*Asian Journal of Chemistry; Vol. 27, No. 4 (2015), 1235-1239*

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17200

# Improving Thermal Properties of Fluoroelastomer Using Carbon Nanotubes in Presence of Air and under Nitrogen Flow

J. HEIDARIAN* and A. HASSAN

Polymer and Composite Materials Research Laboratory, Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

*Corresponding author: Fax: +60 3 79674193; Tel: +60 3 79674249; E-mail: heidarianj@um.edu.my

*Received*: 11 February 2014; *Accepted*: 7 May 2014; *Published online*: 4 February 2015; AJC-16765

Carbon nanotube (CNT)-, carbon black (CB)-filled fluoroelastomer (FE) and unfilled-fluoroelastomer were prepared (CNT/FE, CB/FE and fluoroelastomer). Their thermal gravimetric analysis in presence of air and under nitrogen flow was compared. Results show that in presence of air carbon nanotube improved the thermal properties of fluoroelastomer, resulting in higher amount of fluoroelastomer and char remaining after TGA runs in the temperatures range of 520-900 °C, relative to fluoroelastomer and CB/FE. Moreover in all fluoroelastomer samples at 900 °C most of the fluoroelastomer, char and carbon nanotube or carbon black burned, degraded and evaporated and therefore most mineral additives remained compared to nitrogen surroundings. In TGA runs for the aforementioned temperature range, the percentage of undegraded fluoroelastomer or char remained in the compounds is more for tests under nitrogen flow compared to tests in presence of air. Changing the environment from nitrogen to air is not effective on $T_{onset}$, $T_{5\,\%}$, $T_{10\,\%}$ and $T_{50\,\%}$. Carbon nanotube does not affect these parameters of CNT/FE compared to CB/FE or fluoroelastomer.

**Keywords: Fluoroealstomer, Carbon nanotube, Thermal gravimetric analysis, Air, Nitrogen.**

## INTRODUCTION

Viton is a synthetic rubber and a fluoroelastomer (FE). Viton® GF-600S is a terpolymer of hexafluoro-propylene, vinylidene fluoride and tetra-fluoroethylene with a cure site monomer. It is a peroxide cure and 70 % fluorine fluoroelastomer[1,2].

Normally, in the formulation of fluoroelastomer, carbon black is used. Replacing carbon black with carbon nanotube partially or totally is expected to improve properties of fluoroelastomer which are important in making O-rings, especially for oil and gas industries. The thermal decomposition properties of fluoroelastomers and polytetrafluoroethylene (PTFE) have been examined by Lee[3]. Heating rates of 2-30 °C $min^{-1}$ under a static air atmosphere were employed for the experiments. The decomposition of fluoroelastomers occurs from 400 to 500 °C and PTFE decomposed at a higher temperature (500 to 600°C). The activation energies of decomposition, for the two fluoroelastomers and fluorocarbon resin, ranged from 225 to 266 kJ $mol^{-1}$. The surface morphology of the fluoropolymers after a heat-treatment procedure shows that there were no changes in the morphology when the heat-treatment temperature was under 400 °C for 10 min. However, both fluoropolymers decomposed when the heat-treatment temperature was 500 °C for 10 min.

It was reported that[4] the use of multi-walled carbon nanotubes (MWCNTs)-embedded in fluorinated rubber can lead to a rubber nanocomposite with cellulation structure, giving extreme performance. The O-ring made by this nanocomposites also shows higher resistance when compared to carbon black (CB)-filled fluoroelastomer (CB/FE) O-ring in both low and high temperature ranges. Ito *et al.*[5] used the resulting sealing solution of novel sealing material based on carbon nanotubes (CNT)-FE nanocomposites (CNT/FE) and underwent field test around the world. The results indicate the new sealing solution perform well in both low and high temperature sealing applications and it marks a rare success story for use of nanotechnology in the oil field.

