

Viscoelastic Properties of Fly Ash-Filled Natural Rubber Compounds: Effect of Fly Ash Loading

Thanunya Saowapark,¹ Narongrit Sombatsompop,² Chakrit Sirisinha^{1,3}

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

²Polymer Processing and Flow (P-PROF) Group, School of Energy, Environment, and Materials,

King Mongkut's University of Technology Thonburi (KMUTT), Bangmod, Thungkru, Bangkok 10140 Thailand

³Research and Development Center for Thai Rubber Industry (RDCTRI), Faculty of Science, Mahidol University, Salaya Campus, Salaya, Nakhon Pathom 73170, Thailand

Received 4 July 2008; accepted 17 November 2008

DOI 10.1002/app.29700

Published online 18 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Fly ash (FA) as a by-product of power station plants is known to consist of silicon dioxide similar to precipitated silica. The use of FA as filler in natural rubber (NR) was of interest to reinforce and/or reduce product cost. In this article, viscoelastic properties of FA-filled NR composites with various FA loadings were investigated with the utilization of two different modes of shear flow, namely, oscillatory and steady shear flow. It is found that the addition of FA to NR increases storage modulus (G') and shear viscosity under both oscillatory and steady shear flow. Moreover, the oscillatory test results exhibit the unexpected increase in magnitude of viscous response with increasing FA loading in FA-filled NR compounds. The explanation is proposed in terms of the ball-bearing effect of FA with spherical shape associated with the

occurrence of molecular degradation induced by inorganic constituents particularly manganese, iron, and copper in nonrubber component of NR as well as the small amount of heavy metals including iron, copper in FA. An isoprene rubber (IR) containing no nonrubber component was used to validate the proposed explanation. In addition, with the use of Cox-Merz concept, the results of both complex viscosity under oscillatory shear flow and apparent shear viscosity under steady shear flow can effectively be superimposed in the case of FA-filled compounds, supporting the promotion of viscous response by FA. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2552–2558, 2009

Key words: fly ash; natural rubber; viscoelastic properties; filler; rheology

INTRODUCTION

Fillers are added to rubber for a variety of purposes, of which the most important are enhancements in reinforcement, processability and material costs.¹ Typically, fillers used in rubber industry are classified into reinforcing and nonreinforcing fillers. In some cases, fillers are divided into black and non-black types. There are basically two categories of reinforcing fillers—carbon black and mineral or 'white' fillers such as fumed and precipitated silica.² In rubber industry, because of its fine particle size (high specific surface area), such silica is widely used as nonblack reinforcing filler to improve mechanical properties of vulcanizates, particularly hardness and resistances to tension, tear and abra-

sion. Although, silica is still well accepted among rubber technologists, the use of some other fillers from the natural resources as alternative reinforcing fillers in NR has been carried out to replace silica in rubber compounds.³ Such fillers include clay, lignin, black rice husk ash (BRHA) and white rice husk ash (WRHA), and cellulose fiber.

Ash residues are wastes of coal-fired power plants; these include fly ash (FA) and bottom ash.^{4,5} FA is a relatively inexpensive by-product, and its usages have the benefit of decreasing environmental problems. Furthermore, FA has been used in industry as a consequence of such advantages as low cost, smooth spherical surface and good processability of the filled materials.⁶ In previous study,^{3,7–12} it has been reported that FA particles consist of silicon dioxide similar to silica but with the lower content of silicon dioxide than silica. Consequently, the addition of FA to rubber compounds is able to enhance rubber properties similar to that of commercial silica, but with the much smaller magnitude. It must be noted that if the reinforcement effect provided by FA is carefully considered particularly when compared with precipitated silica, FA can hardly be considered as filler with a real reinforcement potential

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

Contract grant sponsors: Development and Promotion of Science and Technology Talent Project (DPST), Commission on Higher Education (Research fund for the Centre for Utilizations of Polymers and Natural Resources, CUP-NATURE).

TABLE I
List of Materials Used in the Present Study

Materials	Trade name/grade	Suppliers	Amount (phr)
Natural rubber (NR)	STR 5L	Union rubber products, Thailand	100
Synthetic <i>cis</i> -1,4-polyisoprene (IR)	NIPOL IR 2200	Nippon zeon, Japan	100 ^a
Fly ash (FA)	–	Mae Moa power station of KNR group, Thailand	Variable

^a Only used for comparing with NR to exclude a non-rubber effect on compound properties.

because of its much lower structure and surface reactivity. However, in terms of environmental concerns, FA is an interesting filler giving reinforcement to some extent and its role on viscoelastic properties of NR compounds is of interest in the present study.

