

# STORAGE INSTABILITY OF FLY ASH FILLED NATURAL RUBBER COMPOUNDS

THANUNYA SAOWAPARK<sup>1</sup>, PONGDHORN SAE-OUI<sup>2</sup>, NARONGRIT SOMBATSOMPOP<sup>3</sup>,  
CHAKRIT SIRISINHA<sup>1,4</sup> \*

<sup>1</sup> Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

<sup>2</sup> National Metal and Materials Technology Center, 114 Thailand Science Park Paholyothin Rd.,  
Pathumthani, 12120, Thailand

<sup>3</sup> Polymer 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

<sup>4</sup> Research and Development Centre for Thai Rubber Industry (RDCTRI), Faculty of Science, Mahidol  
University, Salaya Campus, Phutthamonthon 4 Rd., Salaya, Nakhon Pathom, 73170, Thailand

\* Corresponding author: [sccsr@mahidol.ac.th](mailto:sccsr@mahidol.ac.th)  
Fax: x662.4410511

Received: 16.12.2011, Final version: 22.5.2012

## ABSTRACT:

Generally, fly ashes (FA) could function as either semi-reinforcing or non-reinforcing fillers in polymeric systems, depending on particle size, specific surface areas and surface chemistry of FA particles. Typically, FA particles are spherical with smooth surfaces having significant influences on viscoelastic and mechanical properties. Additionally, the presence of heavy metals in FA particles could play role on degradation process of rubber molecules to some extent. In this article, the storage instability and thermal aging properties of FA filled natural rubber (NR) compounds were focused via changes in viscoelastic responses. Results obtained reveal that the storage duration of FA filled NR compounds leads to decreases in elastic modulus and molecular weight, particularly in the compounds with high FA loading. By replacing NR with polyisoprene (IR) containing no non-rubber substances, the storage stability is significantly enhanced. It is believed that the presence of metal ions in both FA and non-rubber substances in NR could catalyze the degradation process of rubber molecules. Such degradation process could effectively be suppressed by the addition of amine-based antioxidant.

## ZUSAMMENFASSUNG:

Fliegenasche (FA) kann in Abhängigkeit von der Partikelgröße, dem spezifischen Oberflächeninhalt und der Oberflächenchemie der FA-Partikel als semi-verstärkender oder nichtverstärkender Füllstoff in polymeren Systemen wirken. Typischerweise sind FA-Partikel kugelförmig mit einer glatten Oberfläche, die einen signifikanten Einfluss auf die viskoelastischen und mechanischen Eigenschaften haben. Zusätzlich können Schwermetalle in FA-Partikeln zu einem gewissen Ausmaß eine Rolle bei der Zersetzung von Gummimolekülen spielen. In diesem Artikel wird die Speicherinstabilität und die thermischen Alterungseigenschaften von mit FA gefüllten Naturkautschuk (NR)-Kompositen hinsichtlich ihrer rheologischen Eigenschaften untersucht. Die Ergebnisse zeigen, dass die Speicherdauer von mit FA gefüllten NR-Kompositen zu einer Abnahme des elastischen Moduls und des Molekulargewichts führt, insbesondere bei den Kompositen mit einem hohen FA-Gehalt. Durch das Ersetzen von NR mit Polyisopren (IR), das keine Nichtgummimaterialien enthält, wird die Speicherstabilität deutlich erhöht. Es wird davon ausgegangen, dass die Metallionen sowohl in der FA und in den Nichtgummisubstanzen im NR den Zersetzungsprozess der Kautschukmoleküle katalysieren. Dieser Zersetzungsprozess kann durch die Zugabe von Amin-basierenden Antioxidantien unterdrückt werden.

## RÉSUMÉ:

En général, les cendres volantes (FA) pourraient fonctionner comme des charges semi-renforçissantes ou non renforçissantes pour les systèmes de polymères, suivant la taille de la particule, des surfaces spécifiques, et de la chimie de la surface des particules de FA. Typiquement, les particules de FA sont sphériques avec des surfaces lisses et ayant des influences importantes sur les propriétés mécaniques et viscoélastiques. De plus, la présence de métaux lourds dans les particules de FA pourrait, jusqu'à un certain degré, jouer un rôle dans le processus de dégradation des molécules de caoutchouc. Dans cet article, nous nous concentrons sur l'instabilité durant le stockage et sur les propriétés de vieillissement thermique de caoutchouc naturel (NR) chargé de FA, en étudiant les changements dans les réponses viscoélastiques. Les résultats obtenus révèlent que la durée de stockage des NR chargés de FA entraîne une perte de module élastique et de masse moléculaire, particulièrement pour les composés contenant de grandes quantités de charge. En remplaçant le NR par du polyisoprène (PI) ne contenant pas de substances caoutchouteuses, la stabilité durant le stockage est améliorée de manière significative.