Some of the researchers verified the effect of carbon nanotube on improving the thermal properties of fluoroelastomer. Noguchi *et al.*[6] shows that for CNT/FE compared to CB/FE, at high temperature the dynamic modulus of elasticity and rigidity improved. However, the average coefficient of linear expansion decreased. Dai *et al.*[7] for a rubber composite which includes a fluoroelastomer matrix and plasma-modified carbon nanomaterial, showed that storage modulus over temperature range of 50-200 ºC improved compared to the pure fluoroelastomer. FE/MWCNTs hybrid nanocomposites were prepared by Pham *et al.*[8]. With increasing MWCNT loading, there was a steady increase in decomposition temperature. Thermogravimetric analysis results showed that with increasing MWCNT loadings, thermal stability of composite increases. The activation energy of thermal decomposition (77-87 kJ mol$^{-1}$) increased. An annular seal formed from an elastomer material (can be a fluoroelastomer) and carbon nanotube, or nanodiamonds was disclosed for a drill bit with prolong downhole life by Griffo and Keshavan[9].

There are research works showing improving in properties to resist different chemicals using carbon nanotube in fluoroelastomer instead of carbon black. Russell *et al.*[10] reported that the incorporation of carbon nanotubes in fluoroelastomer considerably improves properties over the use of carbon blacks (CBs) in the automotive fuel system. Perfluoroelastomer composition comprising perfluoroelastomer and nanodiamond for sealing semiconductor manufacturing equipment which have significant plasma resistance were reported by Tanaka and Fukuyama[11].

Some changes in the properties of fluoropolymers due to the presence of carbon nanotube were reported by a number of researchers. Carbon nanotube can change thermo-mechanical properties[12-14], physical and mechanical properties[15-17] and other properties[18] of the fluorocarbon. Thermal stability of the PTFE composites is also enhanced by the presence of carbon nanotube[19].

Research on the verification of the effect of carbon nanotube on the amount of residues in TGA runs of CNT/FE nanocomposites in presence of air is quite rare. In addition, the comparison of the amount of residue in TGA runs of fluoroelastomer, CB/FE and CNT/FE in air environment is not available in literature. Comparing the above mentioned results with that of TGA runs under nitrogen influence is also new. Therefore, this investigation is unique in the sense that knowledge of the amount of residue gives an insight into the ability of carbon nanotube to improve the thermal stability of CB/FE and fluoroelastomer composites in presence of air.

In the present work, carbon nanotube was used as filler for Viton® GF-600S with the aim of improving thermal stability of fluoroelastomer in the presence of air. The thermal properties of the composites *vis-à-vis* carbon black filled and unfilled fluoroelastomer were assessed by thermogravimetric analysis (TGA). The results were compared with TGA runs under nitrogen which was done in our previous work[20]. This is to ascertain whether incorporation of carbon nanotube can preserve more of the undegraded fluoroelastomer and char compared to CB/FE or fluoroelastomer in TGA runs in the presence of air.

In addition, in another study[21] we verified the properties of the above mentioned fluoroelastomer and fillers/FE, by dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and X-ray diffraction (XRD).

## EXPERIMENTAL

Materials used were Viton GF-600S (Fluoroelastomer, FE) supplied by ERIKS Sdn. Bhd. (Malaysia), organic peroxide (Luperox 101 XL-45) made by Arkema Sdn. Bhd., carbon nanotube, MWNT TNM8, outside diameter, OD > 50 nm, purity > 95 % and 10-20 µm length manufactured by Chengdu Organic Chemicals Co. Ltd. (Chinese Academy of Sciences), carbon black, CB (Ensaco 250), given by Age D'Or Industrial Sdn. Bhd. (Malaysia), zinc oxide (Red Seal) provided by Texchem Materials Sdn. Bhd. (Malaysia) and triallylisocyanurate (TAIC) clear liquid produced by Liu Yang San Ji Chemical Trade Co. Ltd. (China).

Three formulations were compounded, carbon nanotube filled fluoroelastomer (CNT/FE), carbon black filled fluoroelastomer (CB/FE) and unfilled fluoroelastomer (FE). In all compounds the amount of fluoroelastomer, organic peroxide, zinc oxide and triallylisocyanurate (TAIC) were 70/2.1/2.1/2.1 g, respectively and for CNT/FE and CB/FE, 7 g filler was used.

Mixing fluoroelastomer with additives was done in a laboratory scale two roll mill with a roll temperature of 48 °C. Fluoroelastomer in the above mentioned composition was supplied to open roll. A uniform band was formed while three rolling cuts from each side of the mill were made, so that the polymer was homogenous and sufficiently warmed up. In the next stage, pre blended ZnO and triallylisocyanurate were added uniformly into the gum and then three rolling cuts from each side of the mill were done. After setting the roll distance to 1.1 mm carbon nanotube was then fed in. The compound was then tight milled ten times. The roll distance was then adjusted to 1.1 mm and the peroxide was added and after final 5 to 6 rolled up end passes, the mixture was supplied to the open roll and sheeted. After 24 h, re-milling was done with a roll temperature of 26 °C. The same procedure was used for CB/FE and fluoroelastomer.