The present work aims to further the previous work³ by focusing mainly on viscoelastic properties of FA-filled NR composites measured from oscillatory and steady shear rheometers. The viscoelastic properties of NR compounds filled with various FA loadings will be discussed. It must be noted that the simple compounds containing only NR and FA with various loading are investigated in this work to exclude any interference on viscoelastic properties which might be caused by other compounding ingredients.

EXPERIMENTAL

Materials

The materials used in the present study are summarized in Table I.

Preparation of rubber compounds

Rubber compounds were prepared using a laboratory-sized two roll mill (model LRM150, Labtech, Thailand) at the set temperature of 60°C for 13 min. The loading of FA compounds was varied from 0 to 200 phr. The formulation of compound is given in Table I.

Characterization of FA

The FA originated from coals typical of those burned in electric power plant (Mae Moa Power Station). The chemical composition of FA was determined using the X-ray fluorescence spectrometer (model S4 Pioneer BrukerAXS, Germany). A scanning electron microscope (SEM) (model LEO 1455 VP, UK) was used at an accelerating voltage of 10 kV to examine the morphology of FA particles. Particle size analyzer (model Mastersizer 2000, Marvern Instruments, UK) was also used to measure the FA particle size and its distribution.

Measurement of viscoelastic properties

Viscoelastic properties of compounds under oscillatory shear flow were measured using the Rubber Process Analyzer (model RPA2000, Alpha Technologies, USA) with the time, strain and frequency sweep tests at test temperature of 70°C. For the amplitude strain sweep test, the deformation strain was swept from 0.5 to 1200% and 0.5 to 30% at 1 and 100 rad/s, respectively. In the frequency sweep test, angular frequency of 1 to 100 rad/s was used under a small strain in the linear viscoelastic region. A Goettfert rate-controlled capillary rheometer (model Rheotester 2000, Germany) was also used to measure rheological properties of compounds under steady shear flow at shear rate range of 10–500 s⁻¹ and test temperature of 70°C. A Bagley correction with three die lengths of 10, 20, and 30 mm with a given die diameter of 2 mm was performed to eliminate end effect.

RESULTS AND DISCUSSION

The chemical composition of FA as determined by the X-ray fluorescence spectrometer is shown in Table II. It is evident that the largest amount of composition in FA is of silicate (SiO₂) or silica. Figure 1 depicts SEM micrograph of FA particles used in the present study. It is clear from the micrograph that the shape of FA particles is spherical. In addition, the particle size distribution of FA used is rather broad with the sizes ranging from submicron to 200 microns as illustrated in Figure 2. The reported mean particle size of FA is of 50.311 microns. It

TABLE II
Chemical Compositions of FA Used in the Present Study

Compositions	Content (%)	Compositions	Content (%)
SiO ₂ (silica)	37.6	BaO	0.130
Al ₂ O ₃	22.4	SrO	0.123
CaO	15.1	MnO	0.101
Fe ₂ O ₃	14.5	ZnO	0.0301
K ₂ O	2.97	ZrO ₂	0.0297
SO ₃	2.71	Cr ₂ O ₃	0.0240
MgO	2.29	Rb ₂ O	0.0193
Na ₂ O	1.33	CuO	0.0187
TiO ₂	0.447	NiO	0.0121
P ₂ O ₅	0.171	Y ₂ O ₃	0.00431

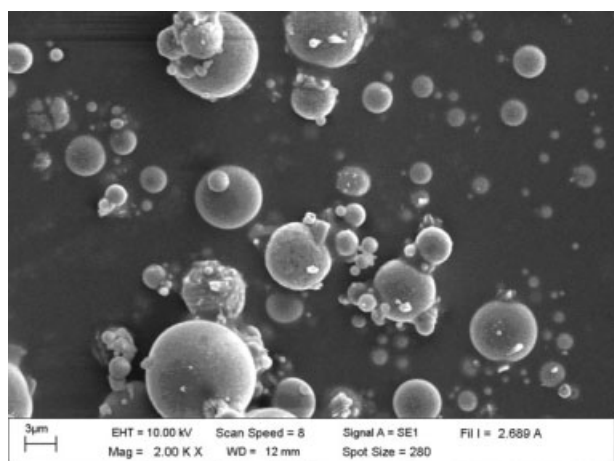


Figure 1 SEM micrograph of FA particles used in the present study.

