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Thermal Properties of Fluoroelastomer Filled With Acidic Surface Modified Carbon Nanotubes

Aziz Hassan, Javad Heidarian
Polymer and Composite Materials Research Laboratory,
Department of Chemistry, University of Malaya,
50603 Kuala Lumpur

Introduction

- Viton: a synthetic rubber, a fluoroelastomer from Du Pont, USA
- Viton® GF-600S: latest development in Viton GF family
- Viton® GF-600S: terpolymer of hexafluoro-propylene, vinylidene fluoride, and tetra-fluoroethylene with a cure site monomer
- Viton® GF-600S, peroxide cure, 70% fluorine fluoroelastomer, new Advanced Polymer Architecture

Introduction

- Viton (FE) formulation: carbon black (CB) filled
- Replacing CB with carbon nanotubes (CNT)
- Using acid surface modified CNT (MCNT) is expected to improve the properties, even more than CNT
- To improve the thermal, physical, mechanical, and chemical properties
- To make O-rings for oil and gas industries

Literature review

- O-rings, for oil in deeper wells, depth in water of 8,000 m
- Higher temperature and pressure reservoirs
- CNT in rubber, at high temperatures and pressures (e.g., 260°C and 239 MPa)
- Compared to CB-filled composites, about 80-100 MPa higher pressure

Literature review

- Increasing CNT loading will increase decomposition temperature in CNT/FE
- FE/CNT were prepared using different surface modified CNTs (by Xu and Yang), better mechanical properties obtained by CF_4 plasma-modified CNT (FCNTs)
- CNT/FE were prepared using plasma-modified CNT

Aim

- MCNT was used as filler for Viton® GF-600S (FE) with the aim of improving thermal stability and thermal aging resistance of FE
- Characterisation by Thermal Gravimetric Analysis (TGA) and Energy Dispersive X-Ray (EDX)

Materials

- Viton GF-600S (Fluoroelastomer or FE), Organic peroxide, Carbon nanotube (CNT), Acid surface modified carbon nanotube MCNT, Zinc oxide, Triallyl Isocyanurate

- Three formulations were used: CNT filled FE (CNT/FE), MCNT filled FE (MCN/FE) and unfilled FE (FE)

Methods

- Equipments: two roll mill, hot press, oven, cure mould, Thermal Gravimetric Analyser (TGA)
- Mixing FE with additives was done in a laboratory size two roll mill
- Curing and post curing
- Thermal Gravimetric Analysis (TGA)
- Thermal aging
- Energy Dispersive X-Ray (EDX) and Field Emission Scanning Electron Microscopy (FESEM) image analyses