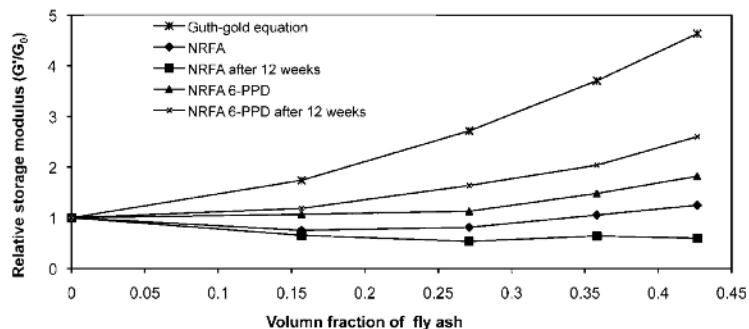
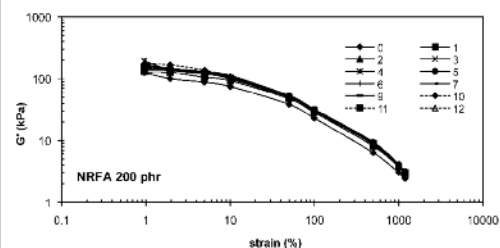
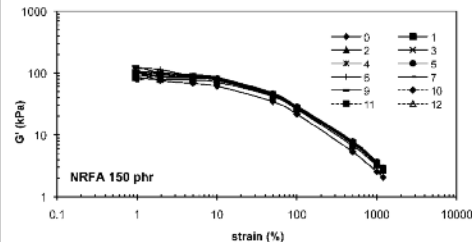
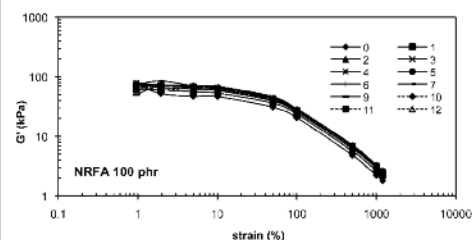
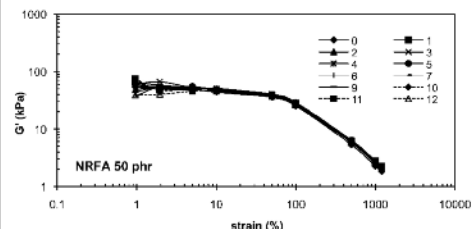
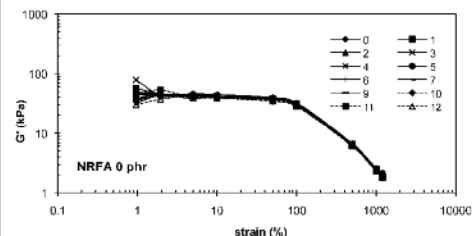


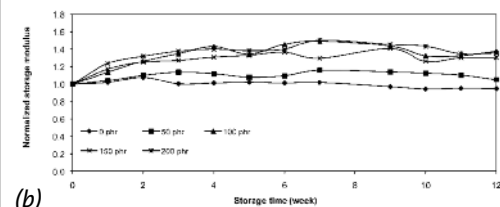
Figure 12 (right): Effect of storage time on modulus of FA filled NR compounds stabilized with 6-PPD antioxidant: (a) storage modulus  $G'$  and (b) retention of  $G'$ .

Figure 13: Relative storage modulus (relative  $G_0$ ) at 1% strain of FA/NR compounds with and without 6-PPD before and after storage of 12 weeks.

