in an increase of time-dependent behaviour [19,21,25]. Consequently, the results of frequency-dependent G' agree with the proposed explanation of molecular chain-scission.

In order to further explore change in viscoelastic properties affected by thermal history, a creep test was conducted. Figure 5 exhibits creep compliance at a function of time at a given shear stress. As expected, creep compliance increases with time for all blends. Also, rate of creep phenomenon is more evident in the blends with high magnitude of thermal experience. According to spring-dashpot model, creep is a result of dashpot response at very low test frequency that means a molecular flow. Thus, the blends with high recycling cycles would reveal high creep values attributed to a large amount of highly chain-scissioned molecules caused by thermal degradation. Notably, the result trends of blends with different recycling cycles are more apparent in the case of creep test, compared with the oscillatory test.