

Rheological Behavior of CPE/NR Blends Filled with Precipitated Silica

Nilobon Phewthongin,¹ Pongdhorn Saeoui,² Chakrit Sirisinha^{1,3}

¹Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

²National Metal and Materials Technology Center, Klong Luang, Pathumthani 12120, Thailand

³Rubber Research Unit, Faculty of Science, Mahidol University, Salaya, Nakhon Pathom 73170, Thailand

Received 26 February 2005; accepted 4 July 2005

DOI 10.1002/app.22550

Published online 2 February 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Blends of elastomeric chlorinated polyethylene (CPE) and natural rubber (NR) at the blend composition ratio of 80/20 CPE/NR with various precipitated silica loadings from 0 to 30 phr were prepared. Their rheological behaviors were determined using two rheometers with different shear modes, i.e., the oscillatory rheometer (Rubber Process Analyzer, RPA2000) and the rate-controlled capillary rheometer (Goettfert Rheotester 2000). Results obtained reveal that the viscoelastic behavior of blends is influenced remarkably by loadings of silica. Within the oscillatory shear strains of 0.3–30%, the unfilled blend appears to be almost insensitive to shear strain that means the unfilled blend possesses a broad linear viscoelastic (LVE) region. As silica is incorporated, the elastic modulus (G') of blends increases, particularly at silica loadings of 20 and 30 phr. The increase in G' as a function of silica loading could be explained by a reinforcing effect via a hydrodynamic effect as well as a strong interaction between chlorine atoms on CPE molecules

and silanol functional groups on silica surfaces associated with a formation of silica tridimensional transient network, usually known as a secondary filler network. Also, all blends with various loadings of precipitated silica reveal an increase in elasticity with increasing frequency, and those with high silica loadings (i.e., 20 and 30 phr) give a more time-independent elastic response, which supports the presence of filler transient network in these blends. By applying the Cox and Merz concept to the rheological results, the superimposition of flow curves determined from the oscillatory shear flow and steady shear flow in the highly silica filled blends is possible if the silica transient network effect is eliminated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2565–2571, 2006

Key words: rheological properties; chlorinated polyethylene; natural rubber; polymer blends; filler

INTRODUCTION

Rheological behavior of polymers is one of important factors affecting processability and properties of final products. It has been reported that flow behavior of polymer melts depends mainly on molecular characteristics,^{1–5} flow geometry,^{6–9} and processing conditions,^{1–3,10,11} such as temperature, shear rate, or frequency. In addition, in the case of polymer blends, rheological properties of polymer blends have been known to rely on many variables, such as nature of polymers, molecular weight and its distribution,^{12,13} blend compositions, the interactions among components including interfacial tension,^{14–16} and blend morphology.^{14–20}

Chlorinated polyethylene (CPE) is widely known for its 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. According to the published work, CPE has been blended with various polymers including polyvinyl chloride (PVC),^{21–24} styrene-acrylonitrile (SAN),^{25,26} and polyurethane (PU)^{27,28} so as to achieve desired properties. Compared to natural rubber (NR), CPE is more expensive and therefore blending CPE with NR is applicable for reducing the production cost of final products requiring CPE properties. Referred to our previous work,^{29–31} 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, in terms of rheological properties of CPE/NR blends, Phewthongin et al.³² found that without the vulcanization of NR phase in blends, the elastic modulus of blends depends strongly on test frequency, mainly because of the viscous response. By contrast, after curing of NR phase in blends, the blends with NR as a matrix demonstrate the time-independent elastic modulus, while those with CPE as a matrix still reveal the time-dependent elastic modulus to some extent depending on NR composition ratio. Recently, a clear evidence of reinforcing effect provided by precipitated silica in

Correspondence to: C. Sirisinha (sccsr@mahidol.ac.th).

Contract grant sponsor: Thailand Research Fund (TRF).