must be noted that the composition of heavy metals in FA depends strongly on source of the coal as also reported by previous work.¹³ Therefore, mechanical properties of NR vulcanizates filled with different sources of ash might be different. However, in this study, the FA used was supplied from a specific source, and effects of composition in FA on properties could be disregarded.

Two different modes of shear flow, namely, oscillatory and steady shear flow were applied to the compounds. Then, the superimposition of data measured under both modes of flow would be performed.

In the case of oscillatory flow as measured from RPA2000, the time sweep test was firstly performed to determine the thermal stability of test specimen within the test duration of 30 min. Evidently, from Figure 3, there is no significant change in storage modulus (G') of all compounds with increasing time up to 30 min. This implies that all of FA-filled NR compounds possess good thermal stability within the test duration to be used for the subsequent strain and frequency sweep tests. In other words, any change to be observed in those tests would not be caused by the thermal degradation occurring during

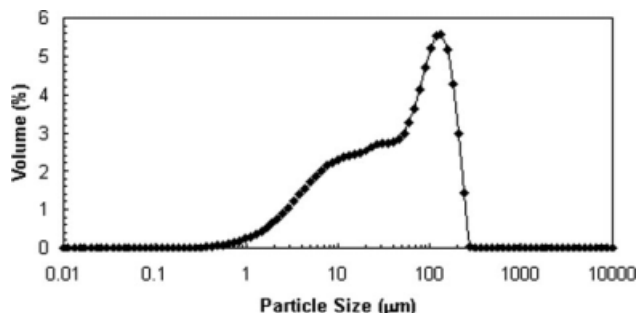


Figure 2 Particle size distribution of FA used in the present study.

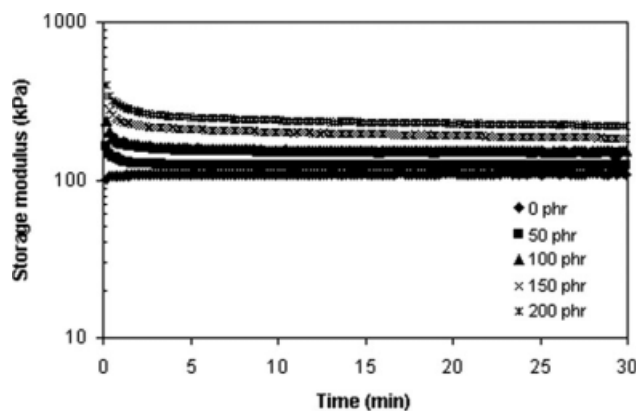


Figure 3 Storage modulus (G') as a function of time of FA-filled NR compounds with various FA loadings.

the test period. Furthermore, it is obvious that G' increases obviously with increasing ash loading, which could be due to the hydrodynamic effect and/or filler network formation.^{14–17}

To further investigate the viscoelastic responses of FA-filled compounds, the strain sweep test was performed, and the results obtained are exhibited in Figure 4. Clearly, at low strain of deformation, G' increases with increasing FA loading similar to the results of time sweep test as shown earlier in Figure 3. However, at high strain, the G' appears to reduce with increasing strain of deformation. Also, the linear viscoelastic (LVE) region (or the strain-independent region) depends strongly on FA loading. The higher the FA loading, the narrower the LVE region. The observed strain-dependent G' is previously explained by the disruption of filler network^{14–18} associated with molecular slippage (particularly in the case of uncured compounds). Apart from the broadness of LVE region, the discrepancy in G' at low and high strains (usually known as Payne effect) are found to be more apparent with increasing filler loading, which supports the disruption of filler network at high strain.^{14–18} Nevertheless, because the amount of silanol groups in FA is relatively small

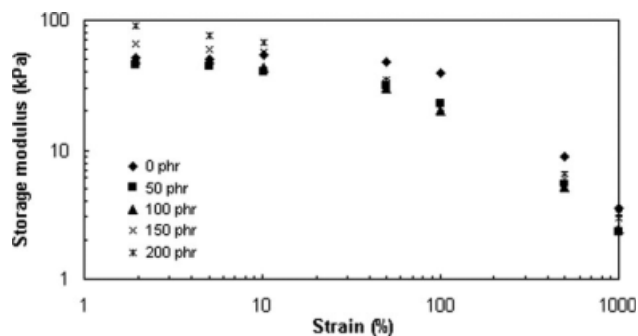


Figure 4 Storage modulus (G') as a function of strain amplitude of NR compounds filled with various FA loadings at 1 rad/s.

