Keywords: Rheology, Viscoelastic properties, Chlorinated polyethylene, Natural rubber, Blends

1. INTRODUCTION

Blending is known to be one of effective techniques to achieve desired properties of final products, and product cost could sometimes be reduced by blending one polymer with another low-cost polymer. Apart from mechanical properties, rheological properties including shear viscosity and elasticity of polymer melts are known to be crucial for polymer processing. There are generally factors affecting rheological properties in polymer melts, e.g. nature of the polymers and their blend composition [1-6] as well as blending conditions [7-8]. In addition, if filled blends are concerned, the uneven distribution of filler in each phase of the blends is reported to affect significantly the mechanical properties of elastomeric blends. [9-11].

Chlorinated polyethylene (CPE) is widely used in applications requiring high resistances to hydrocarbon oil, heat and weathering, which are mainly attributed to the saturated structure and the presence of chlorine atoms on the molecular backbone. In order to achieve desired properties of CPE-based products, CPE has been blended with various polymers including polyvinyl chloride (PVC) [12-15], styrene-acrylonitrile (SAN) [16-17] and polyurethane (PU) [18-19] and natural rubber (NR) [5-6,8,11, 20-22].

Referred to our previous work [5,6,8,11,20-22], it has been reported that a certain amount of CPE could be substituted by NR, giving similar tensile properties to neat CPE, depending on curing systems used for vulcanizing NR phase in blends. In addition, it has been found that viscoelastic properties of CPE/NR blends are governed strongly by curing of NR phase as well as by adding silica to the blends. However, in those work, a premium grade of NR (i.e., STR5L NR) were used in order to minimize complexity of the blend systems which might be affected by a large amount of dirt and non-rubber substances such as protein and fatty acid. Therefore, the present work aims to further reduce a product cost by the use of low-cost grade NR (i.e., STR20 NR) containing a larger amount of dirt and non-rubber substances than the STR5L NR. Cure and viscoelastic behaviors will be discussed.

2. EXPERIMENTAL

2.1 Materials

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

2.2 Mixing procedure

Referred to our previous work [5], CPE/NR blend composition 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 140 and 135 °C for front and back rolls, respectively.

Initially, CPE was allowed 1 minute for melting, and NR was then charged. After blending for 4 minutes, curatives and antioxidant were added to the blends and mixing was carried on for 5 minutes before discharging. The blends were, finally, compression molded into 1-mm thick sheets under pressure of 15 MPa at 155°C. Cure time used was determined from the Rubber Process Analyzer (RPA 2000, Alpha Technologies, USA).

2.3 Measurement of viscoelastic properties

In order to investigate cure behavior of blends, the Rubber Process Analyzer (RPA2000, Alpha Technologies, USA) was utilized according to ASTM D2084 at 155 C. Scorch time (t_{s2}) was and determined from time to achieve torque rise of 2 units above the minimum torque. Cure time used in the present work is the time to reach 90 % cure or t_{c90}.

Viscoelastic properties of blends were measured under 2 different modes of shear, namely, oscillatory and steady shear flow, with the uses of a Rubber Process Analyzer (RPA2000, Alpha Technologies, USA) and a rate-controlled capillary rheometer (Goettfert Rheotester 2000, Germany).

In the case of oscillatory shear flow with RPA2000, the measurement was performed at test temperatures of 170 and 50 °C for uncured and cured blends, respectively. A linear viscoelastic (LVE) region of the blends was initially determined at the test frequencies of 1 and 100 rad/s. Thereafter, the frequency sweep test was performed using the strain within the LVE region.

For the rate-controlled capillary rheometer, an apparent shear stress as a function of apparent shear rate was determined using three dies with different lengths over diameter of 10/2, 20/2 and 30/2.

3. RESULTS AND DISCUSSION

3.1 Cure behavior

In CPE/NR blends, only NR phase is capable of sulfur curing due to the presence of double bonds in NR molecules. Consequently, the cure behavior observed would solely be attributed to the response of NR phase.