TABLE I
Materials Used in the Present Study

Material	Manufacturer/supplier	Amount (phr)	Remarks
Chlorinated polyethylene (CPE; Tyrin 702P)	DuPont Dow Elastomer, USA	80	Raw polymer
Natural rubber (NR; STR5)	Union Rubber Products Co., Ltd., Thailand	20	Raw polymer
Precipitated silica (HiSi1233)	PPG-Siam Silica, Thailand	Varied	Reinforcing filler
Magnesium oxide (MgO; Starmag no. 150)	Boonthavorn Co., Ltd., Thailand	5	Acid receptor
Santoflex 6-PPD ^a	Flexsys, USA	4	Antioxidant

^a *N*-(1,3-dimethylbutyl)-*N'*-phenylenediamine.

CPE/NR blends has been reported, which is explained by a strong interaction between chlorine atoms of CPE and silanol functional groups of silica.³³ Therefore, it is interesting to further the investigation of silica-reinforced CPE/NR blends by focusing on the rheological properties, which is a main objective of the present study. Results measured from two different modes of shear flow, namely, oscillatory and steady shear flow will be discussed.

EXPERIMENTAL

Materials

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

Mixing procedure

Referred to our previous work,³⁰ the CPE/NR blend composition ratio of 80/20 was used for the study, as this blend ratio provides comparable properties to neat CPE with a relatively low product cost. Initially, the premix of NR and antioxidant (6-PPD) was prepared using a laboratory-size internal mixer equipped with Banbury rotors (Brabender Plasticorder, Germany) at the mixing temperature of 55°C to minimize the thermal degradation of NR during blending with CPE. Blending of CPE and NR was also carried out in the Brabender internal mixer at set temperature, rotor speed, and fill factor of 140°C, 30 rpm, and 0.7, respectively. Detail of mixing sequence is illustrated in Table II.

Measurement of rheological properties

Rheological properties of blends were measured using the Rubber Process Analyzer (RPA2000, Alpha Technologies) and a rate-controlled capillary rheometer (Goettfert Rheotester 2000) at the test temperature of 170°C. As for the RPA2000, the 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. In the case of rate-controlled capillary rheometer, an apparent shear stress as a function of apparent shear rate was determined using three dies with a similar die diameter of 2 mm, but different lengths of 10, 20, and 30 mm. To eliminate end effect and to compensate the flow pattern of non-Newtonian melt, the Bagley and the Rabinowitsch corrections were applied to the apparent data, yielding true shear viscosity and corrected shear rate, respectively.²

RESULTS AND DISCUSSION

Referred to our previous work,³² two modes of shear deformation were applied to samples, namely, oscillatory shear flow and steady shear flow. Rheological results based on each mode of shear deformation will be discussed and correlated, as follows.

Oscillatory shear flow

Results of linear viscoelasticity of blends with various silica loadings are illustrated in Figure 1. It is evident that, within the test strains applied to the blends (i.e., 0.3–30%), the unfilled blend appears to be almost insensitive to shear strain that means the unfilled blend possesses a broad LVE region. As precipitated silica

TABLE II
Mixing Sequence Used in the Present Study

Time (min)	Action
0	Add CPE
1	Add 6-PPD premixed NR
2	Add precipitated silica
Varied ^a	Discharge the blends

^a Blends were discharged at 3 min after the occurrence of mixing peak.

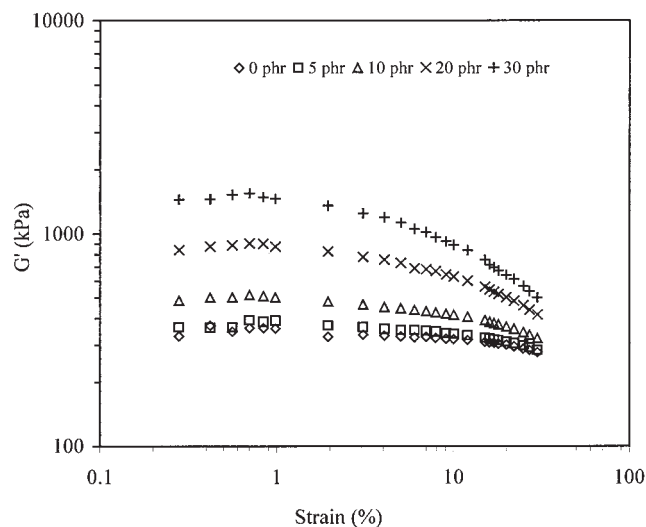


Figure 1 Strain sweep test of CPE/NR blends filled with various silica loadings at a test frequency of 10 rad/s.

