

A Comparative Study of Aging Characteristics and Thermal Stability of Oil Palm Ash, Silica, and Carbon Black Filled Natural Rubber Vulcanizates

Zhong Xian Ooi, Hanafi Ismail, Azhar Abu Bakar

Division of Polymer Engineering, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia

Correspondence to: H. Ismail (E-mail: hanafi@eng.usm.my)

ABSTRACT: Filler-filled natural rubber (NR) vulcanizates were prepared by conventional laboratory-sized two roll mills and cured using sulfuric system. The effect of thermal aging on physical properties and thermogravimetric analysis (TGA) of oil palm ash (OPA) and commercial fillers (i.e., silica vulkasil C and carbon black N330)-filled NR vulcanizates at respective optimum loading and equal loading were studied. Before aging, the OPA-filled vulcanizates showed comparable optimum strength as carbon black-filled vulcanizates. The hardening of aged filler-filled NR vulcanizates happened after aging, thereby tensile strength and elongation at break reduced while the modulus increased. Fifty phr carbon black-filled vulcanizates showed better retention in tensile properties as compared to silica (10 phr) and OPA (1 phr). This was attributed to the addition of different filler loading and this finding was further explained when equal loading of filler-filled vulcanizates was studied. Fourier transform infra-red analysis showed chemical structure had changed and tensile fractured surface exhibited smooth appearance due to the deterioration in tensile properties after aging. TGA also denoted the thermal stability was depending on the amount of filler loading. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 4474–4481, 2013

KEYWORDS: aging; elastomers; thermal properties; thermogravimetric analysis

Received 11 February 2013; accepted 9 June 2013; Published online 24 July 2013

DOI: 10.1002/app.39649

INTRODUCTION

Natural rubber (NR) is produced from the latex of the *Hevea brasiliensis* tree, and is chemically based on *cis*-1,4-polyisoprene except for the chain ends. It is well-known for good elastic properties, resilience properties, abrasion, and impact resistance.^{1,2} However, its resistance to thermal and oxygen is poor³ due to the presence of high amount of carbon double bonds within its structure, and high oxygen content promote the rate of molecular chain scission.⁴ Under thermal condition, most polymers lose their unique properties as a result of molecular chain scission.⁵ Thus, the incorporation of filler to improve the thermal and oxygen resistance is therefore important.

In Malaysia, oil palm ash (OPA) is highly abundant and will be disposed or dumped in an open field. It was reported that 4 million tonnes of OPA is produced annually⁶ and it was forecasted that the ash produced will increase comply with the increasing demand on palm oil commodity. In the previous work, it is worthwhile to note that the incorporation of a small amount of the OPA was capable of showing the reinforcement

that occurred between OPA and rubber matrix and it is found that 1 phr loading gives the optimum value on tensile strength and elongation at break. Meanwhile, other commercial fillers such as silica (10 phr) and carbon black (50 phr) require much larger quantities to reinforce NR properties.^{7,8}

In this article, the thermal properties such as retention properties and thermal stability of different optimum loading of respective filler in NR vulcanizates under thermal aging condition was studied, the optimum loading (1 phr) of OPA⁹ will be compared with two other types of commercial filler (i.e., silica and carbon black) in which optimum loading at 10 phr for silica and 50 phr for carbon black in terms of tensile properties as well as tensile fracture surface before and after thermal aging have been investigated. The equal loading (1 phr) of OPA, silica, and carbon black was also studied and compared with respect to study the effect of filler types.

EXPERIMENTAL

Materials

NR (grade SMR L) was used as the matrix, and was supplied by the Rubber Research Institute of Malaysia (RRIM). The

Table I. Physical Properties of OPA, Silica, and Carbon Black

	OPA	Silica	Carbon black
Mean Particle size (μm)	17.88	10.47	4.60
Density (g/cm^3)	2.63	2.00	1.90
BET surface area (m^2/g)	45.4	38.5	74.9

OPA used in this work was collected from the United Oil Palm Mill, Penang, Malaysia. The OPA was dried in a vacuum oven (model EV 018) at 80°C for 24 h to expel moisture. The dried OPA was then sieved with mesh (size 75) to separate the large and unburned residues. The main elemental composition (wt %) of OPA was analyzed by X-ray fluorescence (XRF) spectrometer (model Rigaku RIX3000) as follows: C (41.5), SiO_2 (34.0), CaO (7.3), Al_2O_3 (3.9), MgO (3.8), K_2O (3.7), P_2O_5 (3.2), Fe_2O_3 (1.9), and trace elements (0.7). Commercial fillers that is carbon black (N330), precipitated silica (grade vulkasil C), and other curing ingredients such as zinc oxide, stearic acid, *N*-Isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD), *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), and sulfur were purchased from Bayer (M) Sdn. Bhd. and used as received. The physical properties of OPA, silica and carbon black are shown in Table I.

Preparation of Filler-Filled NR Vulcanizates

The filler-filled NR vulcanizates were prepared using a conventional laboratory sized two roll mill (model XK 160). A detailed formulation used in this study is shown in Table II. The curing characteristics such as scorch time (t_{s2}), cure time (t_{c90}), and maximum torque (M_H) of the filler-filled NR vulcanizates were determined by Mosanto Moving Die Rheometer (model MDR 2000) according to ISO 3417 at 150°C , followed by compression molded at 150°C according to their respective t_{c90} values. The molded sheets were conditioned in desiccators for 24 h prior to further testing.