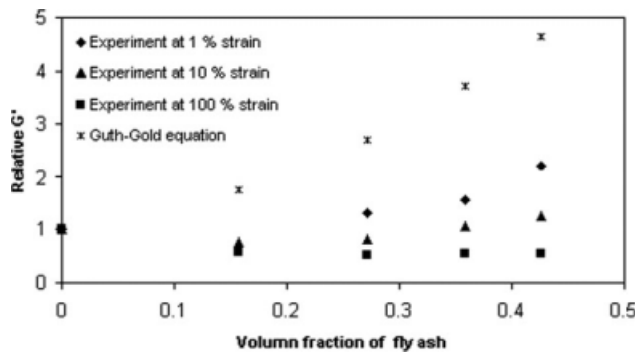


Figure 5 Relative storage modulus (relative G') at 1, 10, and 100% strain of NR compounds filled with various FA loadings as a function of FA loadings.

similar to the silicate-based filler, the interaction via H-bond between silanol groups in FA might be so small that the Payne effect is less obvious than the case of precipitated silica.

However, in the FA-filled system considered in this work, it must be noted that the magnitude of filler network effect might not be as strong as that found in silica-filled system reported previously¹⁴⁻¹⁷ because of the smaller amount of silanol group and surface area in FA particles. It is noticeable that FA particle is very similar to finely ground silicates (with limited reinforcing capabilities in rubber materials) than to precipitated silica (nearly 99.9% SiO₂) as supported by the SEM micrograph (Fig. 1). This means the changes in G' with FA loading is initially believed to be dominated by the hydrodynamic over the filler network effects. To clarify the proposed hypothesis, the Guth-Gold expression as illustrated in eq. (1) is used to generate the theoretical results of relative modulus with the exclusion of filler network effect as shown in Figure 5.^{16,19}

$$\text{Relative } G' = \frac{G'_{\text{filled}}}{G'_{\text{unfilled}}} = 1 + 2.5\phi + 14.4\phi^2 \quad (1)$$

where G'_{unfilled} and G'_{filled} are elastic moduli of unfilled and filled compounds, respectively. The ϕ is the filler volume fraction.

In theory, it is anticipated that the filled compounds would show the positive deviation relative modulus from the Guth-Gold results especially at high filler loading due to the filler network formation as found in silica filled CPE/NR blends.¹⁶ Unexpectedly, the experimental data found in this work show the negative deviation of relative modulus from the calculated Guth-Gold data, which is more pronounced at high deformation strain. It is hypothesized that the hydrodynamic effect is overridden by the strain amplification effect. In general, when strain is applied to the filled rubber compound, the rigid filler in the rubber matrix does not share the deformation of compound. The inclusion

of the undeformable filler in the soft rubber matrix causes the local strain in matrix to go beyond the macroscopic strain.²⁰ Thus, the rubber chains in the highly filled compounds receive greater strain, and lead to the reduction in relative storage modulus via a molecular slippage and/or a disruption of FA-NR interaction. It is noticeable that strain amplification effect would increase with increasing filler loading and strain of deformation. In addition, referred to the spherical shape of FA as shown previously in Figure 1, the molecular slippage would be further promoted via a ball-bearing effect.

Logarithmic plots of G' as a function of frequency of NR compounds filled with various FA loading are shown in Figure 6. It is evident that all compounds show an increase in G' (or elasticity) with increasing frequency which is attributed to the insufficient time for molecular relaxation at high frequency. Additionally, the magnitude of frequency-dependent responses (as determined from slopes) clearly increases with increasing FA loading. The results unexpectedly imply a decrease in elastic behavior of compounds with increasing FA loading, which is on the contrary to the previous findings on chlorinated polyethylene (CPE) system filled with precipitated silica.^{14,15} It has been reported in those work that the strong interaction between polar group of polymer matrix and silanol group of silica could form a tridimensional transient network resulting in a strong elastic response with lowered magnitude of frequency dependent behavior. Clearly, the unexpected results are in accordance with the absence of filler network as proposed previously.