Figs. 1 and 2 illustrate cure behavior of blends with various NR content. It is evident that scorch time and cure time decrease as NR content increases which are believed to be due to the migration of curatives from CPE to NR phase. Curatives is relatively polar and therefore more soluble in CPE than NR phase. As NR content increases, the amount of CPE is simultaneously decreased, leading to a reduction in solubility of curatives in CPE phase. As a consequence, the migration of curatives from CPE to NR phase takes place giving a cure promotion of NR phase. Also, a short scorch time is considered as a poor process safety, and needed to be lengthened. In the present work, the prevulcanization inhibitor or PVI was used for a scorch delay purpose. It can be seen from Fig. 1 that, as expected, scorch time could significantly be increased by PVI addition. It is known that PVI could react stoichiometrically with cure accelerator, and delay vulcanization until all PVI is consumed. In addition, a magnitude of delay is more obvious in the blends with low NR content. This implies that the PVI might be soluble in NR phase rather than CPE phase. In the blends with low NR content, the concentration of PVI in NR phase is high and therefore could effectively delay cure of NR phase.

In the case of crosslink density as determined from torque differences from cure curves, Fig. 3 shows that the crosslink density increases with increasing NR content which is due to the curative migration effect as discussed previously. Also, the addition of 0.5 phr PVI appears to increase crosslink density of NR phase in blends. Further increase in PVI concentration gives no significant change in crosslink density.

3.2 Oscillatory shear flow

3.2.1 Uncured blends

Generally, viscoelastic behavior of polymer under molten state would give informative data on processability. Thus, in the present work, viscoelasticity of uncured blends were determined using the RPA2000 at test temperature of 170 C at which CPE matrix could flow freely.

Results of strain sweep test at various blend ratio are shown in Fig. 4. It can be seen that storage modulus, or usually known as elastic modulus (G'), depends strongly on strain of deformation. At low strain, each blend ratio exhibits a region with strain-independent G' which is usually known as a linear viscoelastic (LVE) region. According to the spring-dashpot model, with the strain in LVE region, molecular entanglement leads to a dominant spring response. At strain greater than the critical strain (γ_c), molecular slippage taking place causes a sharp decrease in G'. With increasing NR content, there is no significant difference in broadness of LVE region. Also, it is evident that the blends with high NR content possess low G' which is caused by a thermal-oxidative degradation of NR phase during blending at high set temperature of 140 C. Notably, the actual batch temperature is much higher than the set temperature caused by shear heating. It is known that NR is prone to thermal degradation due to the presence of unsaturation on its backbone. Similar observation is reported elsewhere [5].

Fig. 5 illustrates the results of damping factor (tanδ). Clearly, all blends show a strong swing up of damping factor at high strain which is due to the energy dissipation via a molecular slippage. In addition, the damping factor is apparently not sensitive to the blend composition ratio, implying that, at high temperature of 170 C, both CPE and NR phases possess similar magnitude of energy dissipation per cyclic deformation of a volumetric unit of rubber.

Regarding the frequency-dependent viscoelasticity of uncured blends, Fig. 6 exhibits an obvious increase in G' as angular frequency increases. Based on the spring-dashpot model, it is known that the deformation in dashpot component is time-dependent. Consequently, a sharp increase in G' with test frequency implies insufficient time for a response of dashpot component to the test frequency, and therefore spring component takes control of the bulk viscoelastic response. In other words, with increasing test frequency, there is insufficient time for molecular relaxation via molecular flow, leading to an increase in elastic energy via molecular entanglement. The blends with relatively high NR content gives relatively low G' associated with high damping factor (see Fig. 7) at any test frequency due to a thermal degradation of NR phase as discussed previously.