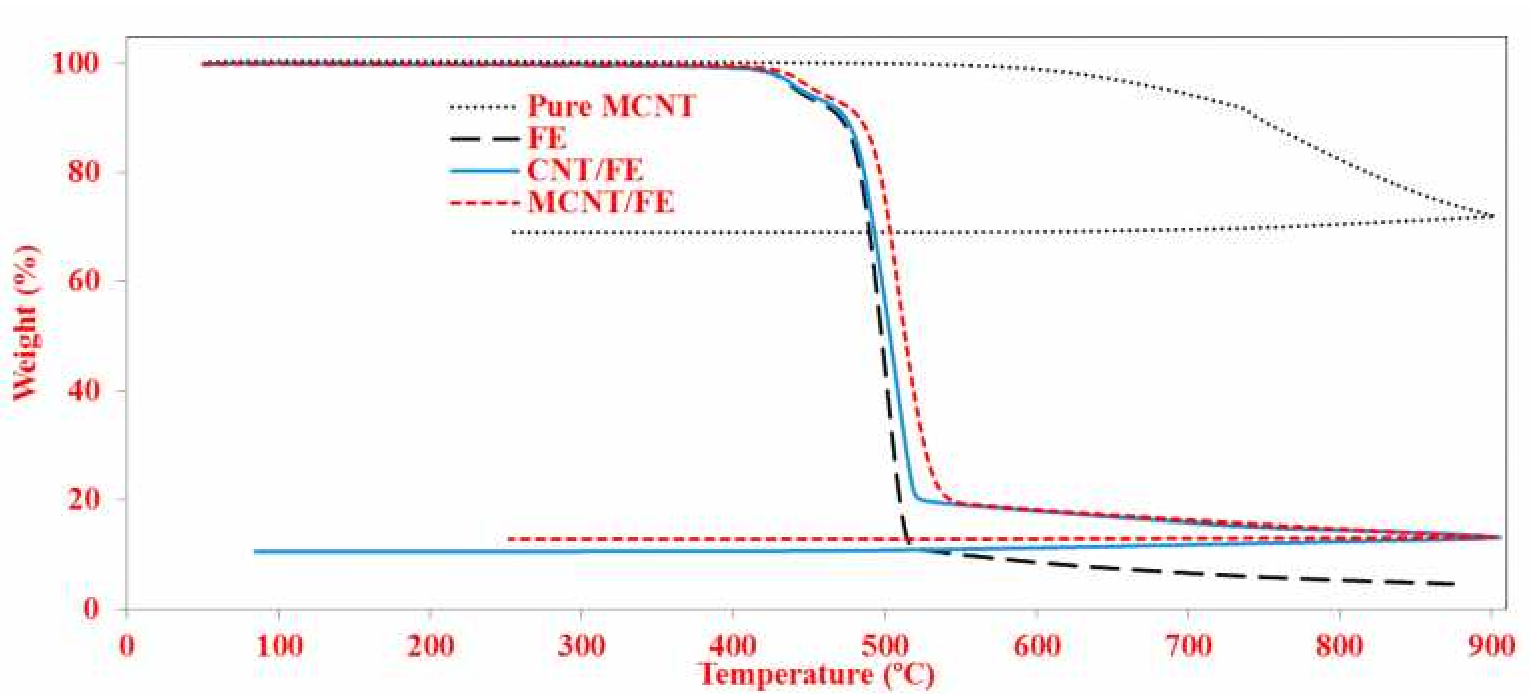
Thermal Gravimetry Analysis (TGA)

- TGA scans from room temperature to 900°C at a scan rate of 20°C.min^{-1}, under nitrogen atmosphere (20 ml.min^{-1})
- Heating-cooling TGA scans up to 560°C