Damping properties of NR compounds with various FA loading are exhibited in Figure 7. Obviously, the reduction in damping factor with increasing frequency could be observed in all compounds indicating a rise in elastic behavior caused by the insufficient time for molecular relaxation as discussed in G' results. Similar to the case of G' , there is the unexpected increase in damping factor with increasing ash loading. As mentioned previously, it

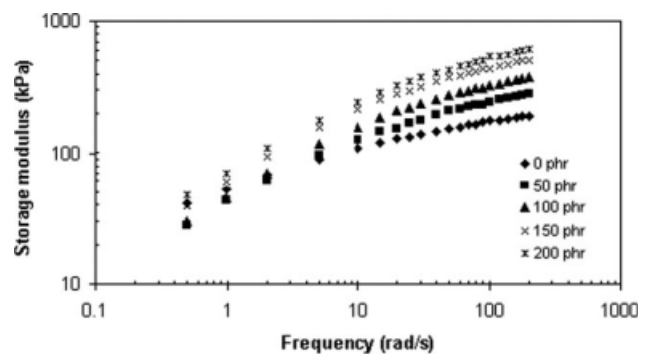


Figure 6 Storage modulus (G') as a function of frequency of NR compounds filled with various FA loadings.

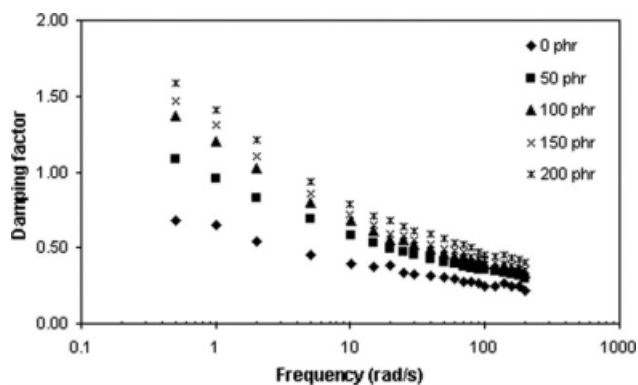


Figure 7 Damping factor ($\tan \delta$) as a function of frequency of NR compounds filled with various FA loadings.

is initially anticipated that there would be the increase in elastic behavior of compounds with increasing FA loading via the filler network formation similar to the previous work on silica-filled CPE system.^{14,15} The unexpected difference in result trends are believed to be the results of a viscous response promotion given by molecular slippage via the FA ball-bearing effect (i) and molecular degradation of NR matrix which might be accelerated by the presence of nonrubber component and/or of metal such as iron and copper in FA as illustrated in Table II (ii).^{21,22}

To validate the proposed explanation of nonrubber component effect, further experiment was performed on a synthetic isoprene rubber (IR) which is free from nonrubber substances. It can be seen from Figure 8 that, with increasing FA loading, the increase in damping factor is still noticeable, but the magnitude of discrepancy in damping factor of compounds with different FA loading is much less apparent than that of NR compounds (Fig. 7). This implies the lower viscous response in IR compounds than NR compounds. Thus, it might be summarized

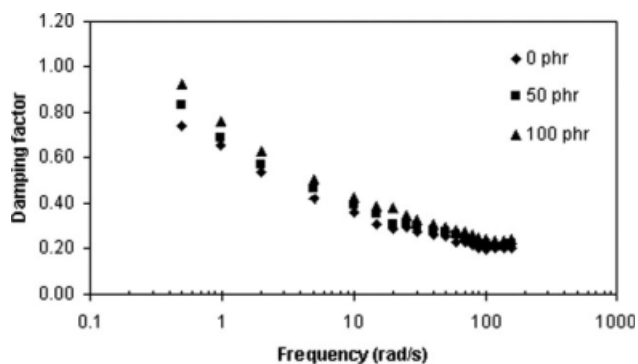


Figure 8 Damping factor ($\tan \delta$) as a function of frequency of synthetic isoprene rubber (IR) compounds filled with various FA loadings.