Retention Properties Under Aging Condition

To evaluate the retention properties under aging condition of OPA, silica, and carbon black-filled NR vulcanizates, five dumb-bell shaped specimen were placed in an oven with air-circulating system at the operating temperature of 100°C for 48 h, according to ASTM D 573. The tensile properties of aged specimens were determined in the same manner as unaged specimen and compared. The retained percentage values of tensile properties were calculated according to eq. (1).

$$\text{Retention (\%)} = \frac{\text{Value}_{\text{aged}}}{\text{Value}_{\text{unaged}}} \times 100 \quad (1)$$

Fourier Transform Infra-Red Spectroscopy

FTIR was used to obtain some qualitative information about the functional groups and chemical characteristics of the fillers-filled NR

Table II. Formulation and Designation of Filler Filled Natural Rubber Vulcanizates

Materials	Sample code (phr ^a)					
	Gum	OPA 1	Silica 1	Carbon black 1	Silica 10	Carbon black 50
NR (SMR L)	100	100	100	100	100	100
OPA	-	1	-	-	-	-
Silica	-	-	1	-	10	-
Carbon black	-	-	-	1	-	50
Zinc oxide	1.5	1.5	1.5	1.5	1.5	1.5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
IPPD	2.0	2.0	2.0	2.0	2.0	2.0
CBS	1.9	1.9	1.9	1.9	1.9	1.9
Sulfur	1.6	1.6	1.6	1.6	1.6	1.6

^a Parts per hundred parts of rubber.

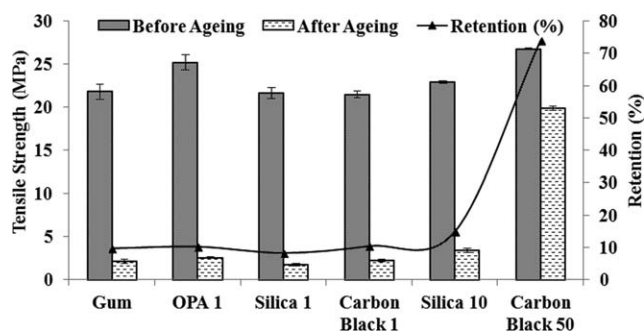


Figure 1. Effect of the filler types on the tensile strength of natural rubber vulcanizates after thermal aging for 2 days at 100°C .

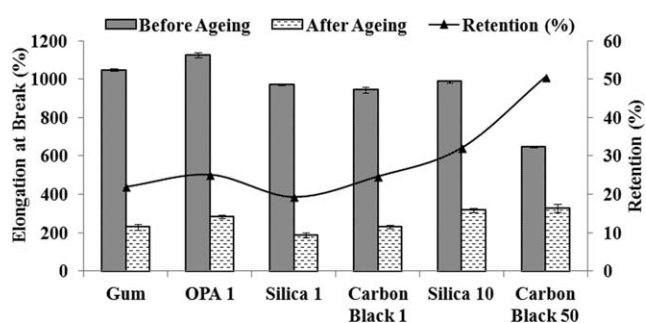


Figure 2. Effect of the filler types on the elongation at break of natural rubber vulcanizates after thermal aging for 2 days at 100°C .

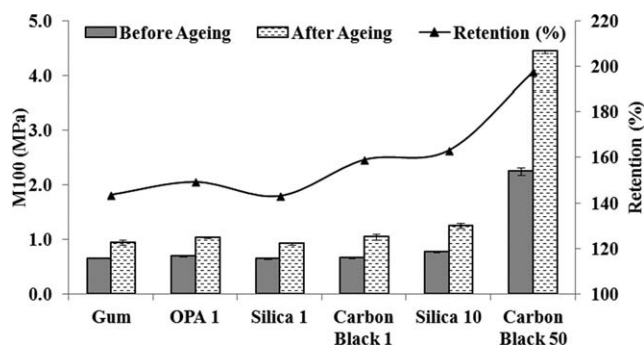


Figure 3. Effect of the filler types on the tensile modulus (M_{100}) of natural rubber vulcanizates after thermal aging for 2 days at 100°C.

vulcanizates and possible chemical structure change between fillers and NR before and after effect of thermal aging. FTIR spectra were obtained and recorded using a Perkin Elmer Spectrometer (Massachusetts, USA) in the range of 550 to 4000 cm^{-1} at resolution of 4 cm^{-1} . For each spectrum, 16 scans were coadded.

Morphological Studies

Tensile fractured surface of different filler-filled NR vulcanizates before aging and after aging were scanned with scanning electron microscope (FESEM: model Zeiss Supra 35 VP) and compared. The fractured specimens were mounted on aluminum stubs and sputter-coated with a thin layer of gold-palladium in order to avoid electrostatic charge and poor resolution during examination. The SEM images observed were used to study the mode of fracture and support the change in tensile properties.