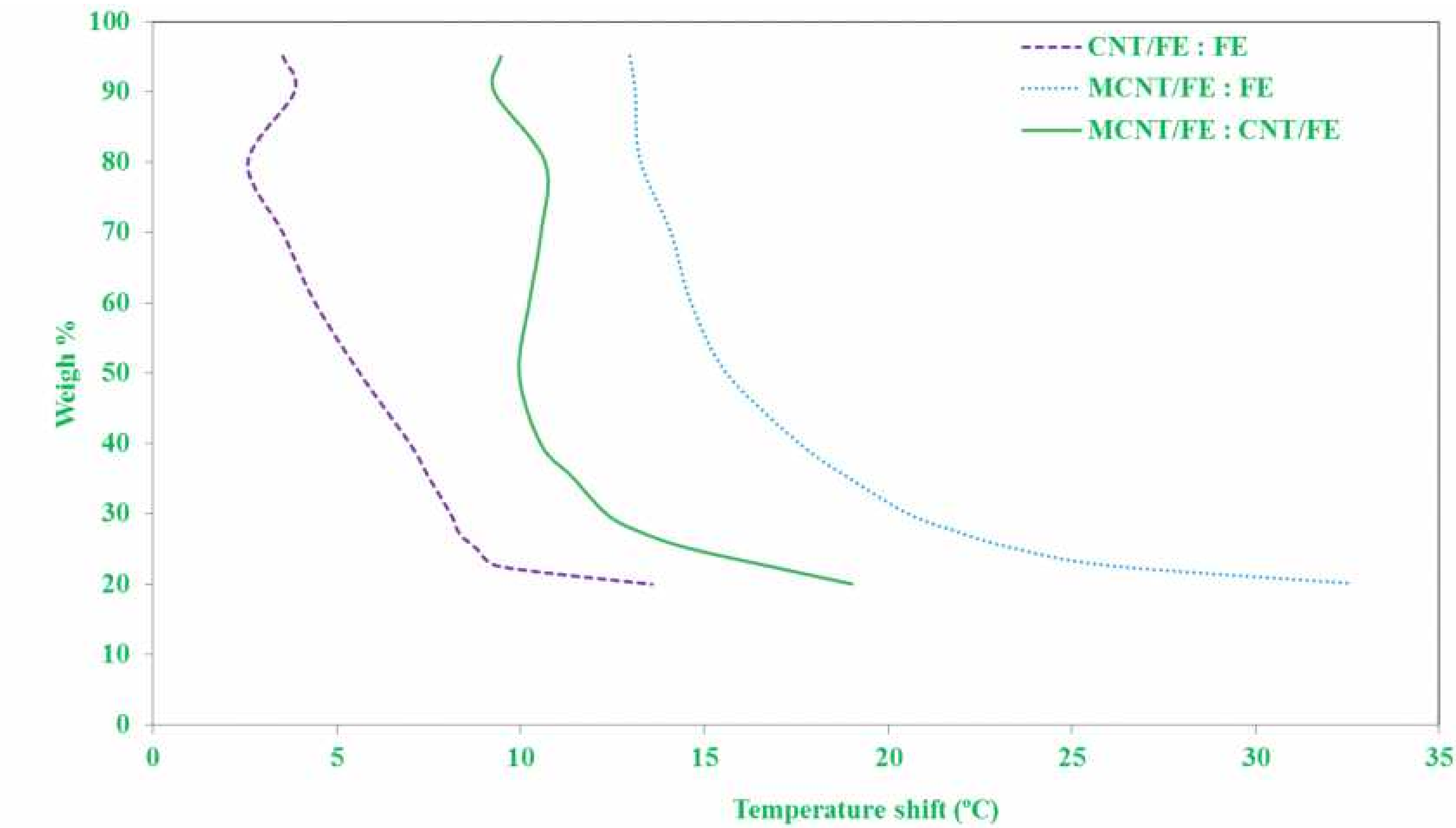
Thermal aging

- Thermal aging was done according to ASTM D-573 for 24, 48 and 72 hours at 250°C in air oven
- EDX analysis was conducted using FESEM coupled with EDX
- Un-aged and aged samples of 5 mm × 5 mm × 2 mm dimensions from the molded post cured rubber sheets were used for EDX analyses, to determine the elements of C, O, F, Si, Ca and Zn

Results and Discussion
TGA under nitrogen



Thermal stability shift curve



TGA data (under nitrogen)

Specimen	T_{Onset} (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)
FE	423.4	442.6	470.7	497.8
CNT/FE	421.1	446.2	475.4	505.1
MCNT/FE	433.1	457.7	485.4	513.7
MCNT	627.7	693.6	748.4	-
CNT	594.5	640.2	692.9	-