that the nonrubber substances presented in NR play role in such increase in magnitude of viscous behavior to some extent. According to previous work, the inorganic constituents found in nonrubber component of NR including manganese, iron and copper are able to catalyze the oxidation breakdown of NR.^{21,22}

An existence of small magnitude of change in viscous response observed in IR compounds filled with FA might be due to the molecular slippage via the ball-bearing effect of FA and/or the occurrence of molecular degradation of rubber matrix by a thermo-oxidative process, as mentioned previously. It is likely that a small amount of heavy metals in FA including iron or copper as shown in Table II could act as good oxidizing agents, which are believed to accelerate the degradation of rubber molecules.²¹

Figure 9 reveals the processability of the NR compounds with various FA loadings via complex viscosity as a function of frequency. As expected, the complex viscosity evidently decreases with increasing frequency indicating the pseudoplastic behavior. Additionally, the increase in complex viscosity with increasing FA loading could be observed. Referred to the results of damping properties shown in Figure 7, the highly filled compounds reveal high damping factor particularly at low frequency that means the increase in complex viscosity is caused by the increase in magnitude of viscous response via molecular slippage as discussed earlier.

In the case of rheological properties under steady shear flow as measured from a capillary rheometer, Figure 10 reveals a similar result trend to that of complex viscosity under oscillatory flow, i.e., there is a slight increase in true shear viscosity with increasing FA loading at any given shear rate. Such small magnitude of increase in shear viscosity of NR compounds filled with FA is in good agreement with previous work.²³ The promotion of viscous response by molecular slippage via the ball-bearing effect

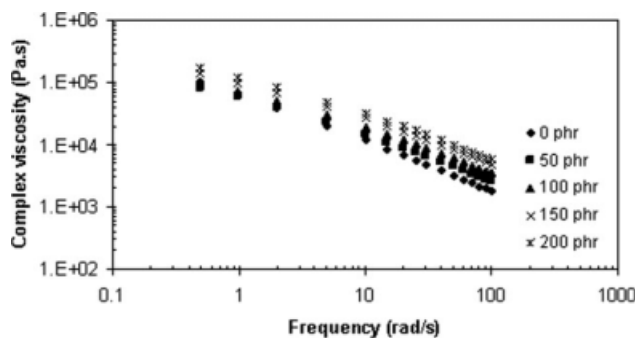


Figure 9 Complex viscosity as a function of frequency of NR compounds filled with various FA loadings.

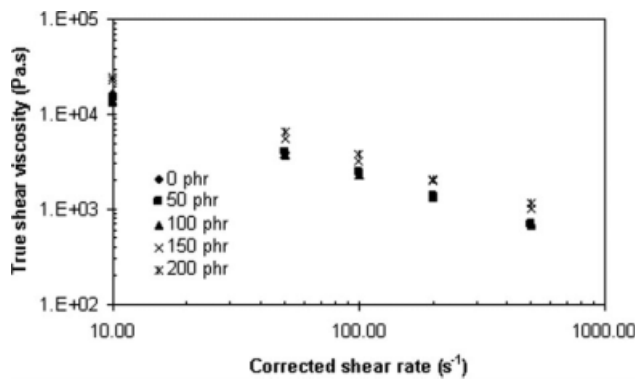


Figure 10 True shear viscosity as a function of corrected shear rate of NR compounds filled with various FA loadings.

and/or molecular chain-scission is believed to be responsible for the slight viscosity rise observed despite with high loading of FA.

To correlate rheological data under oscillatory and steady shear flow, the Cox-Merz concept²⁴ was applied, and the results obtained are illustrated in Figure 11. It is obvious that, in the case of unfilled NR compound, complex viscosity measured under oscillatory shear flow is slightly higher than apparent shear viscosity measured under steady shear flow, which is due probably to the end effect taking place via elasticity of compounds. This end effect leads to an additional pressure measured. On the contrary, in FA-filled compounds, both plots of