Thermogravimetric Analysis of Filler-Filled NR Vulcanizates

To evaluate the thermal stability of each type of filler-filled NR vulcanizates, thermogravimetric analysis (TGA) was performed using a Perkin Elmer Pyris 6 Thermogravimetric Analyzer. TGA had proven to be a successful technique in determining the thermal stability of polymers. A small amount (~ 10 mg) of specimen was taken for the analysis. The weight loss was measured as a function of temperature, which was heated from 30 to 600°C at a heating rate of 10°C/min in a nitrogen atmosphere.

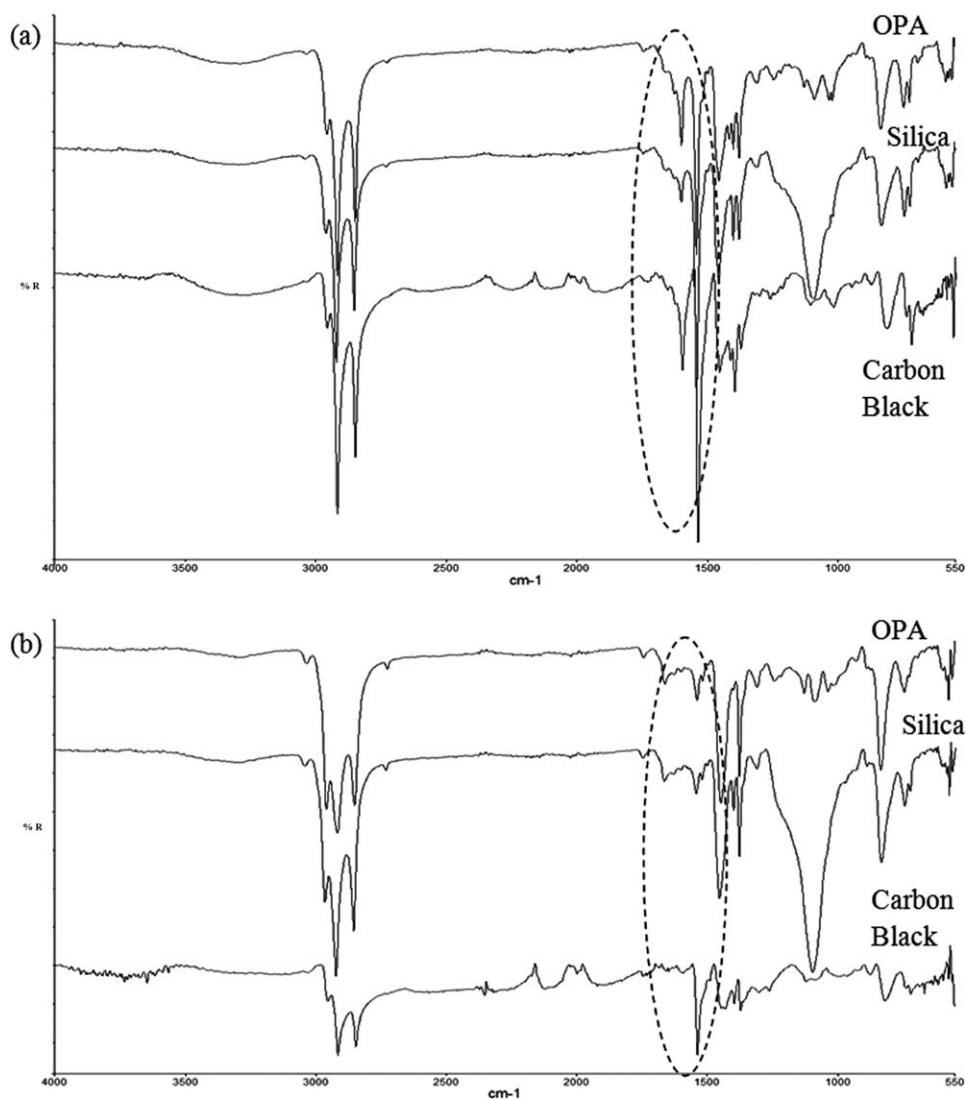


Figure 4. The FTIR spectra for optimum loading of OPA, silica, and carbon black filled natural rubber vulcanizates (a) Before aging, and (b) After aging.