with a relatively large specific surface area of ~ 145 m^2/g is filled, the elastic modulus (G') of the blends increases, particularly at silica loadings of 20 and 30 phr. The increase in G' as a function of silica loading could be explained by a reinforcing effect via a hydrodynamic effect as well as a strong interaction between chlorine atoms on CPE molecules and silanol functional groups on silica surfaces associated with a formation of silica tridimensional transient network, usually known as a secondary filler network.^{34–36} It is known that this secondary filler network is relatively weak and therefore could be disrupted at high strain, leading to an observed drop in G' at high shear strain as shown in Figure 1 (generally known as a Payne effect). In other words, the higher the magnitude of filler transient network, the shorter is the LVE region. The results agree very well with results of elastic modulus in the rubbery region measured from the dynamic mechanical thermal analyzer (DMTA), as reported in our previous work.³³ Consequently, the 1% shear strain as a strain in the LVE region of all blends with various silica loadings has been selected for a subsequent oscillatory measurement as a function of frequency.

Figure 2 exhibits the G' as a function of test frequency. It could clearly be seen that all blends with various loadings of precipitated silica reveal an increase in elasticity with increasing frequency, which is attributed to a decrease in time available for molecular relaxation. Furthermore, G' of the blends with high silica loadings (i.e., 20 and 30 phr) gives relatively shallow slope, indicating a more time-independent elastic response, which supports the presence of filler transient network in these blends. As mentioned earlier, the shear strain of 1% used in a frequency sweep test is so small that the filler transient network is not

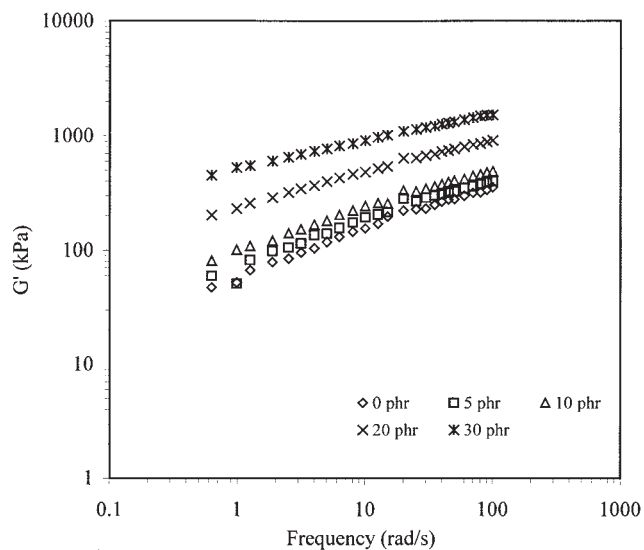


Figure 2 Elastic modulus (G') as a function of frequency in CPE/NR blends filled with various silica loadings.

disrupted, and could consequently act as a pseudo-crosslink and thus a time-independent elastic response.

Regarding a loss modulus (G'') as a function of test frequency illustrated in Figure 3, it is evident that G'' increases with test frequency, which is due to the higher energy required for molecular viscous response. Also, compared to G' of blends at given silica loading, the value of G'' is obviously lower than that of G' , implying the elastic-dominant response in all blends. The magnitude of modulus difference between G' and G'' is more evident in the blends filled with high silica loadings, supporting the increase in elasticity provided by the pseudo-crosslink of filler transient network.

