Alternatively, it could be stated that the molecular structure of polymers determined via rheological response is most sensitive at very low test frequency.

3.2 Effect of magnesium oxide (MgO)

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

Figure 6 illustrates an influence of MgO loading on G' under strain sweep test of 5th recycled blends. It is evident that, at any given strain amplitude of deformation, G' of blends reduces with decreasing MgO loading. Notably, the blend without MgO reveals relatively low G', compared to blends with MgO, implying relatively small magnitude of elasticity and thus poor thermal stability of this blend. Initially, it is anticipated that, by alternating MgO loading, the occurrence of thermal degradation via dehydrochlorination would be observed. A consequence of dehydrochlorination process in chlorinated polymer would generally yield a crosslink and thus a rise in stiffness (or G' in this case) as illustrated previously in Figure 2. However, the overall results of blends with various loadings of MgO reveal the opposite result trend, i.e., a decrease in G'. Based on the results obtained, it is hypothesized that the decrease in G' might deal with a molecular change of NR phase rather CPE phase.

In order to prove such proposed hypothesis, the DMTA test was performed, and the results of glass transition temperatures (T_g) in each phase of blends are summarized in Table 2. It is evident that, within the experimental error of 2 °C as an instrument temperature tolerance, values of T_g as determined from damping peaks of each phase is affected by MgO loading in different ways. It is apparent that the morphology of this blend system is a two-phase morphology with individual T_g. By decreasing MgO loading, T_g of NR phase significantly shifts to the lower temperature implying a molecular change of NR phase. On the contrary, T_g of CPE phase is almost unchanged by varied loading of MgO. The explanation is proposed as follows: with low loading of acid acceptor (MgO), a large amount of hydrochloric acid released from CPE dehydrochlorination reaction might cause acidity of the bulk, accelerating molecular change of NR phase via chain-scission mechanism. It is also noticeable that the trend of T_g shift to the lower temperature is similar to that found in blends with various recycling cycles as illustrated in Table 3. As discussed previously, by increasing thermal history, the NR phase with unsaturation structure is prone to be degraded leading to its greater molecular mobility and thus a shift in T_g to the lower temperature. This is, therefore, logical to state that changes in viscoelastic properties of blends by varying MgO loading and recycling cycle are attributed dominantly to similar molecular mechanism of thermal degradation, i.e., a molecular chain-scission in NR phase.

4. Conclusions

Blends of chlorinated polyethylene (CPE) and natural rubber (NR) at blend composition ratio of 80/20 were prepared and recycled. Changes in viscoelastic properties of blends by recycling were monitored. The following conclusions could be dawn from the results obtained:

1. With increasing recycling cycles, a decrease in blend elastic modulus associated with a noticeable shift in T_g of NR phase are observed. The results imply a molecular change in NR phase via thermal chain-scission mechanism.

2. By reducing the amount of magnesium oxide (MgO) as an acid acceptor for CPE, the major change is unexpectedly found in NR rather than CPE phases with similar manner to the increase in recycling cycles. It is therefore believed that changes in viscoelastic properties of blends by varying MgO loading and recycling cycle are attributed to similar molecular mechanism of thermal degradation, i.e., molecular chain scission in NR phase.

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Table captions

Table 1 Materials used in the present study

Table 2 Glass transition temperature (T_g) of CPE and NR phases in 5^{th} recycled CPE/NR blends

Table 3 Glass transition temperature (T_g) of CPE and NR phases in CPE/NR blends with various recycling cycles

Figure captions

Figure 1 Storage modulus (G′) as a function of strain amplitude at 1 rad/s CPE/NR blends with various recycling cycles

Figure 2 Storage modulus (G′) of neat CPE and NR as a function of test duration at 170 °C

Figure 3 Damping factor (tanδ) as a function of strain amplitude at 1 rad/s of CPE/NR blends with various recycling cycles

Figure 4 Storage modulus (G′) as a function of angular frequency at 10% strain of CPE/NR blends with various recycling cycles