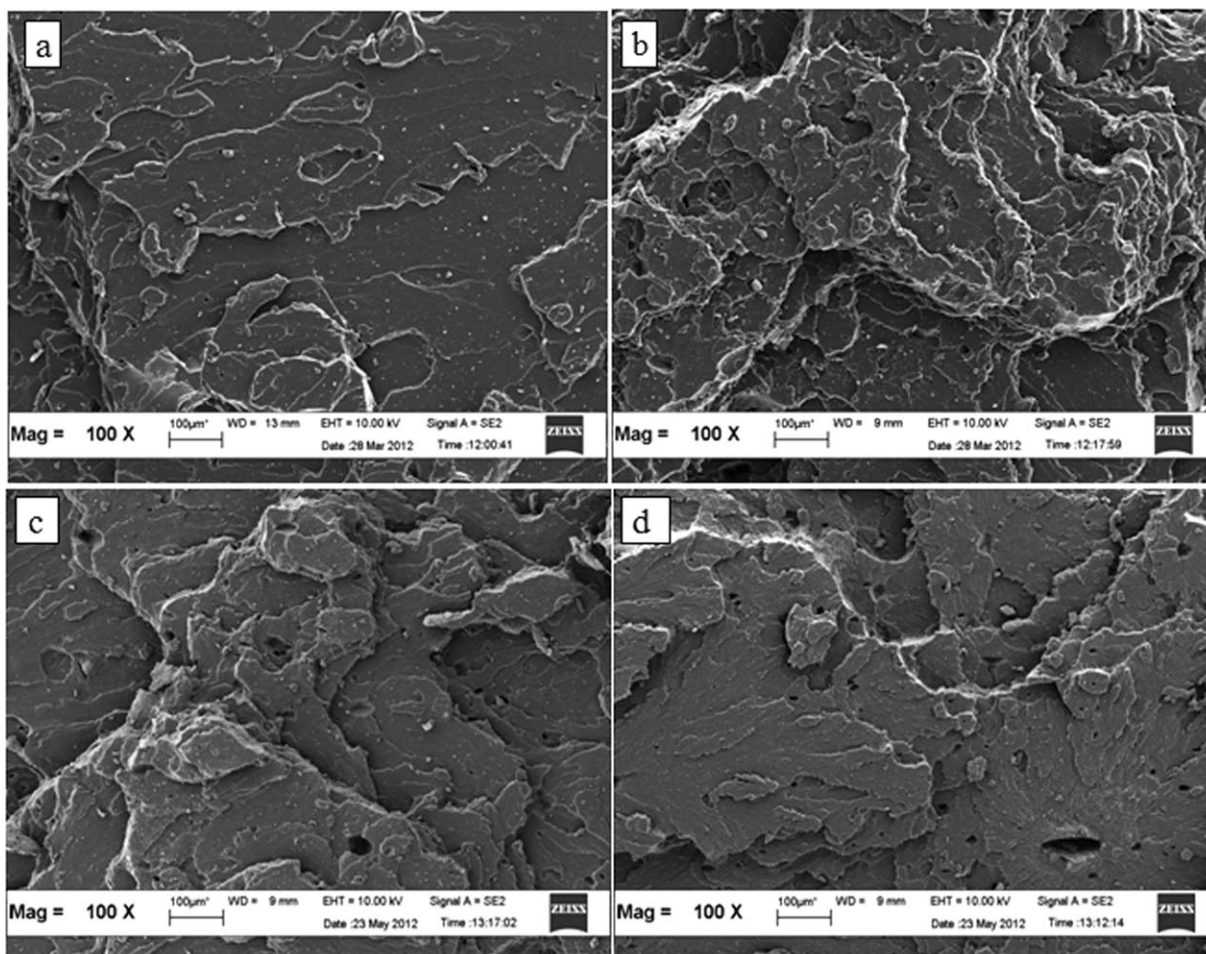


Figure 5. Tensile fractured surface of different filler (a) Gum, (b) 1 phr OPA, (c) 10 phr silica, (d) 50 phr carbon black before thermal aging.

The TGA curve was recorded and drawn in order to study the thermal stability of the OPA filled NR vulcanizates.

RESULTS AND DISCUSSION

Retention Properties

Figures 1 and 2 show the tensile strength and elongation at break of gum and different filler-filled vulcanizates before and after thermal aging for 2 days at 100°C. Before thermal aging, at the same filler loading, the tensile strength, and elongation at break of the OPA-filled vulcanizates were higher than those of the corresponding silica and carbon black-filled NR vulcanizates. When compared to 1 phr OPA loading, the 1 phr of silica and 1 phr of carbon black-filled NR vulcanizates were not effectively strengthen the NR vulcanizates as low filler loading may affected the formation of stretched straight NR chains between neighbor particles thus reduced the slippage of the absorbed NR chains on the filler surface when external force was applied.¹⁰ This showed the unique characteristic for the OPA, which naturally showed the irregular shaped particles with rough surfaces, and porous structures that allowed NR chains to penetrate into the pores of OPA and became bound rubber. This only applicable at a very low OPA loading as OPA particles tended to

agglomerate at higher loading because of its hydrophilic characteristics causing poor dispersion as reported in previous work.⁹

However, amongst the optimum loading of filler-filled NR vulcanizates, indicating the 50 phr carbon black-filled NR vulcanizates exhibited the highest tensile strength followed by 1 phr OPA and then the 10 phr silica-filled vulcanizates. This reinforcement efficiency may be correlated to the interaction between filler and NR. Ismail et al.¹¹ reported that the smaller particle size normally gives better interaction with NR matrix. The carbon black has the smallest particle size (Table I), so it exhibited the highest tensile strength as compared to silica and OPA. In terms of elongation at break, the silica and carbon black-filled vulcanizates showed decreasing value while OPA had improved the elongation at break. Again, this may attributed to the surface characteristic of OPA that able to support the stress transferred from the NR matrix and withstand the elongation when external forces applied on it. Thus, the strength of NR matrix could be reinforced as well as elongation before fracture. Also, it was worth noting that the tensile strength of 1 phr OPA filled NR vulcanizates (25.2 MPa) was comparable to 50 phr carbon black filled vulcanizates (26.8 MPa) and even higher than 10 phr silica filled vulcanizates although the mean particle