Curing of fluoroelastomer compound was done with the mold (15 cm × 15 cm × 1 mm) in a heated press, at 177 °C under high pressure of (10 MPa) for 7 min. The post curing was done in air oven at 232 °C for 2 h. Conditions for curing and post curing were recommended by the supplier.

**Thermal gravimetric analysis:** 25-35 mg of post-cured samples was subjected to TGA runs from room temperature to 900 °C. It was carried out on a Perkin-Elmer Pyris Diamond TG/DTA thermal analysis system at a scan rate of 20 °C min$^{-1}$, in the presence of air. The same procedure was applied for 3.5-5 mg of pure carbon nanotube. The latter was also used for pure carbon black.

**Field emission scanning electron microscopy (FESEM) image analyses:** Image analysis was conducted using FESEM Philip XL-40 (UK). The post-cured CNT/FE (5 × 5 × 1 mm) was first applied on aluminum stub using double sided copper tape (3M Company), while the razor cut (cross-section) surface of it was coated with gold and subjected to FESEM image analyses.

## RESULTS AND DISCUSSION

**Thermogravimetric analysis in presence of air-weight of residual:** Fig. 1 shows the TGA plots of CNT/FE, CB/FE, fluoroelastomer, carbon nanotube and carbon black in the presence of air, extracted data from these plots are presented in Table-1. In Table-1, $T_{onset}$, $T_{5\%}$, $T_{10\%}$ and $T_{50\%}$ are the onset temperature at which the compound starts to lose weight (degrade), temperature at which the compound loses 5, 10 and 50 % weight respectively. It shows that carbon nanotube does not really affect these parameters of CNT/FE compared to CB/FE or fluoroelastomer.

TABLE-1
THERMAL GRAVIMETRIC ANALYSIS PROPERTIES OF FILLER/FE, FE AND PURE FILLER IN THE PRESENCE OF AIR

| FE Composite | $T_{Onset}$ (°C) | $T_{5\%}$ (°C) | $T_{10\%}$ (°C) | $T_{50\%}$ (°C) |
|---|---|---|---|---|
| Unfilled FE | 419.6 | 440.3 | 471.0 | 502.3 |
| CB filled FE | 418.1 | 440.6 | 471.3 | 497.9 |
| CNT filled FE | 419.0 | 444.4 | 473.5 | 499.3 |
| CB | 680.3 | 665.0 | 689.0 | 772.0 |
| CNT | 594.6 | 585.6 | 612.2 | 730.0 |

Carbon nanotube (CNT); Carbon black (CB); fluoroelastomer (FE)

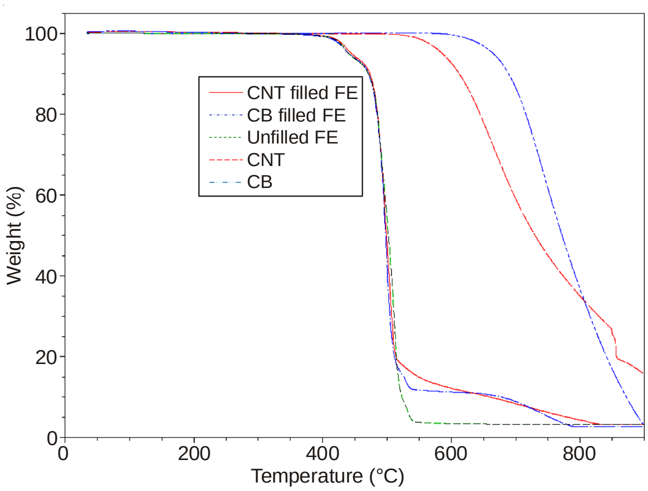

Fig. 1. TGA curves of pure filler, fluoroelastomer and filler/fluoroelastomer in the presence of air