3.2.2 Cured blends

In the case of viscoelastic properties of cured blends at 50 C (which is referred to be a service temperature of final products), it is found that similar trend of G' to those at 170 C (see Fig. 4) could be observed, i.e., G' decreases with NR content. Notably, the damping factor results as shown in Fig. 8 illustrate clearly an almost frequency-independent behavior in the blends with a large amount of NR. Also, these blends with NR as a major component show relatively low damping factor. Undoubtedly, the presence of sulfidic linkages as chemical crosslinks in NR phase is responsible for the results. It is known that the molecular restriction via chemical crosslink is analogous to the spring response, and therefore is not affected by deformation strain (i.e., the LVE region is broadened). In addition, the results of damping factor are in good accordance with those of crosslink density as illustrated previously in Fig. 3. With increasing NR content in blends, the crosslink density increases, leading to a reduction damping factor of these blends.

Figs. 9 and 10 exhibits the outstanding role of sulfidic linkages on viscoelastic properties as a function of test angular frequency. Obviously, G' and tanδ of the blends with cured NR as a major component is almost independent of test frequency. The is a strong evidence that the viscoelastic properties of these blends is governed mainly by a spring component. By contrast, the blends with CPE as a major component still show sharp dependence of viscoelasticity on test frequency. The higher the frequency, the higher the G' due to the insufficient time for viscous or dashpot response (i.e., molecular relaxation). A relatively low damping factor in blends with a relatively high content of cured NR phase is attributed to a limited molecular flow and thus a small magnitude of energy loss per cyclic deformation of a volumetric unit of rubber.

3.3 Steady shear flow

Since a rate-controlled capillary rheometer was utilized to determine flow properties under steady shear flow of CPE/NR blends, only uncured blends could be characterized. Apparently, Fig. 11 shows that all blends exhibit a strong pseudoplastic behavior (i.e., shear viscosity decreases with increasing shear rate) due to molecular disentanglement at high shear rate. Furthermore, shear viscosity of blends decreases with increasing NR content which could be explained by a decrease in molecular weight via thermal degradation of NR phase during blending at high temperature as discussed previously.

In order to correlate the oscillatory to the steady shear results, the Cox and Merz's concept (i.e., a complex viscosity as a function of frequency is equivalent to an apparent shear viscosity as a function of shear rate) was applied to the rheological data obtained, and the results are shown in Fig. 12. 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 STR5L reported elsewhere [6]. Phewthongin and co-workers found that the oscillatory and steady shear results could be superimposed only if the elastic effect was removed from the results with the uses of dynamic viscosity and Bagley correction. Also, it has been reported that the blends with STR5L NR as a major component still exhibit slightly greater values of shear viscosity determined from oscillatory rheometer. The results illustrate that the rheological responses of CPE blended with STR5L NR are different from those with relatively low-cost STR20 NR to some extent. A possible explanation of discrepancy in rheological behavior of the blends with premium and low-cost grades of NR is proposed in terms of lubricating effect. It is known that non-rubber substances in NR include natural fatty acids whose is larger in low-cost grade NR. Such fatty acids could act as internal lubricants. This would lead to a promotion of molecular flow and thus viscous response.

4. CONCLUSIONS

Elastomeric blends of CPE and a low-cost grade NR (STR20 NR) with various blend composition ratios were prepared, and their rheological behavior were investigated with the uses of oscillatory and steady shear rheometers. The following conclusions could be drawn. The use of low-cost NR possessing a relatively large amount of dirt and non-rubber substances shows poor scorch safety which could be overcome by the addition of prevulcanization inhibitor (PVI). Scorch and cure times are found to be affected strongly by NR content. In the blends with low NR content, their viscoelastic properties are dominated by viscous response, i.e., the time-dependent viscoelastic properties of CPE matrix. By contrast, as NR content increases, NR with sulfidic linkages becomes a matrix exhibits a strong elastic response with time-independent behavior. Unexpectedly, 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 a premium grade NR (STR5L).