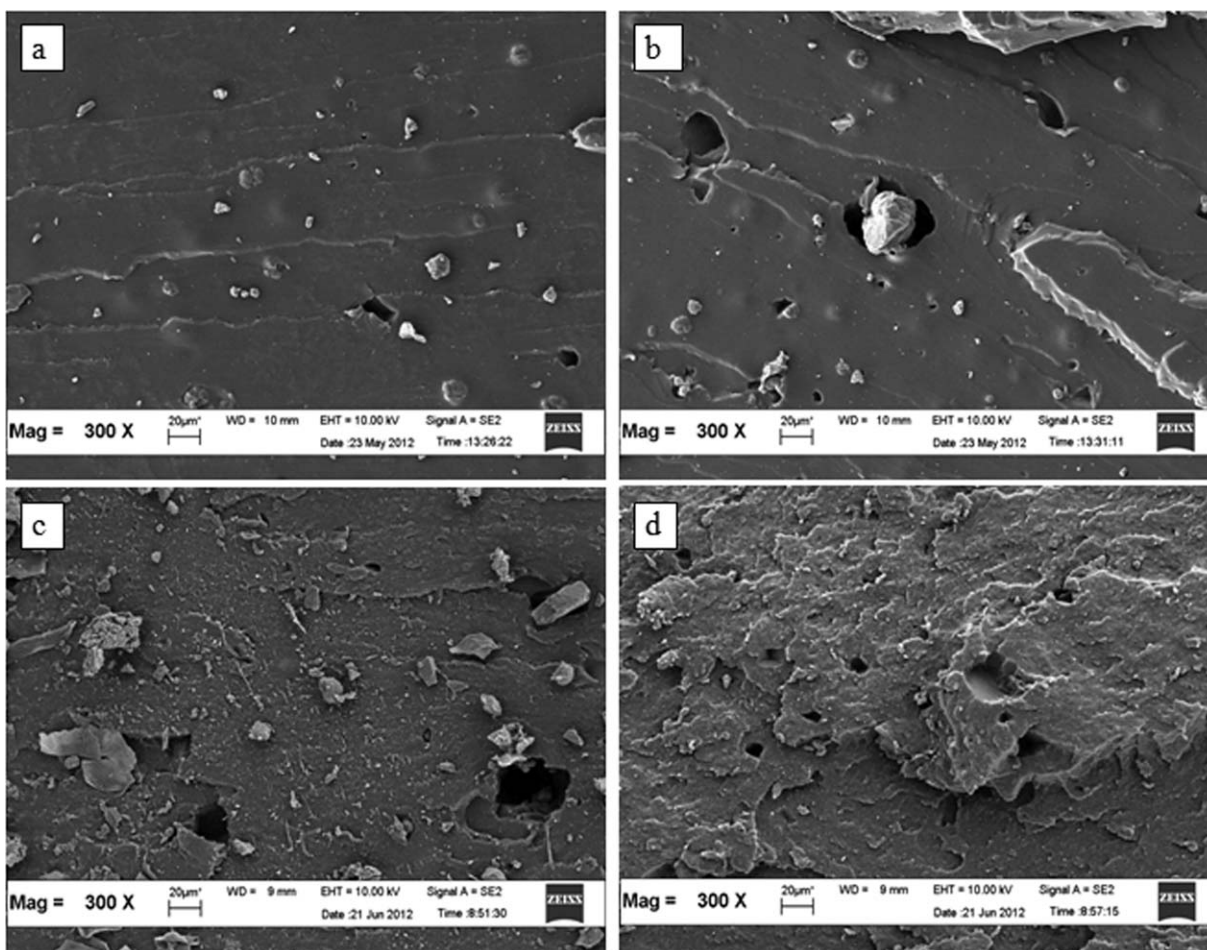


Figure 6. Tensile fractured surface of different filler (a) Gum, (b) 1 phr OPA, (c) 10 phr silica, (d) 50 phr carbon black after thermal aging for 2 days at 100°C.

size of OPA was larger than the commercial filler. The observed trend might have contributed to the porous structure of OPA itself and allowed the rubber chain to penetrate into the pores of OPA as discussed earlier.

When various filler-filled vulcanizates were subjected to the effect of thermal aging for 2 days at 100°C, it had resulted in the reduction of tensile strength and elongation at break irrespective to the types of fillers. The strength reduction of various filled vulcanizates was due to the oxidation of NR matrix, which contained high amount of C=C bonds and this could promote the molecular chain scission.⁴ Another reason was due to hardening and embrittlement to the NR matrix, which had resulted in the stress was unable to be transferred from matrix to filler (poor load-bearing) and consequently leading to catastrophic failure to the rubber product. However, in terms of the retention properties, the carbon black filled NR vulcanizates showed the highest retained tensile strength and elongation at break, followed by silica and OPA-filled vulcanizates. This might be attributed to the different optimum loading, i.e., OPA (1 phr), silica (10 phr), and carbon black (50 phr). Arayaprane and Rempel¹² reported that the retention in tensile strength increased when the filler loading was

increased and this suggested that the composition amount of matrix to be degraded was decreased with an increase in filler loading. The addition of high filler loading would hamper the NR matrix from heat degradation. Ismail et al.¹³ also mentioned that the filler type had no significant effect on the retention properties when the same loading of various fillers were added. This was in agreement with the results shown in Figures 1 and 2 in which the retention properties of the same loading of OPA, silica, and carbon black-filled vulcanizates were comparable as unfilled NR vulcanizates, which ranged from 8 to 10% (Figure 1) and 20 to 24% (Figure 2).