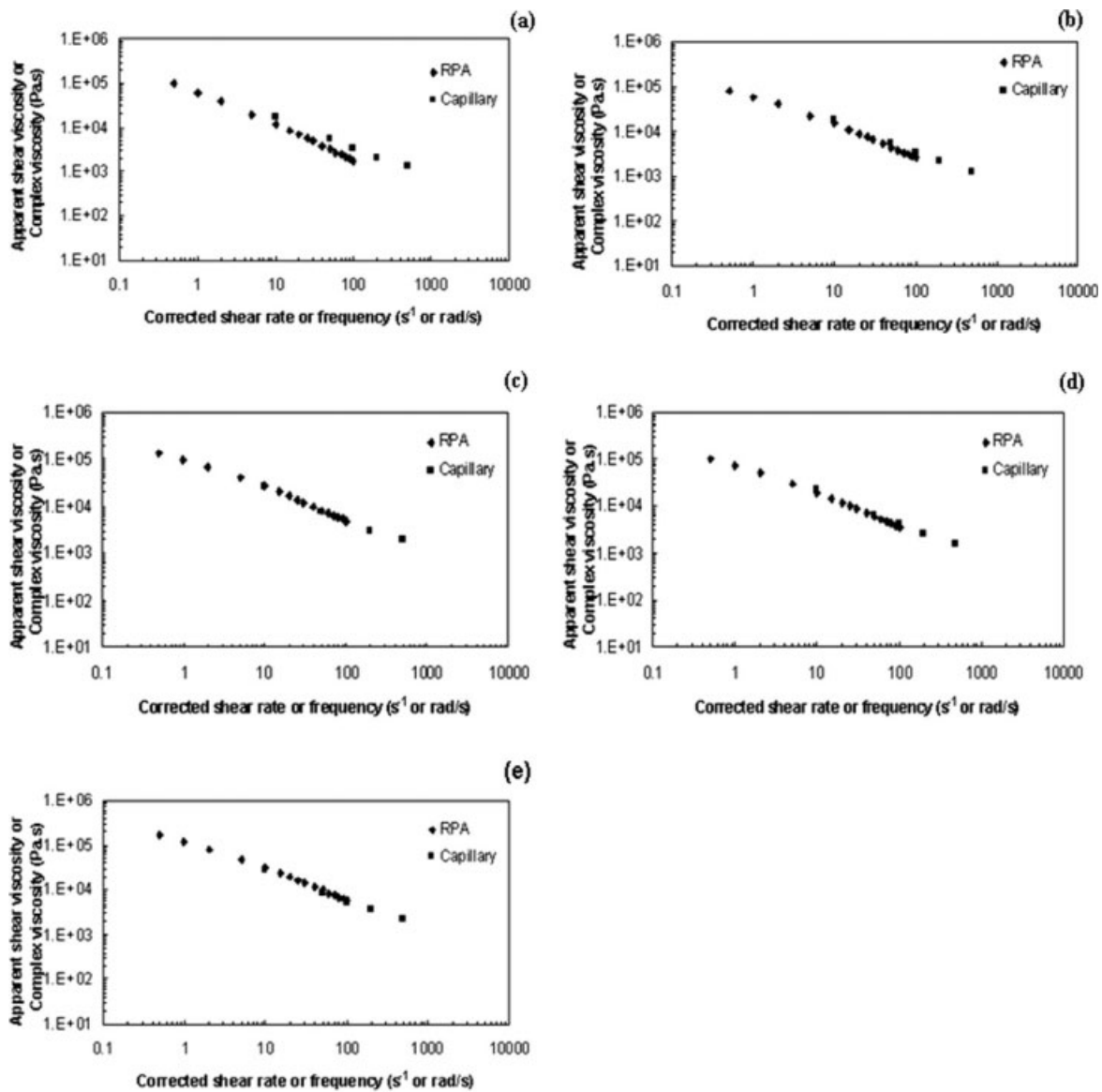


Figure 11 Plots of complex viscosity determined from RPA2000 as a function of frequency (◆) and apparent shear viscosity measured from capillary rheometer as a function of shear rate (■) of NR compounds filled with various FA loadings : (a) 0, (b) 50, (c) 100, (d) 150, and (e) 200 phr.

complex and apparent shear viscosity become superimposed. This is because of the flow promotion via viscous response provided by FA and/or nonrubber component, as discussed earlier.