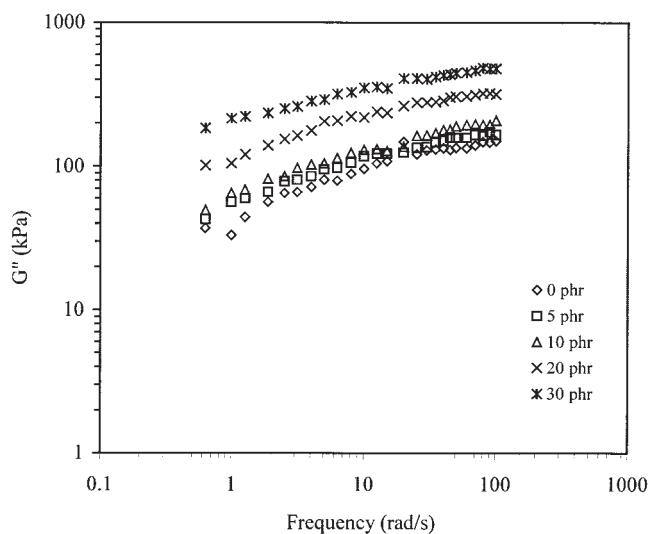


Figure 3 Loss modulus (G'') as a function of frequency in CPE/NR blends filled with various silica loadings.

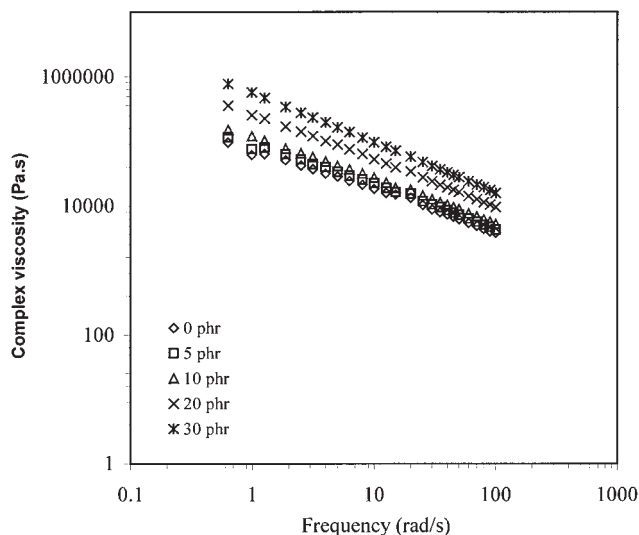


Figure 4 Complex viscosity (η^*) as a function of frequency in CPE/NR blends filled with various silica loadings.

Figure 4 reveals the processability of the blends via a complex viscosity (η^*) as a function of frequency. Clearly, all blends exhibit pseudoplasticity, i.e., a decrease in η^* with increasing frequency. At any given test frequency, there is a slight increase in η^* with silica loadings up to 10 phr. Beyond this loading, η^* markedly increases, supporting the presence of pseudo-crosslink of filler transient network, as discussed previously. Also, the correlation of η^* to G' results clearly indicates that the processability of all blends is controlled strongly by the elastic response via the presence of filler transient network. In addition to the strong interaction of CPE-silica and the formation of silica transient network, the hydrodynamic effect is known to yield an increase in viscosity as a function of filler loading. To eliminate the hydrodynamic effect from the experimental results, the Einstein equation as shown in eq. (1) was used to calculate the relative viscosity ($\eta_{\text{filled}}/\eta_{\text{unfilled}}$) as a function of silica volume fraction as illustrated in Figure 5. According to the Einstein equation, the relative viscosity depends only on volume fraction of silica.

$$\frac{\eta_{\text{filled}}}{\eta_{\text{unfilled}}} = 1 + 2.5\phi \quad (1)$$

where η_{filled} and η_{unfilled} are the extrapolated zero shear viscosity of filled and unfilled blends, respectively, while ϕ is a volume fraction of silica.

It is clearly evident that the relative viscosity of the blends measured from RPA2000 is higher than that calculated from the Einstein equation, particularly at high loading of silica (i.e., 20 and 30 phr of silica). The results support the proposed explanation of the relatively high complex viscosity of the blends with high silica loading