- [6] Da Costa HM, Visconte LLY, Nunes RCB, Furtado CRG: Rice-husk-ash-filled natural rubber. II. Partial replacement of commercial fillers and the effect on the vulcanization process, *J. Appl. Polym. Sci.* 87 (2003) 1405–1413.
- [7] Siriwardena S, Ismail H, Ishiaku US: A comparison of white rice husk ash and silica as fillers in ethylene-propylene-diene terpolymer vulcanizates, *Polym. Int.* 50 (2001) 707–713.
- [8] Kosíková B, Gregorová A, Osvald A, Krajčovicová J: Role of lignin filler in stabilization of natural rubber-based composites, *J. Appl. Polym. Sci.* 103 (2007) 1226–1231.
- [9] Hua D, Ningjian A, Tuo Y, Li Z, Chubo H: The reinforcement of red clay on natural rubber and its reinforcing mechanism, *J. Appl. Polym. Sci.* 112 (2009) 3418–3422.
- [10] Goharpey F, Mirzadeh A, Sheikh A, Nazockdast H, Katbab A: Study on microstructure, rheological, and mechanical properties of cellulose short fiber reinforced TPVs based on EPDM/PP, *Polym. Composite.* 30 (2009) 182–187.
- [11] Ahmaruzzaman M: A review on the utilization of fly ash, *Prog. Energ. Combust.* 36 (2010) 327–363.
- [12] Sombatsompop N, Thongsang S, Markpin T, Wimolmala E: Fly ash particles and precipitated silica as fillers in rubbers. I. Untreated fillers in natural rubber and styrene-butadiene rubber compounds, *J. Appl. Polym. Sci.* 93 (2004) 2119–2130.
- [13] Kongvasana N, Kositchaiyong A, Wimolmala E, Sirisinha C, Sombatsompop N: Fly ash particles and precipitated silica as fillers in NR/CR vulcanizates under thermal and thermal-oil ageing, *Polym. Adv. Technol.* 22 (2011) 1014–1023.
- [14] Kantala C, Wimolmala E, Sirisinha C, Sombatsompop N: Reinforcement of compatibilized NR/NBR blend by fly-ash particles and precipitated silica, *Polym. Adv. Technol.* 20 (2009) 448–458.
- [15] James EM, Burak E, Frederick RE: *The Science and technology of rubber*, Elsevier Academic Press, London (2005).
- [16] Saowapark T, Sombatsompop N, Sirisinha C: Viscoelastic properties of fly ash-filled natural rubber compounds: Effect of fly ash loading, *J. Appl. Polym. Sci.* 112 (2009) 2552–2558.
- [17] Cibulková Z, Šimon P, Lehocký P, Balko J: Antioxidant activity of *p* phenylenediamines studied by DSC, *Polym. Degrad. Stabil.* 87 (2005) 479–486.
- [18] Herbert M: *Progress in polymer degradation and stability research*, Nova Science Publisher, New



(a)



(b)

York (2008).

- [19] Kumar A, Commereuc S, Verney V: Ageing of elastomers: a molecular approach based on rheological characterization, *Polym. Degrad. Stabil.* 85 (2004) 751–757.
- [20] Cibulková Z, Šimon P, Lehocký P, Balko J: Antioxidant activity of 6PPD derivatives in polyisoprene matrix studied by non-isothermal DSC measure-