As can be seen in Fig. 1, in the presence of air, with incorporating of carbon nanotube, higher amount of the fluoroelastomer remained and produced char preserve in the temperatures range of 520-900 °C compared to CB/FE or fluoroelastomer. Pham *et al.*[8], used SEM micrograph of the ash residue collected after 90 % degradation of CNT/FE under nitrogen. The authors showed that less or partial degradation of the polymer chains attached to the nanotubes occurs whereas extensive degradation is occurring in the bulk. Based on amount of fluoroelastomer remaining in the temperature range of 520-900 °C and the previous reported work[8], it can be concluded that in the presence of air, the fluoroelastomer attached or near the carbon nanotube at this temperature range will not be degraded or degrade less. Therefore more percentage of fluoroelastomer and char were preserved compared to CB/FE or fluoroelastomer. Consequently, carbon nanotube enhanced the thermal stability of fluoroelastomer and more percentage of this nanocomposite remained undegraded at higher temperatures in the presence of air.

The percentage of carbon nanotube remained within the nanocomposites can be calculated by multiplying the percentage of carbon nanotube obtained from the TGA data at that temperature by 8.4 % (the initial percentage of carbon nanotube in fluoroelastomer). These amounts are shown in Table-2. Fig. 1 and Table-2 indicate that pure carbon nanotube lost more weight at temperatures up to 900 °C than pure carbon black. Again in the TGA of nanocomposite, at each temperature, the percentage of "undegraded FE + char + mineral additives" can be calculated. The calculation can be done by subtracting the percentage of "carbon nanotube remained" in the nanocomposite (Table-2) from the percentage of nanocomposite remained in TGA curve extrapolated in Fig. 1 at that temperature. Results of these calculations are shown in Table-3. The same calculations were done for CB/FE.

TABLE-2
PERCENTAGE OF FILLER REMAINING IN PURE FILLER AND FILLER/FE AT DIFFERENT TEMPERATURES IN THE PRESENCE OF AIR

| Temperature (°C) | Carbon nanotube (%) | Carbon nanotube/ FE (%) | CB (%) | CB/FE (%) |
|---|---|---|---|---|
| 523 | 99.6 | 8.4 | 100 | 8.4 |
| 542 | 99.1 | 8.2 | 100 | 8.4 |
| 562 | 97.7 | 8.2 | 100 | 8.4 |
| 600 | 92.7 | 7.8 | 99.7 | 8.4 |
| 650 | 78.0 | 6.6 | 96.9 | 8.1 |
| 700 | 59.1 | 5.0 | 86.5 | 7.3 |
| 800 | 35.0 | 2.9 | 36.7 | 3.1 |
| 875 | 15.6 | 1.3 | 2.9 | 2.4 |

Carbon black (CB); fluoroelastomer (FE)

TABLE-3
PERCENTAGE OF "UNDEGRADED FE + CHAR + MINERAL ADDITIVES" REMAINED IN THE COMPOUNDS AT DIFFERENT TEMPERATURES IN THE PRESENCE OF AIR

| Temperature (°C) | Unfilled FE | CB/FE | CNT/FE |
|---|---|---|---|
| 523 | 10.8 | 8.7 | 11.0 |
| 542 | 4.0 | 3.7 | 10.2 |
| 562 | 3.7 | 3.3 | 6.7 |
| 600 | 3.4 | 3.2 | 5.2 |
| 650 | 3.3 | 2.6 | 4.0 |
| 700 | 3.3 | 1.7 | 3.4 |
| 800 | 3.3 | 0 | 1.4 |
| 875 | 3.3 | 0 | 1.4 |

Carbon nanotube (CNT); Carbon black (CB); fluoroelastomer (FE)

**Thermogravimetric analysis under nitrogen atmosphere-weight of residual:** Fig. 2[20] shows the TGA plots of CNT/FE, CB/FE, fluoroelastomer, carbon nanotube and carbon black under nitrogen influence, extracted data from these plots are presented in Table-4. Table-4 shows that $T_{onset}$, $T_{5\%}$, $T_{10\%}$ and $T_{50\%}$ in TGA test was almost unaffected when using carbon nanotube in fluoroelastomer compared to CB/FE or fluoroelastomer, similar to the results under the presence of air atmosphere.