The tensile modulus of the various filler-filled NR vulcanizates is illustrated in Figure 3, before and after subjected to the thermal aging. As expected, the tensile modulus increased when the filler was added since the modulus of filler was higher than that of NR matrix. Modulus is an alternative indication for hardness of the materials.¹¹ After subjected to the effect of thermal aging, the opposite trend was observed for tensile modulus and shifted to a higher value. Again, this might be attributed to the hardening and embrittlement of the NR matrix when subjected to the thermal aging. Similar observation was reported for NR/EPDM blends by Arayaprane and Rempel.¹⁴ The tensile

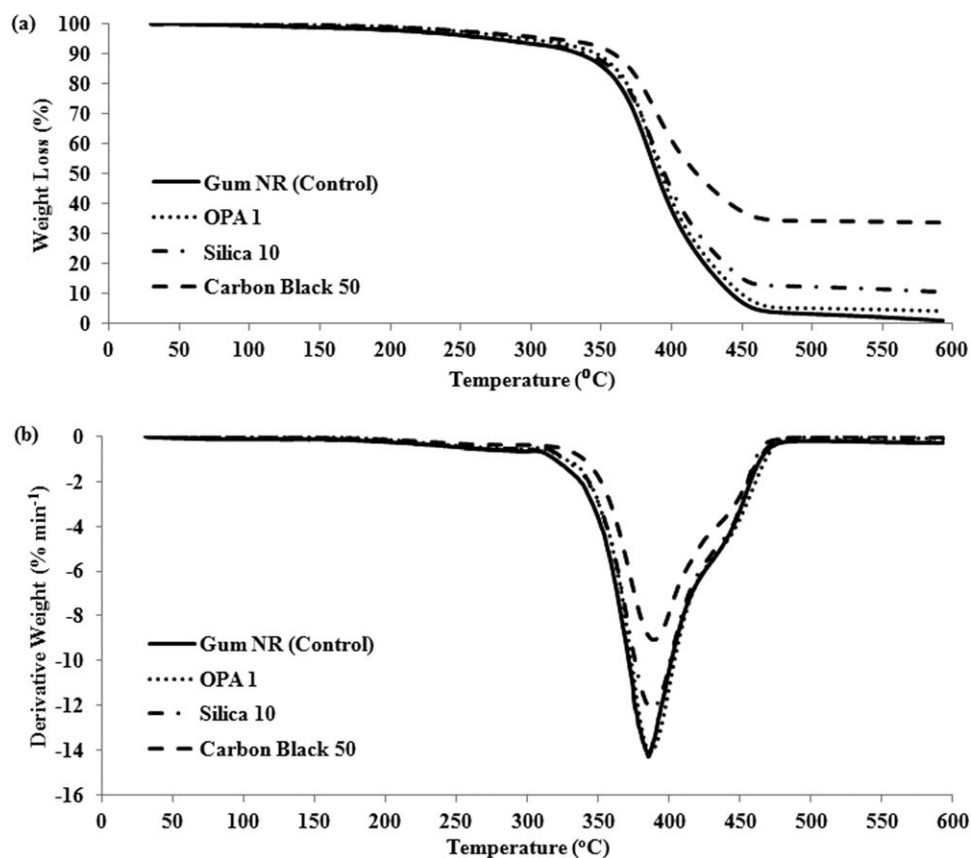


Figure 7. Thermal stability of gum NR vulcanizate and vulcanizates filled with optimum loading of oil palm ash, silica, and carbon black (a) TGA curve and (b) DTG curve.

modulus after aging increased due to scissoring of chain segments and sulfuric crosslink into shorter chain as reported by Ismail et al.¹³ The 50 phr carbon black-filled vulcanizates exhibited the highest retention because of high loading of carbon black. At the same filler loading, the carbon black showed the slightly higher tensile modulus than that of corresponding silica and OPA-filled NR vulcanizates. The experimental results were similar as previous work by Hamed and Zhao¹⁵ in which carbon black filler could promote the stiffening of NR matrix. Another reason might be due to the high thermal stability of carbon black as compared to silica and OPA.

FTIR Studies

To prove the deterioration of filler-filled NR vulcanizates, the IR spectra of OPA, silica, and carbon black filled NR vulcanizates were studied and recorded before and after subjected to thermal condition at 100°C for 2 days, as shown in Figure 4. A high intensity of the peak in the range of vibrations 1530–1570 cm⁻¹ (as highlighted with the eclipse) was observed for all the fillers-filled NR vulcanizates, which corresponded to the bond C=N, R-CH=N-R', S-S-C=N as previously reported by Murgic and Jelencic.¹⁶ These bonds are known as crosslink due to the addition of accelerators (CBS) and sulfur that are present in the NR vulcanizates. However, after subjected to aging condition, the intensity of those peaks was clearly attenuated suggesting that the chain scissoring had undergone deterioration as well as

polysulfide crosslinks when exposed to the high thermal condition. The role of IPPD is an antioxidant, however, the aging temperature and exposure time was 100°C and 2 days, which might not effective for the IPPD to take role into protecting the NR under such adverse condition. For the reason that the intensity band at 1660 cm⁻¹, which was assigned to the C=C-C=O¹⁷ tended to increase after aging especially for the OPA and silica-filled NR vulcanizates. The increase of these peaks was due to the oxidation at the main polymeric chain, which was attacked by the oxygen. Rohana Yahya et al.³ also observed this absorption band and the intensity increased when the aging time was increased. The chemical structure change in NR vulcanizates happened to deteriorate its properties; therefore the filler-filled NR vulcanizate lost its tensile strength and ductility.