Initial CNT or MCNT remained in CNT/FE and MCNT/FE

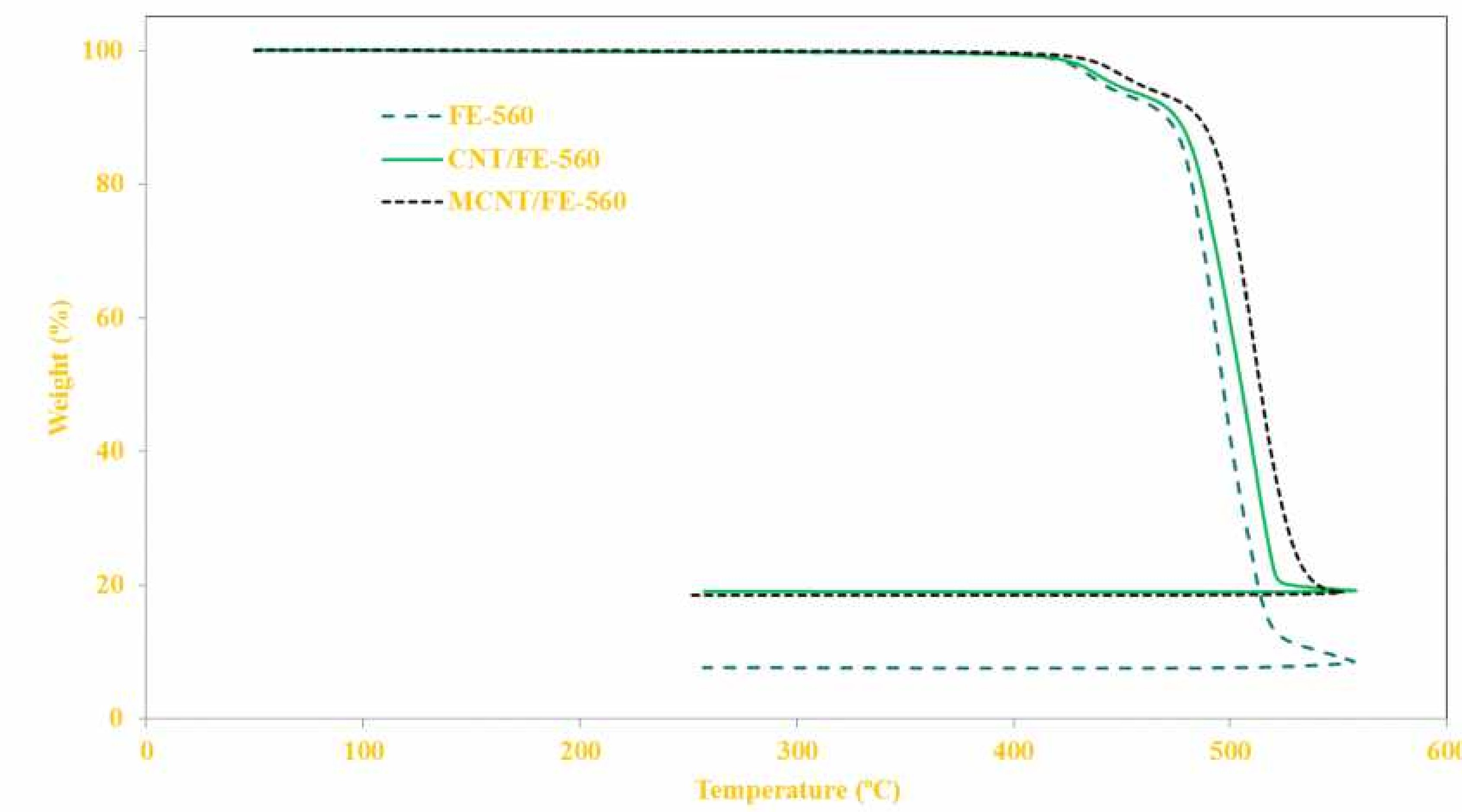
Temperature (°C)	MCNT	MCNT/ FE	CNT	CNT/ FE
520	100.00	8.40	100.00	8.4
530	99.94	8.39	100.00	8.4
540	99.87	8.39	99.70	8.4
560	99.67	8.37	99.30	8.3
600	99.04	8.32	97.90	8.2
650	97.21	8.17	94.50	7.3
700	94.39	7.93	89.30	7.5
800	82.52	6.93	66.60	5.6
875	74.15	6.23	54.80	4.6

TGA under nitrogen

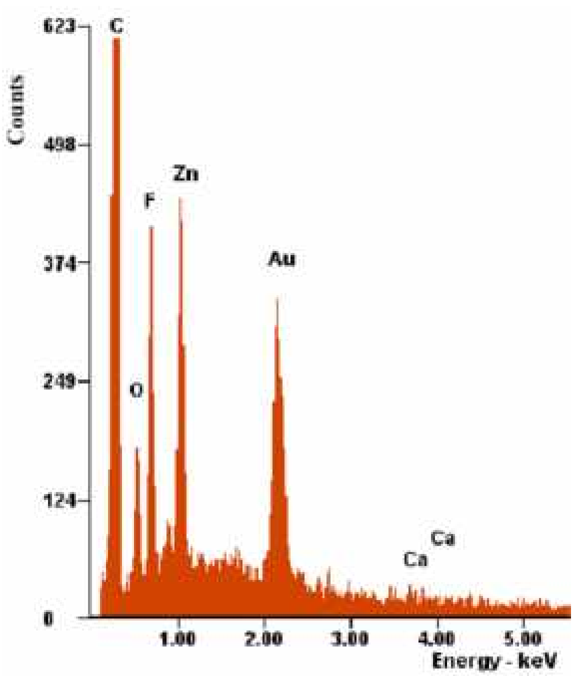
The percentage of “undegraded FE + char + mineral additives” and “undegraded FE + Char” remained in the compounds at different temperatures.