TABLE-4
THERMAL GRAVIMETRIC ANALYSIS PROPERTIES OF FILLER/FE, FE AND PURE FILLER UNDER NITROGEN FLOW[20]

| FE Composite | $T_{Onset}$ (°C) | $T_{5\%}$ (°C) | $T_{10\%}$ (°C) | $T_{50\%}$ (°C) |
|---|---|---|---|---|
| Unfilled FE | 423.4 | 442.6 | 470.7 | 497.8 |
| CB filled FE | 420.7 | 439.6 | 465.8 | 499.9 |
| CNT filled FE | 418.9 | 441.2 | 468.5 | 497.7 |
| CB | 720.0 | 748.8 | 797.6 | - |
| CNT | 589.6 | 639.3 | 693.1 | - |

Carbon nanotube (CNT); Carbon black (CB); fluoroelastomer (FE)

Tables 5 and 6 were obtained with the same calculations that were done for Tables 2 and 3. Table-5 shows the percentage of filler remained from pure filler and filler/FE in TGA runs at different temperatures and under nitrogen flow. Table-6 shows that of "undegraded fluoroelastomer + char + mineral additives" remained within the compounds. Table-6 also shows the "undegraded FE + char" percentage at different temperatures.

TABLE-5
PERCENTAGE OF FILLER REMAINING IN PURE FILLER AND FILLER/FE AT DIFFERENT TEMPERATURES UNDER NITROGEN FLOW[20]

| Temperature (°C) | CNT (%) | CNT/FE (%) | CB (%) | CB/FE (%) |
|---|---|---|---|---|
| 523 | 100.0 | 8.4 | 100.0 | 8.4 |
| 542 | 99.7 | 8.4 | 100.0 | 8.4 |
| 562 | 99.3 | 8.3 | 100.0 | 8.4 |
| 600 | 97.9 | 8.2 | 100.0 | 8.4 |
| 650 | 94.5 | 7.3 | 99.7 | 8.3 |
| 700 | 89.3 | 7.5 | 98.3 | 8.3 |
| 800 | 66.6 | 5.6 | 90.0 | 7.6 |
| 875 | 54.8 | 4.6 | 80.4 | 6.8 |

Carbon nanotube (CNT); Carbon black (CB); fluoroelastomer (FE)

TABLE-6
PERCENTAGE OF UNDEGRADED FE + CHAR + MINERAL ADDITIVES AND UNDEGRADED FE + CHAR REMAINED IN THE COMPOUNDS AT DIFFERENT TEMPERATURES UNDER NITROGEN FLOW[20]

| Temp. (°C) | Undegraded FE + char + mineral additives | | | Undegraded FE + char |
|---|---|---|---|---|
| | FE (%) | CB/FE (%) | CNT/FE (%) | CNT/FE (%) |
| 523 | 10.4 | 9.9 | 10.8 | 8.3 |
| 542 | 9.4 | 8.9 | 10.1 | 7.6 |
| 562 | 9.2 | 7.6 | 9.6 | 7.1 |
| 600 | 7.9 | 6.6 | 8.8 | 6.3 |
| 650 | 7.0 | 5.1 | 8.7 | 6.2 |
| 700 | 6.1 | 3.6 | 7.6 | 5.1 |
| 800 | 4.9 | 2.4 | 7.6 | 5.1 |
| 875 | 4.3 | 1.9 | 7.6 | 5.1 |

Carbon nanotube (CNT); Carbon black (CB); fluoroelastomer (FE)

Fig. 2 and Tables 5 and 6 also show that using carbon nanotube in fluoroelastomer increases the thermal stability of fluoroelastomer compared to CB/FE or fluoroelastomer samples. Again as can be seen in Fig. 2, under nitrogen flow, with incorporating of carbon nanotube, higher amount of the fluoroelastomer remained and produced char preserve in the temperatures range of 520-900 °C compared to CB/FE or fluoroelastomer.

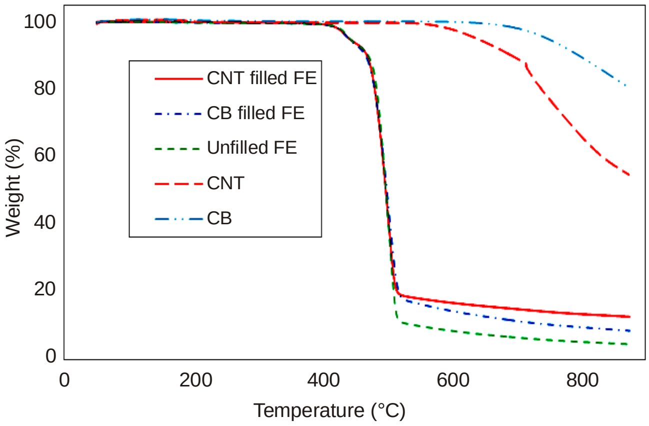

Fig. 2. TGA curves of pure filler, fluoroelastomer and filler/FE under nitrogen flow [Ref. 20]