- ments, *J. Therm. Anal. and Calorim.* 80 (2005) 357–361.
- [21] Phewthongin N, Saeoui P, Sirisinha C: Comparison of viscoelastic behaviour in silica filled cured and uncured CPE/NR blends with various mixing time, *Appl. Rheol.* 16 (2006) 182–189.
- [22] Abu-Jdayil B, Mohameed H, Snobar T, Sa'id M: Rheology and storage tests of Dead Sea shampoo, *Appl. Rheol.* 14 (2004) 96–103.
- [23] Navarro-Gonzalez M, Wagner MH: Storage stability of bitumen modified by the addition of ground rubber, swollen SBS and polymeric short fibers, *Appl. Rheol.* 22 (2012) 24691.
- [24] Navarro-Gonzalez M: Rheology and engineering parameters of bitumen modified with polyolefins, elastomers and reactive polymers, Technische Uni Berlin, Berlin (2010).
- [25] Narathichat M, Sahakaro K, Nakason C: Assessment degradation of natural rubber by moving die processability test and FTIR spectroscopy, *J. Appl. Polym. Sci.* 115 (2010) 1702–1709.
- [26] Juan Z: Network model for the entangled polymer melts: A review, *Physics Procedia* 3 (2010) 1775–1780.
- [27] Barnes HA, Hutton JE, Walters K: *An Introduction to Rheology*, Elsevier Science Publishers, Amsterdam (1988).
- [28] Giancarlo L, Luciano G: Dependence of zero-shear viscosity on molecular weight distribution, *J. Polym. Sci. Pol. Lett.* 11 (1973) 95–101.
- [29] William HT, Warren HB, Dewey LK: Rheological molecular weight distribution determinations of ethylene/tetrafluoroethylene copolymers: implications for long-chain branching, *Macromolecules* 26 (1993) 499–503.
- [30] Soobum C, Chang DH: Molecular Weight Dependence of Zero-Shear Viscosity of Block Copolymers in the Disordered State, *Macromolecules* 37 (2004) 215–225.
- [31] Jean-Marc C, Laurent C, Laurent G, Yves B, Catherine G: Molecular weight between physical entanglements in natural rubber: A critical parameter during strain-induced crystallization, *Polymer* 48 (2007) 1042–1046.
- [32] Bateman L, Moore CG, Porter M, Saville B: *The chemistry and Physics of rubber like substance*, L.Maclaren & Sons, London (1963).
- [33] Jabulani SM, Elsabé PK, Richard AK: Effect of fly ash characteristics on the behaviour of pastes prepared under varied brine conditions, *Miner. Eng.* 24 (2011) 923–929.
- [34] Jenkins R, Snyder RL: *Introduction to X-Ray Powder Diffraction*, Wiley-Interscience, New York (1996).
- [35] Ozlem C, Erdem D, Sabriye P: Characterization of fly ash and its effects on the compressive strength properties of Portland cement, *Indian J. Eng. Mater. S.* 15 (2008) 433–440.
- [36] Andreas AL: Data reduction, and cluster and discriminant analysis of aluminosilicate infrared spectra-fly ash reacted at 860 °C with sodium carbonate as a model system, *Vib. Spectrosc.* 37 (2005) 209–216.
- [37] Temuujin J, Williams RP, Riessen AV: Effect of mechanical activation of fly ash on the properties of geopolymer cured at ambient temperature, *J. Mater. Process. Tech.* 209 (2009) 5276–5280.
- [38] Hasma H, Othman AB: Role of some non-rubber constituents on thermal oxidative, *J. Nat. Rubb. Res.* 5 (1990) 1–8.
- [39] De SK, White JR: *Rubber Technologist's handbook*, Rapra Technology Limited Shropshire (2001).
- [40] Seng-Neon G, Kow-Fong T: Effect of treating latex with some metal ions on storage hardening of natural rubber, *Polymer* 34 (1993) 2142–2147.
- [41] Kawahara S, Kakubo T, Sakdapipanich JT, Isono Y, Tanaka Y: Characterization of fatty acids linked to natural rubber-role of linked fatty acids on crystallization of the rubber, *Polymer* 41 (2000) 7483–7488.
- [42] Albert H, Smith GEP JR, Gottschalk GW: Effect of iron on aging of GR-S, *Ind. Eng. Chem.* 40 (1948) 482–487.
- [43] Aronniemi M, Sainio J, Lahtinen J: Chemical state quantification of iron and chromium oxides using XPS: the effect of the background subtraction method, *Surf. Sci.* 578 (2005) 108–123.
- [44] Elka K, Daniela P, Alla S, Ivan M, Lacezar P: Study of iron state in titania-supported FeMo catalysts of hydrodesulfurization, *React. Kine. Catal. Lett.* 85 (2005) 283–290.
- [45] Olefjord I: Application of electron spectroscopy for chemical analysis (ESCA) to the study of iron-based battery electrodes, *J. Appl. Electrochem.* 5 (1975) 145–150.
- [46] Kelber JA, Lin TC, Seshadri G: A consistent method for quantitative XPS peak analysis of thin oxide films on clean polycrystalline iron surface, *Appl. Surf. Sci.* 119 (1997) 83–92.
- [47] Ratnayuke UN, Senevirantne G, Siriwardene S, Prasad W: Effect of Iron (Fe) on quality of crepe rubber, *International Seminar on Elastomer* (2003) 47.
- [48] Brendan Ro: *Rubber compounding: chemistry and applications*, Marcel Dekker, New York (2004).
- [49] Phewphong P, Saeoui P, Sirisinha C: Mechanism of silica reinforcement in CPE/NR blends by the use of rheological approaches, *J. Appl. Polym. Sci.* 107 (2008) 2638–2645.
- [50] George W: *Handbook of fillers*, William Andrew Inc, New York (1999).