	“undegraded FE + char + mineral additives”			“undegraded FE + Char”	
Temperature (°C)	FE	MCNT/FE	CNT/FE	MCNT/FE	CNT/FE
520	-	30.58	12.56	28.08	10.06
530	-	17.63	11.58	15.13	9.08
540	-	12.19	10.88	9.69	8.38
560	-	10.54	10.48	8.04	7.98
600	7.90	9.65	9.68	7.15	7.18
650	7.00	8.84	9.52	6.34	7.02
700	6.10	8.24	8.32	5.74	5.82
800	4.90	7.65	8.32	5.15	5.82
875	4.30	7.30	8.32	4.80	5.82

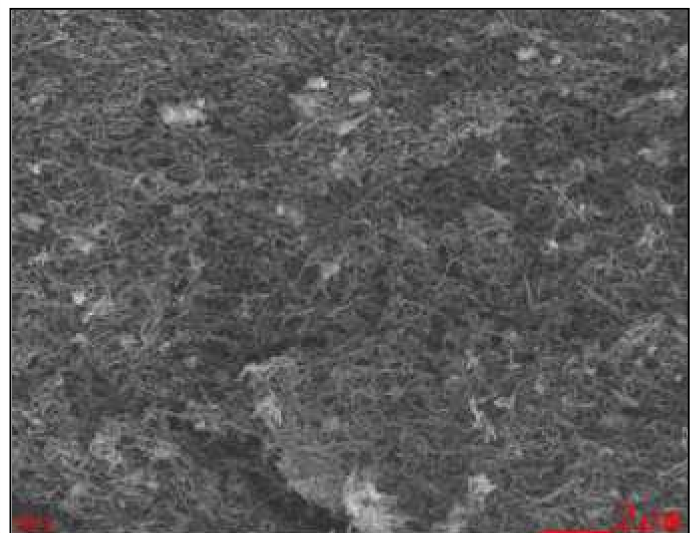
Heat and cool TGA curves of FE and filled FE up to 560 ºC



EDX spectra (a) and FESEM images (b) of MCNT/FE-560°C



a



b

Amount of element remained based on initial weight of compound

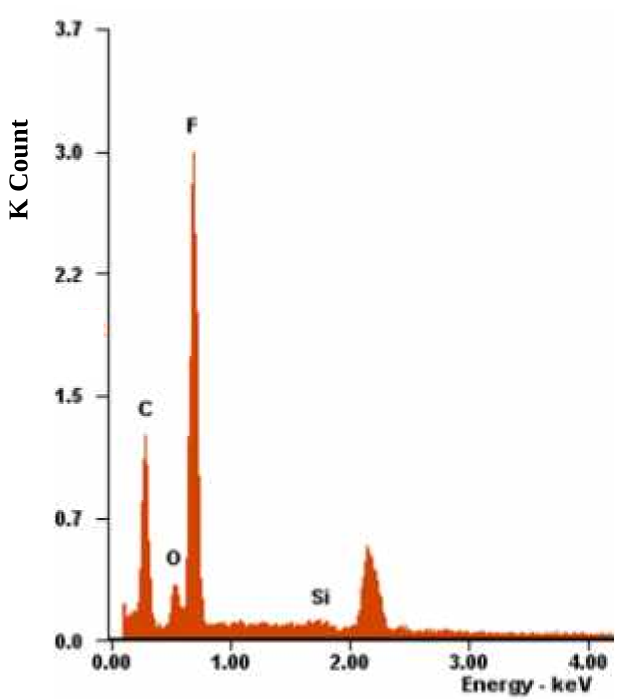
Element	Element remained (%)				
	FE-560°C	MCNT/FE-560°C	CNT/FE-560°C	MCNT/FE-900°C	CNT/FE-900°C
C	3.42	13.38	13.13	10.69	6.26
F	0.85	1.75	2.00	0.20	0.24
Zn	2.08	2.75	1.76	0.92	2.00
Ca	0.27	0.28	0.16	0.15	0.20
Si	-	-	0.09	-	-

TGA properties (N_2 media)