5. ACKNOWLEDGEMENTS

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Figure Captions

Fig. 1 Influences of blend composition ratio and PVI concentration on scorch time (t_{s2}) of blends at cure temperature of 155°C

Fig. 2 Influences of blend composition ratio and PVI concentration on cure time (t_{c90}) of blends at cure temperature of 155°C

Fig. 3 Crosslink density in terms of torque difference (ΔS) as a function of NR content with various PVI concentrations at cure temperature of 155°C

Fig. 4 Storage modulus (G') as a function of strain amplitude of uncured blends with various blend composition ratios at test temperature of 170°C

Fig. 5 Damping factor (tanδ) as a function of strain amplitude of uncured blends with various blend composition ratios at test temperature of 170°C

Fig. 6 Frequency-dependent storage modulus (G') of uncured blends with various blend composition ratios

Fig. 7 Frequency-dependent damping factor (tanδ) of uncured blends with various blend ratios

Fig. 8 Damping factor (tanδ) as a function of strain amplitude of cured blends with various blend composition ratios at test temperature of 50°C

Fig. 9 Frequency-dependent storage modulus (G') of cured blends with various blend composition ratios

Fig. 10 Frequency-dependent damping factor (tanδ) of cured blends with various blend composition ratios

Fig. 11 Apparent shear viscosity curves of CPE/NR uncured blends with various blend composition ratios

Fig. 12 Plots of complex viscosity determined from RPA2000 (◆) and apparent shear viscosity measured by capillary rheometer (◇) as a function of frequency or shear rate in uncured CPE/NR blends with various blend composition ratios: 100/0 (a); 80/20 (b); 50/50 (c); 20/80 (d); 0/100 (e)

Table 1 Materials used in the present study

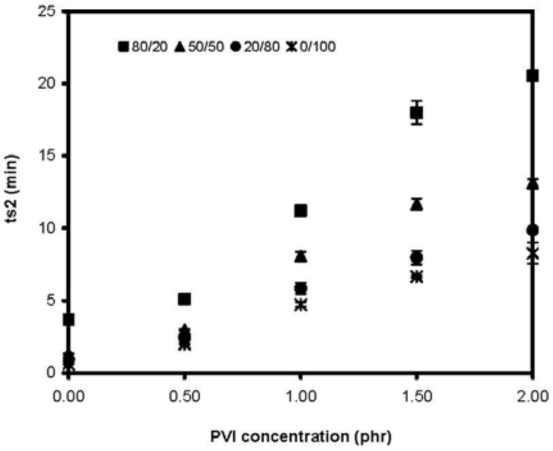
Material/grade	Manufacturer/Supplier	Amount (phr)	Remarks
Chlorinated polyethylene (CPE; Tyrin 702P)	DuPont Dow Elastomer Co., Ltd., USA	a	Raw polymer
Natural rubber (NR) / STR20	Union Rubber Products Co., Ltd., Thailand	a	Raw polymer
Magnesium oxide (MgO) / Starmag#150	Petch Thai Chemical Co. Ltd., Thailand	5	Acid receptor
Stearic acid / Commercial grade	Polychem Co. Ltd., Thailand	2	Cure activator
Santoflex / i-PPD[b]	Flexsys Co. Ltd., Belgium	4	Antioxidant
Santocure / TBBS[c]	Flexsys Co. Ltd., Belgium	1	Cure accelerator
Ordinary sulfur / Commercial grade	Siam Chemicals Co. Ltd., Thailand	2	Curing agent
Santogard / PVI[d]	Flexsys Co. Ltd., Belgium	1	Prevulcanization inhibitor

a = CPE:NR by weight of 100:0, 80:20, 50:50, 20:80 and 0:100

b = N-Isopropyl-N'-phenyl-phenylenediamine

c = N-t-butyl-2-benzothiazolesulfenamide

d = N-(Cyclohexylthio)phthalimide



■ 80/20 ▲ 50/50 ● 20/80 ✱ 0/100
ts2 (min)
25
20
15
10
5
0
0.00
0.50
1.00
1.50
2.00
PVI concentration (phr)