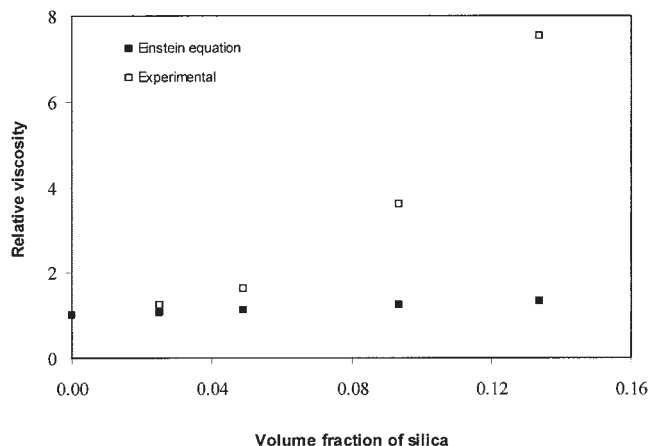


Figure 5 A comparison of relative viscosity as a function of silica volume fraction as determined from RPA2000 and calculated from the Einstein equation.

due to the presence of pseudo-crosslink of silica transient network, as discussed previously. Notably, the deviation of relative viscosity at high silica loading could also be caused by the use of a simplified model where particle-particle interactions would play role on rheological properties to some extent.

Steady shear flow

Expectedly, an apparent shear viscosity (η_a) at any given shear rate determined from the capillary rheometer would increase with increasing silica loading, similar to the result of complex viscosity measured from RPA2000. The rise in η_a as a function of silica loading is apparently attributed to the hydrodynamic effect associated with the strong interaction between CPE and silica surfaces as discussed previously. To

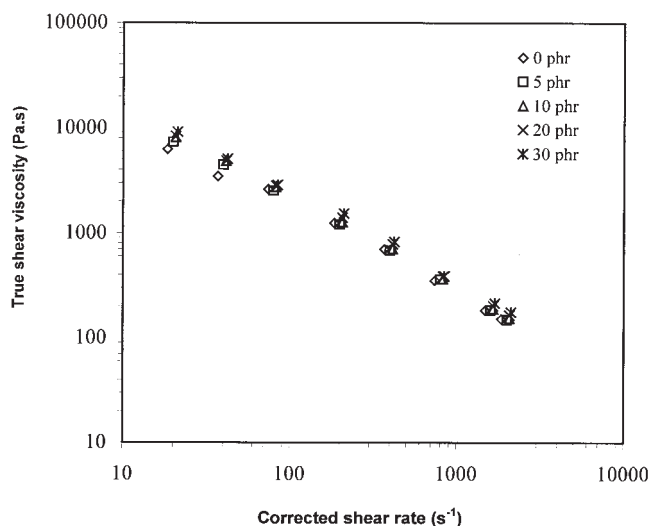
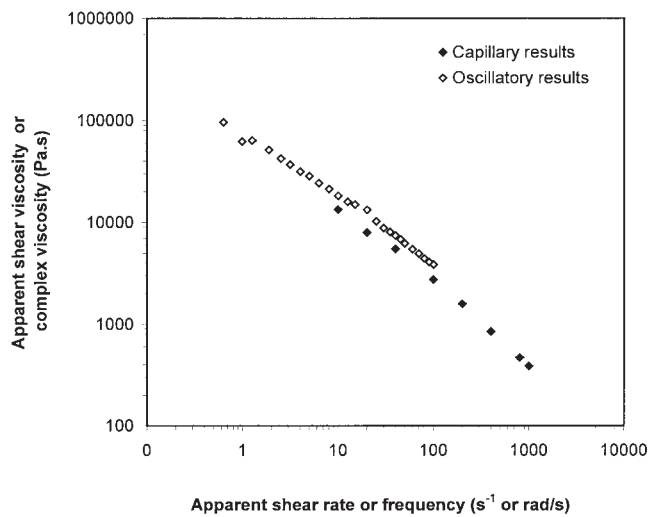
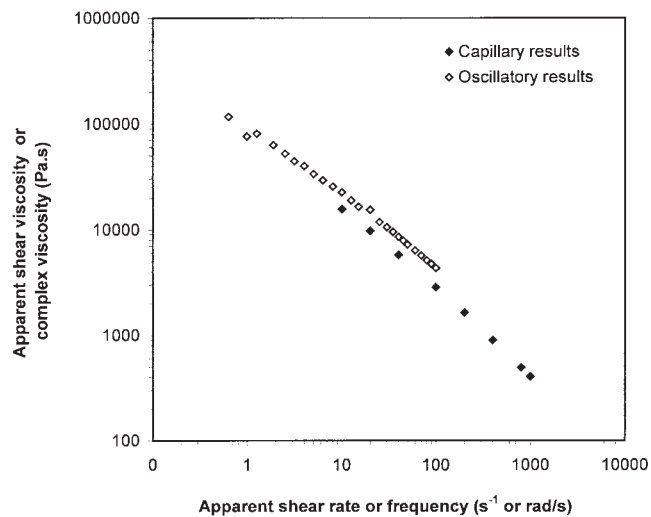