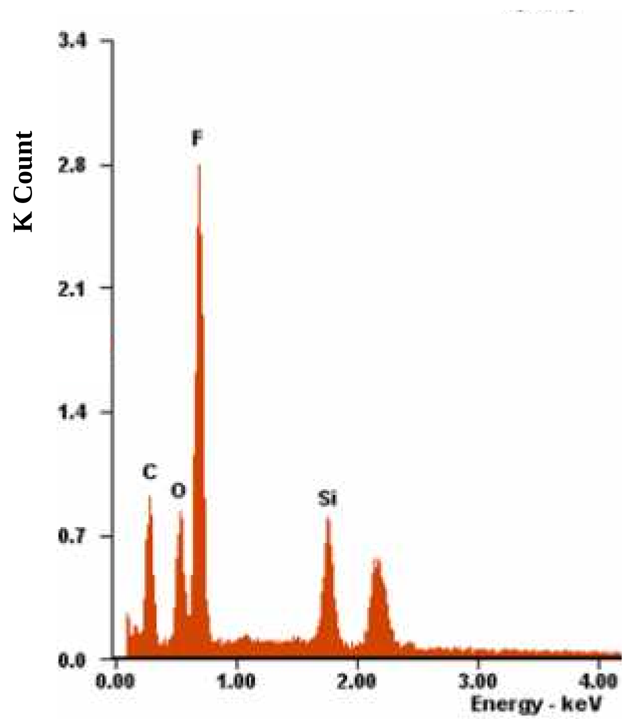
- Using MCNT thermal stability increased
- MCNT/FE curve shifted slightly to higher temperatures and the thermal stability improved compared to CNT/FE
- MCNT causes more percentage of FE and produced char stay in the temperatures range of 520° - 900°C compared to FE and CNT/FE
- Part of FE which is near or attached to the MCNT showed less or partial degradation compared to that of CNT/FE or FE
- The percentage of carbon and fluorine in the residue of TGA scan up to 560°C of MCNT/FE are the same as that of CNT/FE and was higher than FE (The amount of remaining fluorine represents the undegraded FE)

Thermal Aging

EDX spectra of (a) MCNT/FE and (b) MCNT/FE-72



(a)



(b)

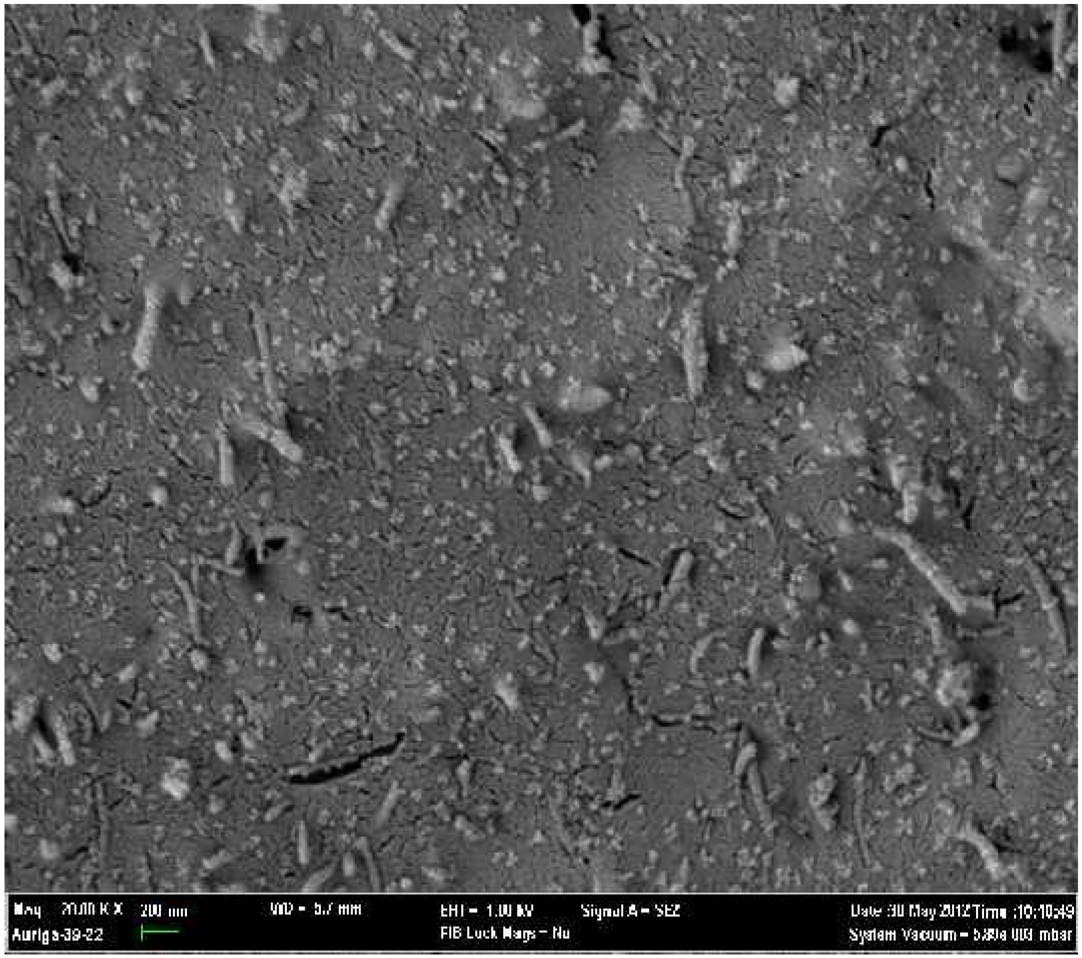
The surface composition of the composites before and after different times of aging, obtained by EDX and initial element loss percentage after aging