Fig. 1

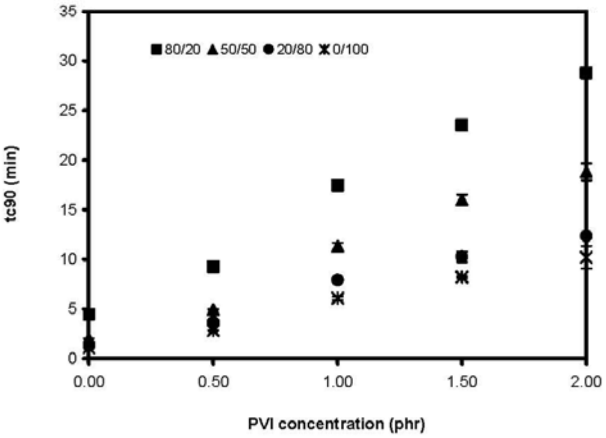

■ 80/20 ▲ 50/50 ● 20/80 ✱ 0/100
tc90 (min)
0
5
10
15
20
25
30
35
0.00
0.50
1.00
1.50
2.00
PVI concentration (phr)

Fig. 2

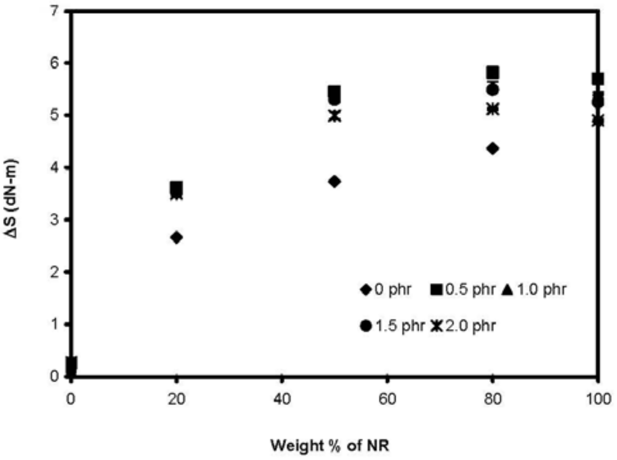

ΔS (dN-m)
0
1
2
3
4
5
6
7
0
20
40
60
80
100
Weight % of NR
◆ 0 phr
■ 0.5 phr
▲ 1.0 phr
● 1.5 phr
✱ 2.0 phr

Fig. 3

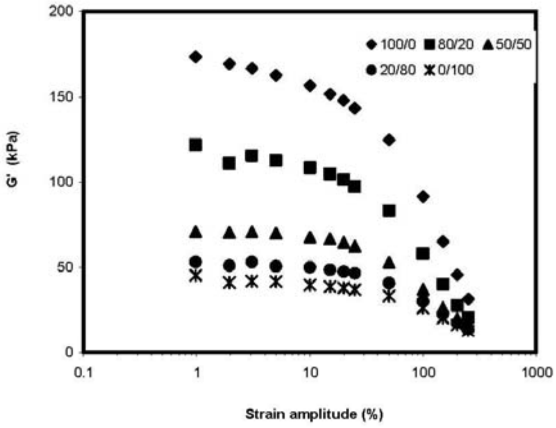

200
150
100
50
0
G' (kPa)
0.1
1
10
100
1000
Strain amplitude (%)
◆ 100/0
■ 80/20
▲ 50/50
● 20/80
✱ 0/100

Fig. 4

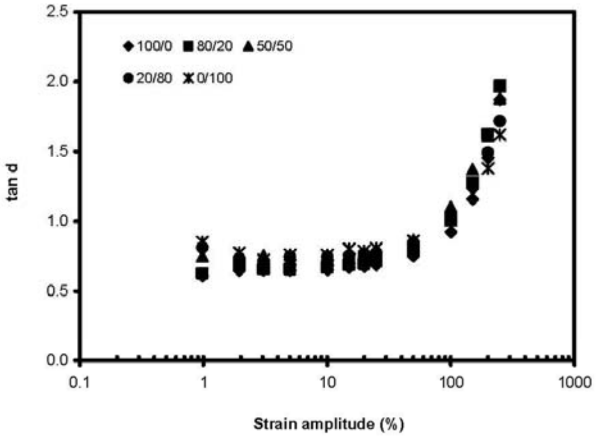

2.5
2.0
1.5
1.0
0.5
0.0
tan d
◆ 100/0
■ 80/20
▲ 50/50
● 20/80
✱ 0/100
0.1
1
10
100
1000
Strain amplitude (%)