Based on amount of fluoroelastomer remaining in the temperature range of 520-900 °C and Pham *et al.*[8] work, it can be concluded that the fluoroelastomer attached or near the carbon nanotube within this temperature range will not be degraded or degrade less. Therefore, more percentage of fluoroelastomer and char preserved compared to CB/FE or fluoroelastomer under nitrogen flow. Besides, in CNT/FE, most of the char is stable up to 900 °C while in CB/FE, most of the char decomposed, degraded and evaporated. Therefore, due to the presence of carbon nanotube, thermal stability of fluoroelastomer enhanced and more percentage of nanocomposite can withstand higher temperatures compared to the fluoroelastomer or CB/FE (under nitrogen environment). Fig. 2 and Table-5 indicate that pure carbon nanotube lost more weight at high temperature up to 900 °C than pure carbon black (under nitrogen environment).

**Comparison between thermogravimetric analysis runs in presence of air and under nitrogen atmosphere:** Fig. 3 shows the FESEM images of CNT/FE (the razor cut surface). This figure shows good distribution and dispersion of carbon nanotube in fluoroelastomer.

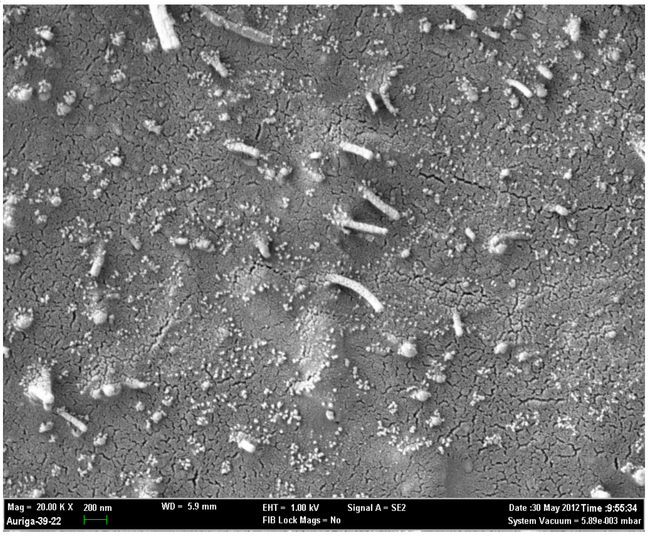

Fig. 3. FESEM images of CNT/FE (the razor cut surface)

The reasons that cause the carbon nanotube preserve more percentage of undegraded fluoroelastomer and char in TGA runs under nitrogen atmosphere[4,8] are also valid for runs in presence of air. Firstly, the presence of carbon nanotube in fluoroelastomer makes the active centres of fluoroelastomer main chains inactive, preventing the degradation, thus can save the fluoroelastomer nearer the carbon nanotube. Secondly, the interactions between carbon nanotube and fluoroelastomer results in increased physical and chemical cross-linking points which prevent the degradation of the polymer chains. Besides, considering that the degradation of fluoroelastomer is a radical chain reaction, it is therefore susceptible to inhibition by reagents capable of trapping such radicals. Furthermore, the antioxidant nature of carbon nanotube attributed to the high electron affinity (around 2.65 eV) enables it to act as a radical scavenger particularly for oxide radicals produced due to the presence of air. The last reason is the bounded rubber to carbon nanotube. It is because this structure can prevent the decomposition of rubber at high temperatures by resisting the molecular mobility[4].

Comparing Tables 3 and 6 and Figs. 1 and 2, it show that at each temperature, the percentage of "undegraded FE + char

+ mineral additives" remained within the compounds tested under nitrogen flow are more than those tested in the presence of air. The reason is burning carbons with oxygen in the presence of air while under nitrogen flow, there will be no oxygen to burn the carbon off. In the case of using air, the oxygen will also cause more degradation of fluoroelastomer and loses weight as it is a degradation agent especially at this temperature range. Besides, comparing Tables 2 and 5, it shows that at each temperature, filler remained in pure form under nitrogen atmosphere is more than that remained under air atmosphere. Most fillers for specimens tested in air burned off. Comparing Tables 1 and 4, it shows that changing the environment from nitrogen to air does not affect $T_{onset}$, $T_{5\%}$, $T_{10\%}$ and $T_{50\%}$.