Morphological Studies

Further evidence on the deterioration of fillers-filled NR vulcanizates were proven by the SEM images of the tensile fractured surface of unfilled NR vulcanizates and optimum loading of each filler-filled vulcanizates, which are presented in Figures 5 and 6, before and after the severe aging condition. The appearance of tensile fractured surface for all vulcanizates, especially filler-filled NR vulcanizates showed rougher surface with deeper tearing lines and more cracking path. However, after being subjected to thermal aging, it transformed and become smooth.

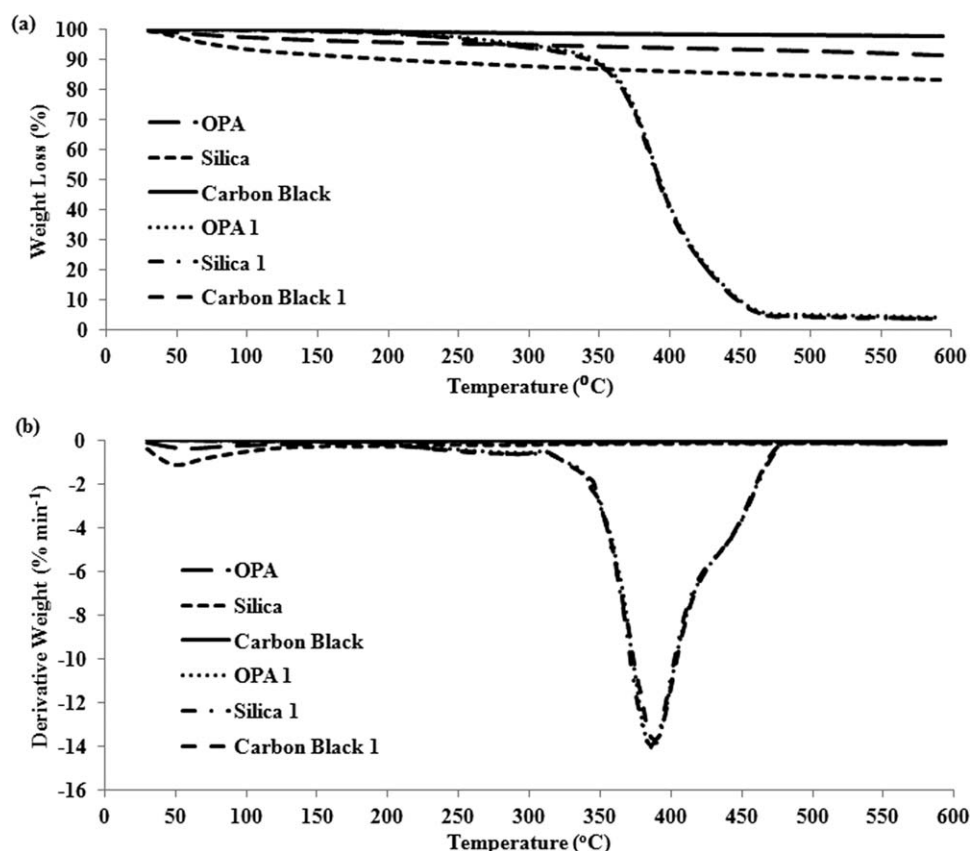


Figure 8. Thermal stability of each types of fillers and vulcanizates filled with same loading of oil palm ash, silica, and carbon black (a) TGA curve and (b) DTG curve.

This phenomenon indicated that the fractured mode of rubber product had transformed from ductile failure to brittle failure as hardening of NR matrix. Besides, the filler detachment had occurred especially for the OPA and silica filled vulcanizates as shown in Figure 5(b,c), respectively. It is worthwhile to note that the tensile fractured surface of carbon black-filled vulcanizates exhibited the rougher surface with some tearing line and angular cracking after thermal aging. This supported the tensile results obtained in which carbon black-filled vulcanizates showed the highest retained properties.

Thermogravimetric Analysis

Figures 7 and 8 show the TGA and derivative thermogravimetric (DTG) results of unfilled NR vulcanizates and NR vulcanizates filled with OPA, silica, and carbon black at optimum loading and same filler loading, respectively. With the addition of filler, there was some improvement in the thermal stability to all filler-filled NR vulcanizates as shown by the temperature variation of 10% weight loss ($T_{10\%}$), 50% weight loss ($T_{50\%}$), 90% weight loss ($T_{90\%}$), temperature at maximum weight loss rate (T_{max}), and char residue (%), which are summarized in Table III. In this study, the TGA on each raw filler also been carried out. Among the types of filler analyzed, the carbon black exhibited the excellent thermal stability, as compared to the OPA and silica fillers. It is well known that silica contains hydroxyl groups, which tend to absorb more moisture from environment and water molecules, were decomposed at elevated

temperature. Thus, the temperature at 10% weight loss for silica filled NR vulcanizates was lower than OPA and carbon black-filled vulcanizates. However, the temperature at 50% weight loss, the filler-filled NR vulcanizates shows an increasing trend corresponding to the amount of filler loading: 1 phr OPA < 10 phr silica < 50 phr carbon black. The addition of filler (i.e., OPA, silica, and carbon black) and their effect had been