Fig. 5

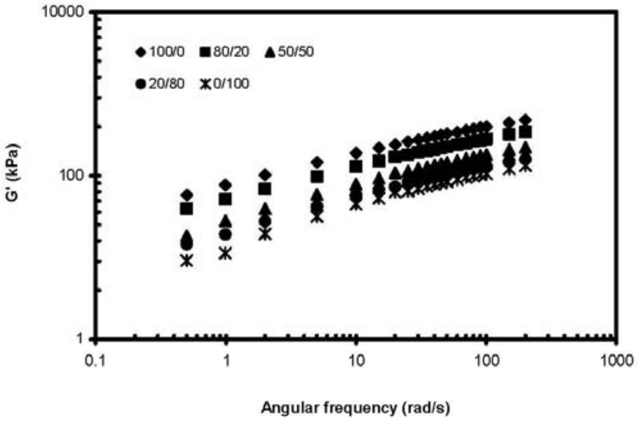

10000
100
1
0.1
1
10
100
1000
G' (kPa)
Angular frequency (rad/s)
◆ 100/0
■ 80/20
▲ 50/50
● 20/80
✱ 0/100

Fig. 6

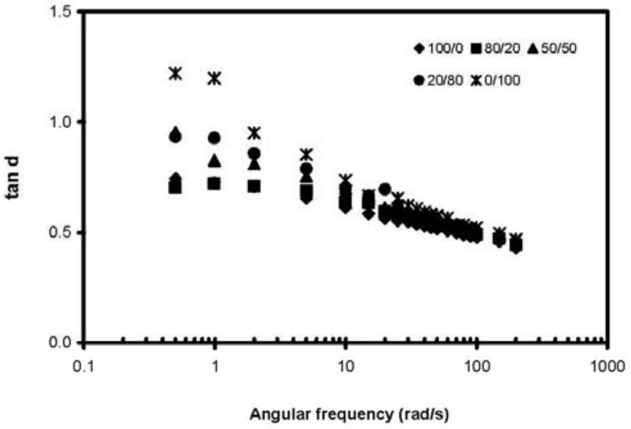

1.5
1.0
0.5
0.0
tan d
0.1
1
10
100
1000
Angular frequency (rad/s)
◆ 100/0 ■ 80/20 ▲ 50/50
● 20/80 ✱ 0/100

Fig. 7

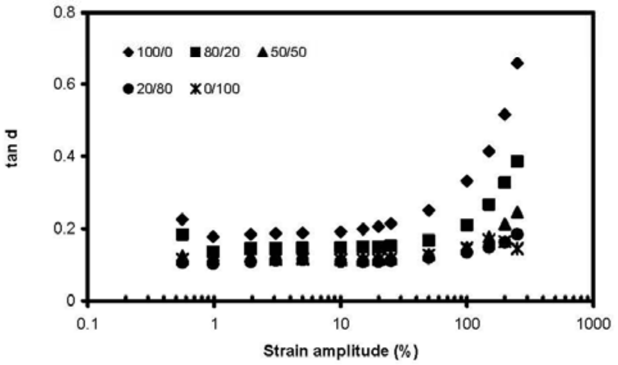

0.8
0.6
0.4
0.2
0
tan d
◆100/0
■80/20
▲50/50
●20/80
✱0/100
0.1
1
10
100
1000
Strain amplitude (%)