In summary, it is proposed that, in NR compounds filled with FA, there is an occurrence of molecular degradation of NR which would therefore cause an increase in magnitude of molecular slippage. Furthermore, the spherical shape of FA would promote such molecular slippage via the ball-bearing effect. These two phenomena would end up with an increase in magnitude of viscous response of NR compounds as FA loading increases. On the contrary, in IR compounds without nonrubber substances, the smaller magnitude of molecular degradation yields the greater degree of molecular entanglement and thus the lower viscous response than NR. The molecular degradation is believed to be attributed to the presence of nonrubber component in NR and heavy metals in FA.

CONCLUSIONS

The FA-filled NR compounds are investigated in this article, and the following conclusions can be drawn. The addition of FA in NR increases G' and viscosity under both oscillatory and steady shear flow. Moreover, the higher FA loading, the larger magnitude of damping properties (viscous response) in the FA-filled NR compounds is observed. The explanation is proposed in terms of ball-bearing effect of FA associated with molecular degradation induced by inorganic constituents particularly manganese, iron and copper in nonrubber component of NR as well as the small amount of heavy metals including iron and copper in FA. The isoprene rubber (IR) containing no nonrubber component was used to validate the explanation. With the use of Cox-Merz concept, the results of both oscillatory and steady shear flows can effectively be superimposed in the case of FA-filled compounds, supporting the

promotion of viscous response provided by the addition of FA.

References

1. Waddell, W. H.; Evans, L. R. *Rubber Chem Technol* 1996, 69, 377.
2. Wolff, S. *Rubber Chem Technol* 1996, 69, 325.
3. Sombutsompop, N.; Thongsang, S.; Markpin, T.; Wimolmala, E. *J Appl Polym Sci* 2004, 93, 2119.
4. Duchesne, J.; Reardon, E. J. *Waste Manage* 1999, 19, 221.
5. Janos, P.; Wildnerova, M.; Loucka, T. *Waste Manage* 2002, 22, 783.
6. Gu, J.; Wu, G.; Zhang, Q. *Mater Sci Eng* 2007, 452–453, 614.
7. Wu, G.; Gu, J.; Zhao, X. *J Appl Polym Sci* 2007, 105, 1118.
8. Atikler, U.; Basalp, D.; Tihminlioglu, F. *J Appl Polym Sci* 2006, 102, 4460.
9. Cokca, E.; Yilmaz, Z. *Waste Manage* 2004, 24, 153.
10. Alkadasi, N.; Hundiwale, D. G.; Kapadi, U. R. *J Appl Polym Sci* 2004, 91, 1322.
11. Hundiwale, D. G.; Kapadi, U. R.; Desai, M. C.; Bidkar, S. H. *J Appl Polym Sci* 2002, 85, 995.
12. Jaarsveld, J. G. S.; Deventer, J. S. J.; Lucky, G. C. *Chem Eng J* 2002, 89, 63.
13. Thongsang, S.; Sombutsompop, N.; Suranaree, J. *Sci Technol* 2007, 14, 77.
14. Phewthongin, N.; Saeoui, P.; Sirisinha, C. *Polym Test* 2005, 24, 227.
15. Phewthongin, N.; Saeoui, P.; Sirisinha, C. *J Appl Polym Sci* 2006, 100, 2565.
16. Phewphong, P.; Saeoui, P.; Sirisinha, C. *J Appl Polym Sci* 2008, 107, 2638.
17. Sirisinha, C.; Saeoui, P.; Pattanawanidchai, S. *J Appl Polym Sci* 2004, 93, 1129.
18. Frohlich, J.; Nieedermeier, W.; Luginsland, H.-D. *Compos Part A: Appl Sci Manuf* 2005, 36, 449.
19. George, W. *Handbook of Fillers*; William Andrew: New York, 1999.
20. James, E. M.; Burak, E.; Frederick, R. E. *Science and Technology of Rubber*, 2nd ed.; Academic Press: New York, 1994.
21. Bateman, L.; Moore, C. G.; Porter, M.; Saville, B. *The Chemistry and Physics of Rubber Like Substance*; L. Maclaren and Sons: London, 1963.
22. Hasma, H.; Othman, A. B. *J Nat Rubber Res* 1990, 5, 1.
23. Thongsang, S.; Sombutsompop, N.; Ansarifar, A. *Polym Adv Technol* 2008, 19, 1.
24. Nicholas, P. C. *Advance Polymer Processing Operation*; William Andrew: New York, 1998.