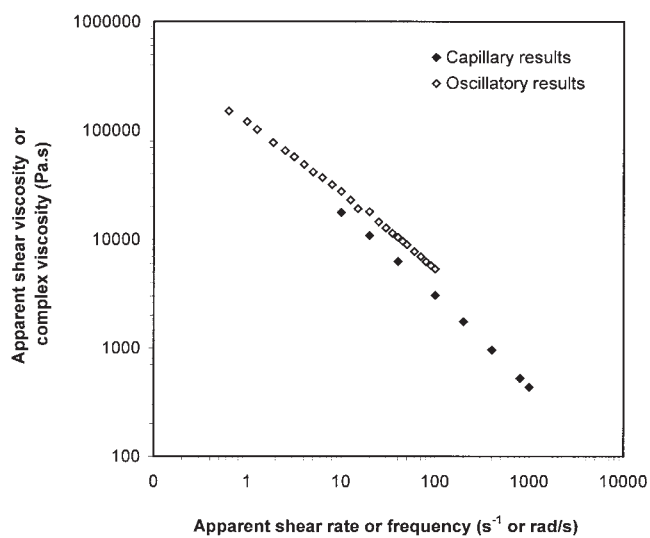
Figure 6 True shear viscosity (η_{true}) as a function of corrected shear rate in CPE/NR blends filled with various silica loadings.



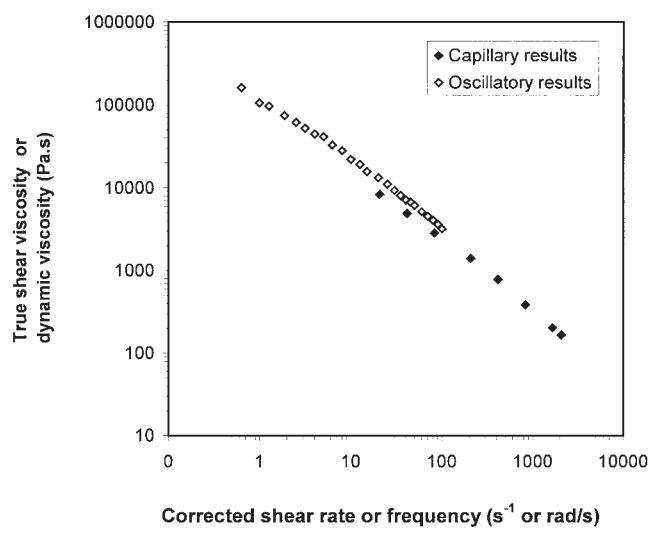
(a)



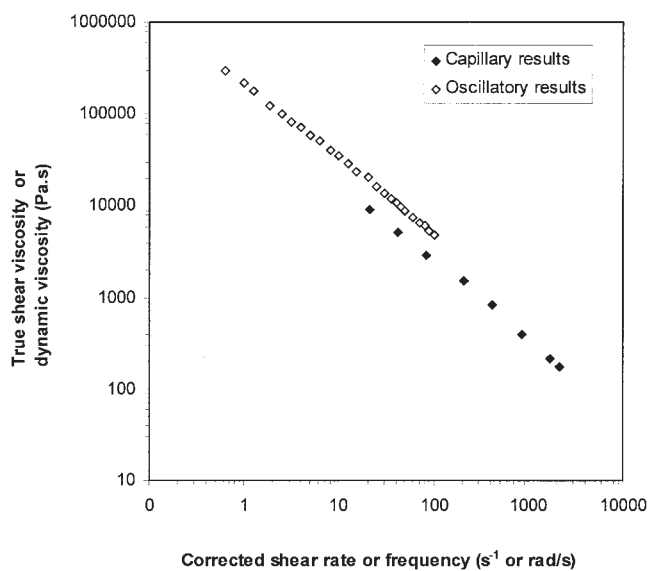
(b)