Fig. 8

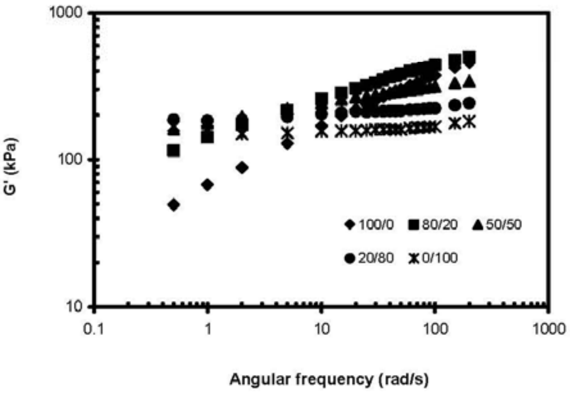

1000
100
10
G' (kPa)
0.1
1
10
100
1000
Angular frequency (rad/s)
◆ 100/0
■ 80/20
▲ 50/50
● 20/80
✱ 0/100

Fig. 9

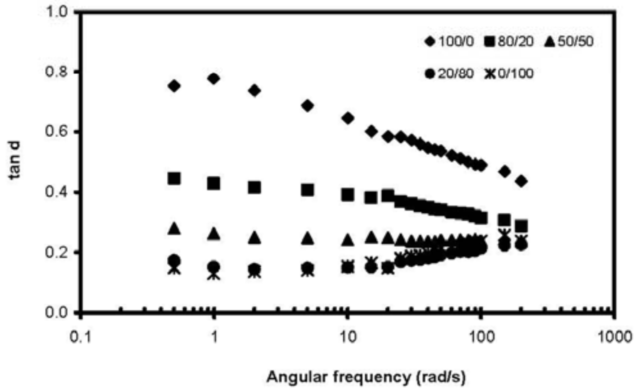
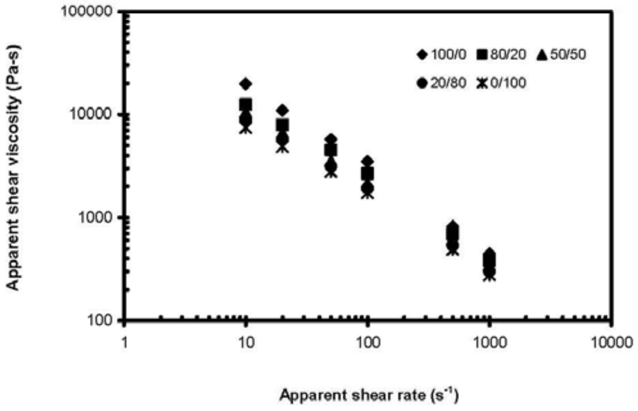
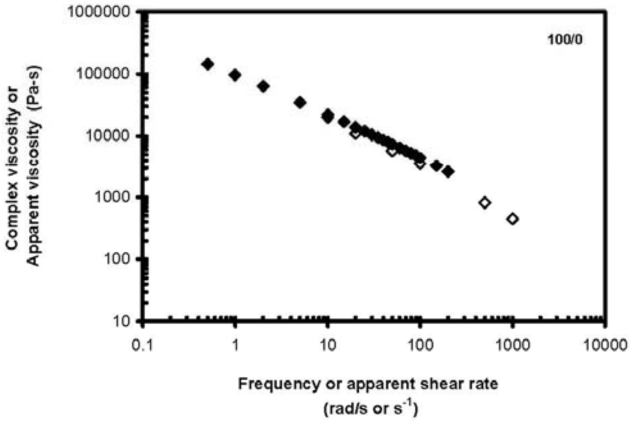

1.0
0.8
0.6
0.4
0.2
0.0
tan d
0.1
1
10
100
1000
Angular frequency (rad/s)
◆100/0 ■80/20 ▲50/50
●20/80 ✱0/100