Element	Wt %	At %	Wt %	At %	Initial Element loss%	Wt %	At %	Initial Element loss%	Wt %	At %	Initial Element loss%
	FE		FE-24			FE-48			FE-72		
C	34.26	44.95	-	-	-	30.65	41.04	41.21	30.89	41.37	64.25
O	04.99	04.92	-	-	-	03.94	03.96	48.11	04.75	04.78	62.25
F	59.82	49.62	-	-	-	64.02	54.20	29.67	62.03	52.52	58.88
Si	00.92	00.52	-	-	-	01.40	00.80	0	02.32	01.33	0
Total	100.00	100.00	-	-	-	100.00	100.00	-	100.00	100.00	-
Element	MCNT/FE		MCNT/FE-24			MCNT/FE-48			MCNT/FE-72		
C	34.06	44.64	30.46	40.63	45.70	31.46	42.11	78.97	26.58	36.95	93.73
O	6.41	06.31	7.36	07.37	30.29	7.07	07.10	74.89	12.95	13.51	83.76
F	58.5	48.48	60.51	51.04	37.20	56.99	48.23	77.82	47.77	41.99	93.44
Si	1.02	00.57	1.68	00.96	0	4.48	02.56	0	12.69	07.55	0
Total	100.00	100.00	100.00	100.00	-	100.00	100.00	-	100.00	100.00	-
Element	CNT/FE		CNT/FE-24			CNT/FE-48			CNT/FE-72		
C	35.43	46.32	36.75	47.92	46.73	31.99	42.60	43.28	30.90	41.39	51.98
O	03.60	03.53	2.79	2.70	60.19	03.53	03.53	38.40	03.69	03.71	43.57
F	59.99	49.60	58.56	48.32	49.86	62.92	52.98	34.11	63.63	53.89	41.60
Si	00.98	00.55	1.91	1.07	0	01.56	00.89	0	01.78	01.02	0
Total	100.00	100.00	100.00	100.00	-	100.00	100.00	-	100.00	100.00	-

Effect of thermal aging on residual elemental composition

- EDX results of aged specimens under air indicates that the percentage of C, F and O lost on the surface of MCNT/FE, CNT/FE and FE increase with increasing aging time
- MCNT preserves less percentage of these elements compared to CNT
- The order of percentage loss in element after 24 hour aging time is MCNT/FE > FE > CNT/FE

FESEM images of FE/MCNT (the razor cut cross section surface)



Conclusion

- MCNT improved the thermal properties of FE, resulting in higher amount of FE and char remaining within the temperature range of 400-900°C relative to unfilled FE and CNT/FE
- The MCNT/FE TGA curve shifted slightly to higher temperatures compared to CNT/FE and FE
- The percentage of carbon and fluorine in the residue of TGA scans up to 560°C of MCNT/FE were the same as CNT/FE and was higher than FE

Conclusion

- EDX analysis of thermal aged specimens under air showed that with increasing aging time, more percentage of C, O and F were lost from the surface of MCNT/FE, CNT/FE and FE
- The order of element loss after 24 hour aging time is: MCNT/FE > FE > CNT/FE