(c)



(d)



(e)

Figure 7 Superimposed plots of oscillatory viscosity determined from RPA2000 and steady shear viscosity determined from capillary rheometer as a function of frequency or shear rate in CPE/NR blends filled with various silica loadings: (a) unfilled; (b) 5 phr; (c) 10 phr; (d) 20 phr; and (e) 30 phr.

eliminate end effect and to compensate the flow pattern of non-Newtonian melt, the Bagley and Rabino-witsch corrections have to be applied to the apparent data, yielding the true shear viscosity (η_{true}) and corrected shear rate ($\dot{\gamma}_{\text{cor}}$), respectively.² A plot of η_{true} as a function of $\dot{\gamma}_{\text{cor}}$ is illustrated in Figure 6. It is obvious that, for all blends, a decrease in η_{true} could be observed, showing a typical non-Newtonian pseudo-plastic behavior, which could be explained by the molecular disentanglement or disruption of silica transient network. Notably, as the ASTM size range of precipitated silica used in this work is considerably smaller than that of capillary diameter (i.e., 20–25 nm³⁷ versus 2 mm), the continuum concept used to determine the apparent data is valid.

Comparison of oscillatory and steady shear flow

Generally, it is possible to compare the oscillatory shear viscosity as a function of test frequency to the steady shear viscosity as a function of shear rate by the use of Cox–Merz concept shown in eq. (2).

$$\eta(\omega) = \eta(\dot{\gamma}) \quad (2)$$

Figure 7(a–e) demonstrate the correlation between oscillatory shear and steady shear flow. It can be seen that there is an agreement between the data determined from the two rheometers depending on the silica loadings. Both complex viscosity (η^*) and apparent viscosity (η_a) could successfully be superimposed as silica loadings is up to 10 phr. By contrast, as the silica loadings are greater than 10 phr, the complex viscosity is considerably higher than the apparent shear viscosity. This is due to the fact that the shear strain of 1% used in frequency sweep test is within the LVE region (see also Fig. 1) that means the silica transient network still exists in the blends with 20 and 30 phr silica loadings. Thus, the results of complex viscosity include the silica transient network effect. On the other hand, in the case of capillary steady shear flow, the shear strain applied is remarkably greater, leading to disruption of silica transient network. To support the proposed explanation, the silica transient network effect found in oscillatory results of the blends with 20 and 30 phr silica loadings must be eliminated by the use of a viscous component, i.e., the dynamic viscosity as a ratio of loss modulus to test frequency. The results obtained are shown in Figure 7(d,e). It is evident that by eliminating the silica transient network effect, results of oscillatory and steady shear flow could successfully superimposed.

CONCLUSIONS

From all rheological results of 80/20 CPE/NR blends with various silica loadings obtained for the present study, the following conclusions could be drawn.

The addition of silica to the blends increases significantly the blend viscosity under both oscillatory and steady shear flow, particularly at silica loadings of 20 and 30 phr, which could be explained by a reinforcing effect via a hydrodynamic effect as well as a strong interaction between chlorine atoms on CPE molecules and silanol functional groups on silica surfaces associated with a formation of silica tridimensional transient network. Also, all blends with various loadings of precipitated silica reveal an increase in elasticity with increasing frequency, and those with high silica loadings (i.e., 20 and 30 phr) gives a more time-independent elastic response, supporting the presence of filler transient network in these blends

With the use of Cox and Merz concept, the superimposition of flow curves determined from of the oscillatory shear flow and steady shear flow in blends with high silica loadings is possible only if the silica transient network effect is eliminated by the use of dynamic viscosity instead of complex viscosity.