Fig. 10

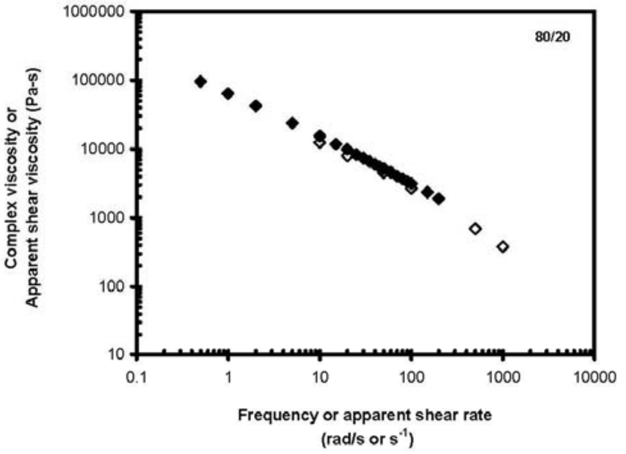


◆ 100/0 ■ 80/20 ▲ 50/50
● 20/80 ✱ 0/100
Apparent shear viscosity (Pa-s)
100000
10000
1000
100
1
10
100
1000
10000
Apparent shear rate (s^{-1})

Fig. 11

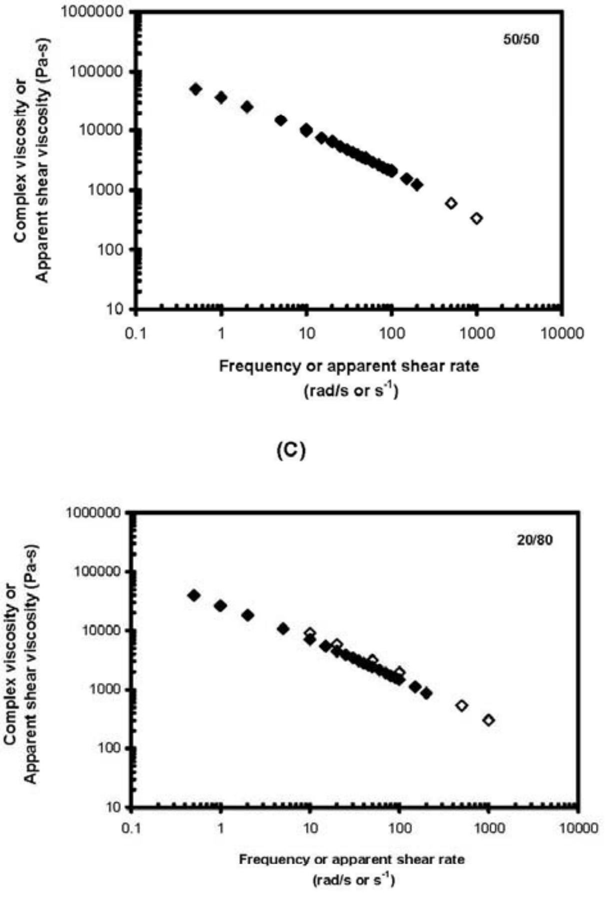

100/0
Complex viscosity or Apparent viscosity (Pa-s)
1000000
100000
10000
1000
100
10
0.1
1
10
100
1000
10000
Frequency or apparent shear rate (rad/s or s^{-1})

(a)


80/20
Complex viscosity or Apparent shear viscosity (Pa-s)
1000000
100000
10000
1000
100
10
0.1
1
10
100
1000
10000
Frequency or apparent shear rate (rad/s or s^{-1})

(b)

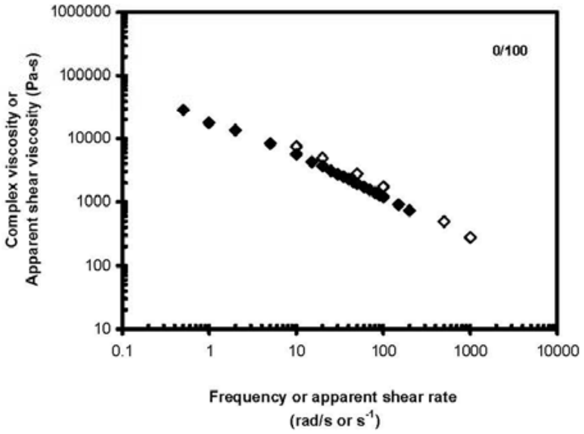
Fig. 12



(C)

(d)

Fig. 12 (Continued)



(e)

Fig. 12 (Continued)