Table III. Thermal Stability Data for Gum NR Vulcanizate and Vulcanizates Filled with Oil Palm Ash, Silica, and Carbon Black

Sample	$T_{10\%}$	$T_{50\%}$	$T_{90\%}$	T_{max}	Char residue (%)
Gum NR	328	389	442	385	0.69
OPA 1	347	393	450	387	4.10
Silica 1	341	391	447	386	3.39
Carbon black 1	342	393	448	388	3.77
Silica 10	340	395	-	387	10.63
Carbon black 50	359	418	-	389	33.73

$T_{10\%}$, temperature at 10% weight loss; $T_{50\%}$, temperature at 50% weight loss; $T_{90\%}$, temperature at 90% weight loss; T_{max} , temperature at maximum weight loss rate.

manifested as superior thermal insulation against the volatile compound during the decomposition of NR matrix under thermal conditions.¹⁸ The addition of reinforcing filler could enhance barrier between thermal source and undecomposed NR matrix regardless of filler types. This also explained the notably increased of char residue as the filler loading was increased, therefore the 50 phr carbon black-filled NR vulcanizates was higher in thermal stability than 10 phr silica-filled vulcanizates, followed by 1 phr OPA-filled NR vulcanizates.

To further prove the effect of filler loading amount on the thermal stability of NR vulcanizates, the same filler loading of the filler-filled NR vulcanizates displayed almost no difference in the weight loss at all the temperature range as shown in Figure 8. Again, this phenomenon certified the fact that the amount of filler would play a significant role to act as thermal insulation in order to protect inherent poor thermal stability of NR matrix.

CONCLUSIONS

On the basis of the experimental results, severe aging condition testified that all the vulcanizates exhibited significant reduction in tensile strength and elongation at break but increased the tensile modulus. The different retention properties of the aged vulcanizates were depending on the NR matrix and the amount of filler loading. With the SEM observation, the tensile fractured surface of aged vulcanizates provided the supportive evidence on the tensile results in which fractured mode transformed from ductile failure to brittle failure. The FTIR analysis also revealed the chemical structures changed in filler-filled NR vulcanizates and therefore deteriorated its tensile strength and ductility.

ACKNOWLEDGMENTS

This work was financially supported by the Ministry of Science, Technology and Innovation (MOSTI) science fund (Project no. 305/PBAHAN/6013380) and MyPhD (Z.X. Ooi).

REFERENCES

1. Van Beilen, J. B.; Poirier, Y. *Trends Biotechnol.* **2007**, *25*, 522.
2. Nga Dang, T. T.; Kim, J. K.; Kim, K. J. *J. Vinyl Addit Technol.* **2010**, *16*, 254.
3. Rohana Yahya, Y. S.; Azura, A. R.; Ahmad, Z. *J. Phys. Sci.* **2011**, *22*, 1.
4. Hamed, G. R. In *Engineering with Rubber*, 2nd ed; Gent, A.N., Ed.; Carl Hanser Verlag: München, Germany, **2007**.
5. Grassie, N.; Scott, G. *Polymer Degradation and Stabilization*. Cambridge University Press: New York, **1985**.
6. Foo, K. Y.; Hameed, B. H. *J. Hazard Mater.* **2009**, *172*, 523.
7. Ismail, H.; Ahmad, Z. *Iran. Polym. J.* **1996**, *5*, 207.
8. Ismail, H.; Osman, H.; Ariffin, A. *Polym. Plast. Technol.* **2005**, *43*, 1323.
9. Ooi, Z. X.; Ismail, H.; Abu Bakar, A. *Polym. Test.*, **2013**, *32*, 38.
10. Wang, Z.; Liu, J.; Wu, S.; Wang, W.; Zhang, L. *Phys. Chem. Chem. Phys.* **2010**, *12*, 3014.
11. Ismail, H.; Rozman, H. D.; Jaffri, R. M.; Mohd Ishak, Z. A. *Eur. Polym. J.* **1997**, *33*, 1627.
12. Arayaprane, W.; Rempel, G. L. *J. Appl. Polym. Sci.* **2008**, *109*, 932.
13. Ismail, H.; Ishiaku, U. S.; Azhar, A. A.; Mohd Ishak, Z. A. *J. Elastom. Plast.* **1997**, *29*, 270.
14. Arayaprane, W.; Rempel, G. L. *Int. J. Mater. Struct. Reliab.* **2007**, *5*, 1.
15. Hamed, G. R.; Zhao, J. *J. Rubber Chem. Technol.* **1999**, *72*, 721.
16. Murgic, Z. H.; Jelencic, J. *Macromol. Mater. Eng.* **2000**, *283*, 21.
17. Calvini, P.; Gorassini, A. *Restaurator (Copenhagen)* **2002**, *23*, 48.
18. Zhu, J.; Uhl, F. M.; Morgans, A. B.; Wilkie, C. A. *Chem. Mater.* **2001**, *13*, 4649.