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

Figure 6 Influence of MgO loading on storage modulus (G′) as a function of strain amplitude at 100 rad/s in 5th recycled blends

Material	Manufacturer/supplier	Functionality	Amount (phr)
Chlorinated polyethylene (CPE; Tyrin 702P)	DuPont Dow Elastomer Co., Ltd, USA	Raw polymer	80
Natural rubber (NR; STR20)	Thailand	Raw polymer	20
Stearic acid (Commercial grade)	Polychem Co., Ltd, Thailand	Cure activator	2
Magnesium oxide (MgO, Commercial grade)	Boonthavorn Co., Ltd, Thailand	Cure activator and acid acceptor	Variable[a]
Sulphur (Commercial grade)	Siam Chemicals Co., Ltd, Thailand	Curing agent	2
Santocure TBBS[b]	Flexsys Co., Ltd, USA	Cure accelerator	1
Santoflex IPPD[c]	Flexsys Co., Ltd, USA	Antioxidant	4
Santogard PVI[d]	Flexsys Co., Ltd, USA	Prevulcanisation inhibitor	1

Footer of Table 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

MgO loading (phr)	Glass transition temperature (°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

Recycling cycle	Glass transition temperature (°C)	
	NR phase	CPE phase
Virgin	-40.4	-0.8
1st	-38.4	-0.8
2nd	-53.3	-0.6
3rd	-54.8	-0.5
4th	-53.2	-0.7
5th	-51.0	-0.8

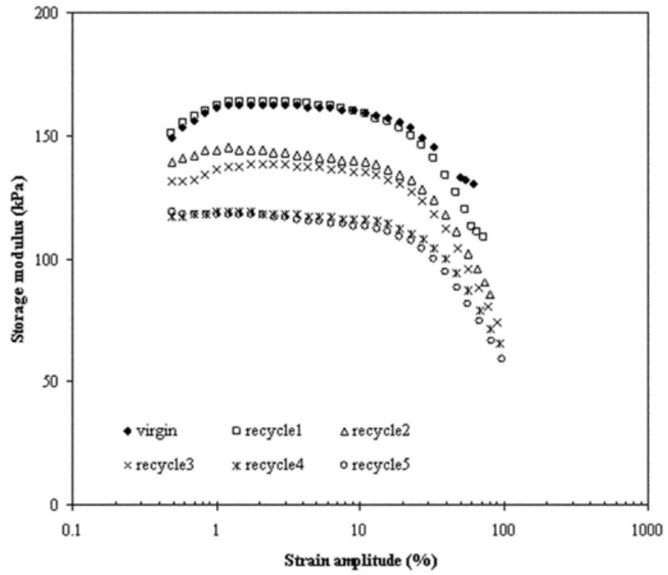

Fig. 1 Storage modulus (G') as a function of strain amplitude at 1 rad/s CPE/NR blends with various recycling cycles
112x99mm (600 x 600 DPI)

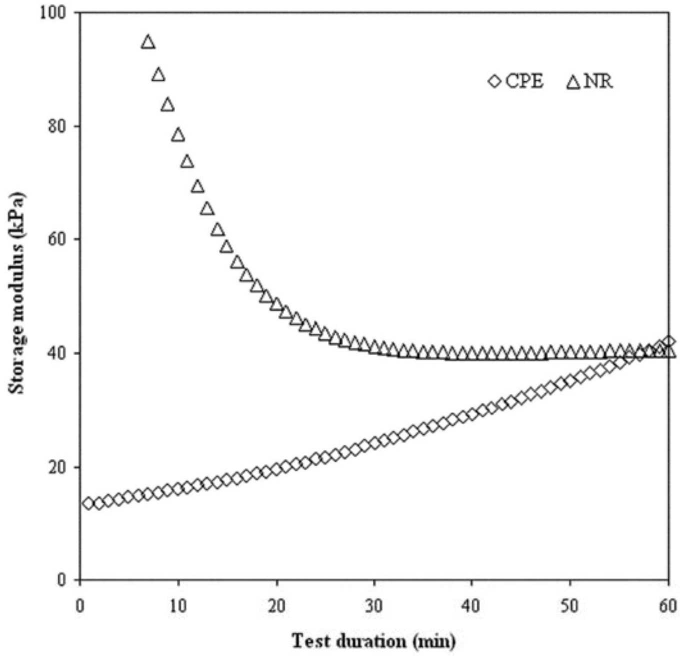

Figure 2 Storage modulus (G′) of neat CPE and NR as a function of test duration at 170 C
123x120mm (600 x 600 DPI)