## Conclusion

When comparing carbon nanotube filled- with unfilled- or carbon black filled-FE in TGA runs, the presence of carbon nanotube produced compounds with more thermal stability of fluoroelastomer in media of air or nitrogen. Besides, more percentage of CNT/FE in the form of undegraded fluoroelastomer or char, remained at higher temperatures compared to that of CB/FE or fluoroelastomer. At each temperature in the range of 520-900 °C, the percentage of undegraded fluoroelastomer or char remained in the compounds is more for tests under nitrogen flow compared to tests in presence of air. Changing the environment from nitrogen to air does not effect the $T_{onset}$, $T_{5\%}$, $T_{10\%}$ and $T_{50\%}$. Carbon nanotube does not affect these parameters of CNT/FE compared to CB/FE or fluoroelastomer.

## ACKNOWLEDGEMENTS

The authors acknowledge to the University of Malaya for the financial support through grant number RG150-11AFR.

## REFERENCES

1. PSP Global Co. (USA), Comparison of General Use and High Performance Grades of Viton, Technical Data Sheet, Accessed on February 12 (2014), from: http://www.pspglobal.com/nfVitongrades.html.
2. R.E. Fuller, *Sea Technol*., 6 (2006).
3. J.-S. Lee, *J. Appl. Polym. Sci*., **97**, 2054 (2005).
4. M. Endo, T. Noguchi, M. Ito, K. Takeuchi, T. Hayashi, Y.A. Kim, T. Wanibuchi, H. Jinnai, M. Terrones and M.S. Dresselhaus, *Adv. Funct. Mater*., **18**, 3403 (2008).
5. M. Ito, T. Noguchi, H. Ueki, K. Takeuchi and M. Endo, *Mater. Res. Bull*., **46**, 1480 (2011).
6. T. Noguchi, H. Ueki, S. Inukai, K. Takeuchi and S. Iinou, EP 2270266 A1 (2011).
7. L. Dai, W. Chen, Z.R. Xu and F. Espinosa, US Patent Application 2008/0318026Al (2008).
8. T.T. Pham, V. Sridhar and J.K. Kim, *Polym. Compos*., **30**, 121 (2009).
9. A. Griffo and M.K. Keshavan, US Patent Application 2009/0038858 Al (2009).
10. T. Russell, J. Walder and A. Rich, *Seal. Technol*., 12 (2005).
11. H. Tanaka and K. Fukuyama, US Patent Application 2009/0023852A1 (2009).
12. T. Noguchi, H. Ueki, S. Inukai, S. Iinou and M. Ito, US Patent Application 2011/0160375 A1 (2011).
13. L. He, Q. Xu, C. Hua and R. Song, *Polym. Compos*., **31**, 921 (2010).
14. R.W. Faulkner, K.J. Mumby, A. Fischer, T. Jozokos and S. Zhou, Multiwall Carbon Nanotube Reinforcement of HNBR and FKM. In Proceeding of Fall 176th Technical Meeting of the Rubber Division, American Chemical Society, Pittsburgh, PA, October 13-15 (2009).
15. L. He, J. Sun, X. Zheng, Q. Xu and R. Song, *J. Appl. Polym. Sci*., **119**, 1905 (2011).
16. N. Levi, R. Czerw, S. Xing, P. Iyer and D.L. Carroll, *Nano Lett*., **4**, 1267 (2004).
17. Y. Xu, Z. Wei-Tao, Y. Wen-Xue, H. Li-Gui, Z. Yu-Jie and Z. Zhu-Di, *Chem. Res. Chin. Univ*., **26**, 491 (2010).
18. K. Pal and J.K. Kim, Role of Fillers on Dispersion of MWCNT/Fluoroelastomeric Composites for High Performance Dielectric Energy Storage Application, IN Proceeding of International Rubber Conference & Exhibition, Mumbai, India, Paper: S-16/4, 17-19 November (2010).
19. E. Park, S. Hong, D. Park and S. Shim, *Colloid Polym. Sci*., **288**, 47 (2010).
20. J. Heidarian, A. Hassan and R.A. Lafia-Araga, *Compos., Part B Eng.*, (communicated).
21. J. Heidarian and A. Hassan, *Compos., Part B Eng*., **58**, 166 (2014).