References

- Dealy, J. M.; Wissbrun, K. F. *Melt Rheology and its Role in Plastic Processing: Theory and Applications*; Van Nostrand Reinhold: New York, 1990.
- Cogswell, F. N. *Polymer Melt Rheology*; Woodhead Publishing: Cambridge, 1994.
- Brydson, J. A. *Flow Properties of Polymer Melts*; Godwin: London, 1981.
- Jacovic, M. S.; Pollock, D.; Porter, R. S. *J Appl Polym Sci* 1979, 23, 517.
- Huang, D. C.; Shroff, R. N. *J Rheol* 1981, 25, 605.
- Yoo, H. J.; Han, C. D. *J Rheol* 1981, 25, 115.
- Liang, J. Z.; Huang, Y. O.; Tang, G. J.; Ness, J. N. *Plast Rubber Compos Process Appl* 1992, 18, 311.
- Ma, C. Y.; White, J. L.; Weissert, F. C.; Min, K. *J Non-Newtonian Fluid Mech* 1985, 17, 275.
- Ma, C. Y.; White, J. L.; Weissert, F. C.; Isayev, A. I.; Nakajima, N.; Min, K. *Rubber Chem Technol* 1985, 58, 815.
- Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
- Williams, M. L.; Landel, R. F.; Ferry, J. D. *J Am Chem Soc* 1955, 77, 3701.
- Ajji, A.; Sammut, P.; Huneault, M. A. *J Appl Polym Sci* 2003, 88, 3070.
- Hameed, T.; Hussein, I. A. *Polymer* 2002, 43, 6911.
- Moly, K. A.; Oommen, Z.; Bhagawan, G. *J Appl Polym Sci* 2002, 86, 3210.
- Lovisi, H.; Silva, A. L.; Maria, L. C. *J Appl Polym Sci* 2003, 89, 1690.
- Huang, J. M.; Cheng, H. J.; Wu, J. S. *J Appl Polym Sci* 2003, 89, 1471.
- Silva, A. L.; Rocha, M. C.; Coutinho, F. M. *Polym Test* 2002, 21, 289.
- Li, S.; Jarvela, P. K.; Jarvela, P. A. *J Appl Polym Sci* 1999, 71, 1649.
- Yang, J.; Shi, D.; Gao, Y. *J Appl Polym Sci* 2003, 88, 206.
- Gao, J.; Li, D.; Wang, D. *Eur Polym J* 2000, 36, 2517.
- Yang, W.; Wu, Q.; Zhou, L.; Wang, S. *J Appl Polym Sci* 1997, 66, 1455.
- Koklas, S. N.; Sotiropoulou, D. D.; Kallitsis, J. K.; Kalfoglou, N. K. *Polymer* 1991, 32, 66.

23. Oommen, Z.; Groeninckx, G.; Thomas, S. *J Appl Polym Sci* 1997, 65, 1245.
24. Siegmann, A.; Hiltner, A. *Polym Eng Sci* 1984, 24, 869.
25. Hwang, I. J.; Lee, M. H.; Kim, B. K. *Eur Polym J* 1998, 34, 671.
26. Hwang, I. J.; Kim, B. K. *J Appl Polym Sci* 1998, 67, 27.
27. Koscielnicka, A. *Eur Polym J* 1993, 29, 23.
28. Maity, M.; Das, C. K. *Polym Int* 2000, 49, 757.
29. Sirisinha, C.; Sae-oui, P.; Guaysomboon, J. *J Appl Polym Sci* 2002, 22, 84.
30. Sirisinha, C.; Sae-oui, P.; Pattanawanidchai, S. *J Appl Polym Sci* 2004, 93, 1129.
31. Sirisinha, C.; Sae-oui, P.; Guaysomboon, J. *Polymer* 2004, 45, 4909.
32. Phewthongin, N.; Sae-oui, P.; Sirisinha, C. *Polym Test* 2005, 24, 227.
33. Pattanawanidchai, S.; Sae-oui, P.; Sirisinha, C. *J Appl Polym Sci*, to appear.
34. Medalia, A. I.; Laube, S. G. *Rubber Chem Technol* 1978, 51, 89.
35. Payne, A. R. *J Polym Sci* 1972, 16, 1191.
36. Leblanc, J. L. *Prog Polym Sci* 2002, 49, 627.
37. Wagner, M. P. *Rubber Chem Technol* 1976, 49, 703.