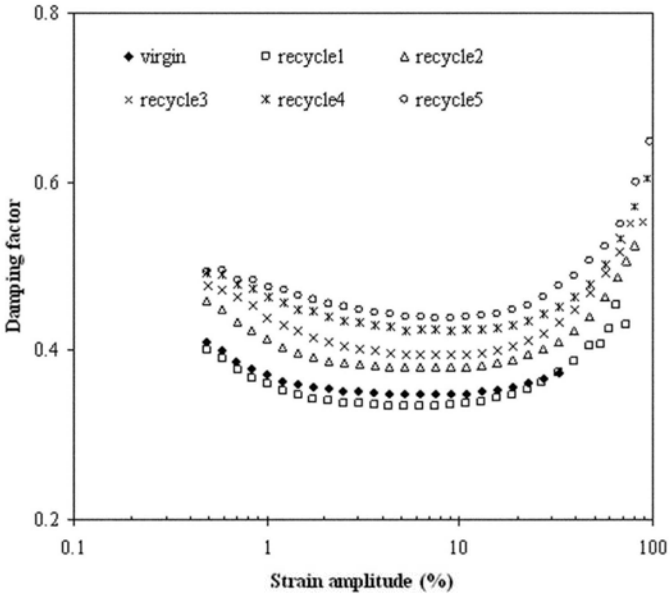

Figure 3 Damping factor (tanδ) as a function of strain amplitude at 1 rad/s of CPE/NR blends with various recycling cycles
116x106mm (600 x 600 DPI)

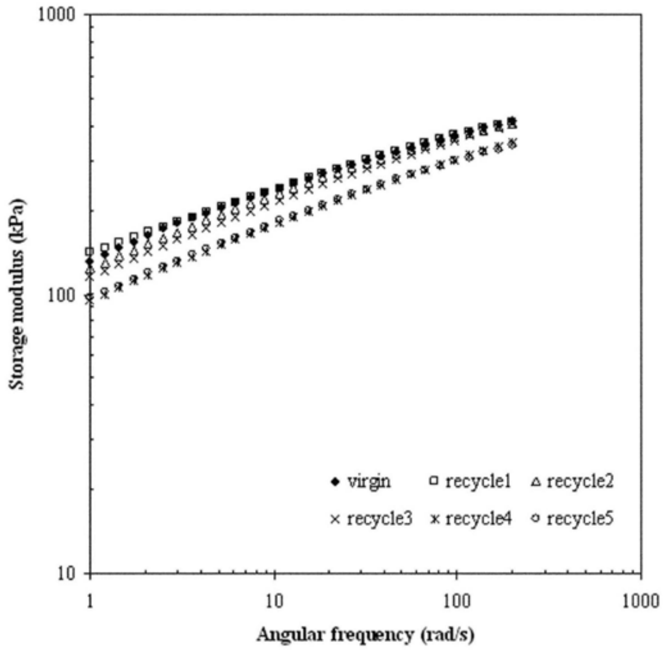

Figure 4 Storage modulus (G′) as a function of angular frequency at 10% strain of CPE/NR blends with various recycling cycles
125x123mm (600 x 600 DPI)

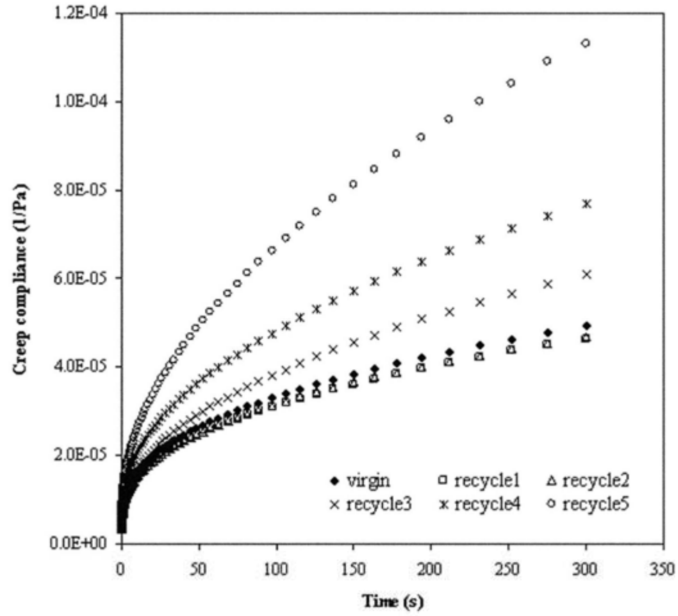

Figure 5 Creep compliance of CPE/NR blends with various recycling cycles
121x115mm (600 x 600 DPI)

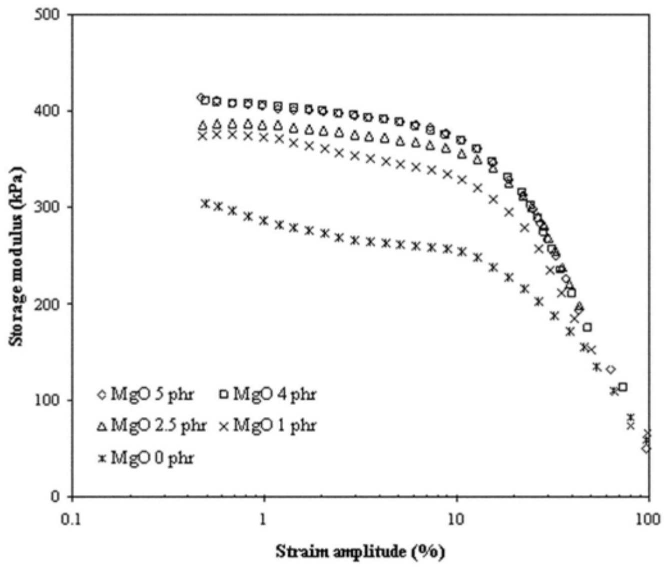

Figure 6 Influence of MgO loading on storage modulus (G′) as a function of strain amplitude at 100 rad/s in 5th recycled blends
111x97mm (600 x 600 DPI)

เรื่องที่ 5

P. Wongwitthayakool, P. Sae-oui, C. Sirisinha, Rheological properties of chlorinated polyethylene blended with low-cost grade natural rubber, International Polymer Processing (accepted with revision)

RHEOLOGICAL PROPERTIES OF CHLORINATED POLYETHYLENE BLENDED WITH LOW-COST GRADE NATURAL RUBBER

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ABSTRACT

A low-cost grade natural rubber (STR20 NR) was used for partly substituting elastomeric chlorinated polyethylene (CPE) and cured by sulfur. Rheological properties of blends with various blend composition ratio under oscillatory and steady shear flows were investigated. Cure behavior is found to be promoted by increasing NR content. Viscoelastic behavior of CPE/NR blends as determined from the Rubber Process Analyzer (RPA2000) is controlled strongly by blend composition. Uncured blends show relatively poor storage modulus associated with high damping factor probably due to the thermal degradation of NR phase. By contrast, after curing NR phase in blends, bulk rheological properties change remarkably. Blends with NR as a major component reveal frequency-independent with broad linear viscoelastic (LVE) region. Flow properties under capillary shear of uncured blends agree well with those under oscillatory shear, i.e., the greater the NR content, the lower the apparent shear viscosity. Surprisingly, even without the elimination of elastic effect by the Bagley correction, it is still possible to superimpose plots of complex viscosity against test frequency over those of apparent shear viscosity against wall shear rate, which are different from the rheological properties of CPE blended with premium grade of NR (STR5L).