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# Materials Advances

## **ARTICLE TYPE**

# Supporting Information

# Soft, ternary, X- and gamma-ray shielding materials: paraffin-based iron-encapsulated carbon nanotube nanocomposites <sup>†</sup>

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#### Abstract

In the field of radiological protection, there is a growing interest in nano- and microcomposites due to their unique physicochemical properties, flexibility in the component selection (the base ingredient as well as the fillers), and lower toxicity in comparison to the lead-(Pb-based) ones. In this study, we manufactured paraffin-based composites with different concentrations of iron-encapsulated multi-walled carbon nanotubes (Fe@MWCNTs) (10 and 20 wt.%), which were prone to shape change at the average room temperature. Long Fe@MWCNT arrays were synthesized by catalytic chemical vapor deposition (c-CVD) using the saturated (at 293.15 K) toluene solution of ferrocene (FeCp<sub>2</sub>) (9.6 wt.%) as a feedstock toward the highest efficiency of a complete Fe-encapsulation. The experimental data indicate that the shielding properties against gamma- and X-ray radiation are influenced by the filler concentration – the higher CNT content resulted in a greater ability to attenuate incident ionizing radiation. Finally, Fe@MWCNT-paraffin composites demonstrated corrosion resistance, as they did not react with 1 M aqueous solutions of NaCl, NaOH, and HCl.

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Fig. S1: Optical micrographs of: Fe@MWCNTs (a), neat paraffin (b), Paraffin + 10 wt.% Fe@MWCNT (c), and Paraffin + 20 wt.% Fe@MWCNT (d) composites



Fig. S2: EDX spectra of Fe@MWCNTs (a), neat paraffin (b), Paraffin + 10 wt.% Fe@MWCNT (c), and Paraffin + 20 wt.% Fe@MWCNT (d) composites. Field of view: 26.9  $\mu$ m, Mode: 15 kV – Point, Detector: backscattered electron detector.

## Rheological properties

Table S1:	Storage modulu	is and loss	modulus for pu	re paraffin	samples and	composites	with Fe@MW	/CNTs additio	n in a	function c	of
strain, f	= 1 Hz, $T = 309$	.75 K									

<b>C</b> t	Para	ffin	Paraffin + 10 w	rt% Fe@MWCNTs	Paraffin + 20 w	rt% Fe@MWCNTs
Strain	G'	G''	G'	$\widetilde{G''}$	G'	$\widetilde{G''}$
[-]	[Pa]	[Pa]	[Pa]	[Pa]	[Pa]	[Pa]
0,001006	110900	42823,33	675666,67	256600	709933,33	258266,67
0,001273	111233,33	42593,33	682166,67	251666,67	721333,33	263466,67
0,001615	112466,67	42486,67	683933,33	255700	749033,33	268466,67
0,00204	113633,33	42420	690900	255133,33	764000	271833,33
0,002591	113600	42876,67	690600	255700	769966,67	270600
0,003277	114333,33	43173,33	693533,33	255366,67	772333,33	270100
0,00414	114933,33	42920	692866,67	253400	774566,67	270366,67
0,005243	114766,67	42666,67	694300	251100	775966,67	269033,33
0,006644	115000	42693,33	691433,33	251600	776700	269133,33
0,008417	115566,67	43163,33	688900	249866,67	777200	270566,67
0,01066	114100	43153,33	686833,33	250533,33	776766,67	269100
0,0135	113170	43273,33	681200	250233,33	773466,67	269266,67
0,0171	111893,33	43386,67	673200	249600	769200	269200
0,02165	109780	43566,67	662800	249100	762400	269000
0,02742	104696,67	44410	649300	248566,67	754566,67	268233,33
0,03473	95836,67	45236,67	631833,33	247566,67	743700	267900
0,04397	82200	45293,33	609000	246766,67	729666,67	267300
0,05568	65810	44153,33	578033,33	246266,67	711700	266433,33
0,07052	49496,67	40686,67	535033,33	246666,67	688400	265566,67
0,08931	38950	36643,33	475233,33	246966,67	657033,33	265666,67
0,1131	30006,67	32413,33	402500	243000	609600	267800
0,1432	22406,67	28353,33	325233,33	231266,67	531700	274900
0,1814	16080	23773,33	257333,33	210633,33	416933,33	282033,33
0,2297	11800	19840	203766,67	184266,67	305633,33	268400
0,2909	8676,67	16583,33	163333,33	157433,33	222966,67	235433,33
0,3684	6627,67	14120	131600	133233,33	171666,67	195166,67
0,4665	4852,33	11743,33	105586,67	112500	140633,33	157200
0,5907	3617	9780,33	83393,33	95506,67	116800	127700
0,7481	2483,33	7926,67	64613,33	81376,67	90120	108866,67
0,9474	1844,67	6682	49263,33	69090	67010	92830
1,2	1356,67	5746	37460	58503,33	50140	77520
1,519	1000,33	4974,67	28026,67	49316,67	37533,33	64500
1,924	739,83	4299	20760	41443,33	27846,67	53623,33
2,437	554,9	3765,33	15203,33	34753,33	20490	44533,33
3,086	412,97	3287	10979	29090	14973,33	36900
3,908	307,2	2901	7867,33	24323,33	10900	30580
4,949	229,27	2585,67	5657	20326,67	7887	25436,67
6,267	167,83	2312,33	4188,33	16976,67	5717,67	21186,67
7,936	119,1	2057	3125,33	14246,67	4258,33	17673,33
10,05	81,67	1828,33	2330	12000	3213,67	14783,33

Table S2:	Storage	modulus	and loss	modulus	for pure	paraffin	samples	and	composites	with	Fe@MWCNTs	addition	in a	function	of
temperate	ure, $\gamma = 0$	0.01%, <i>f</i> =	= 1 Hz												

	Para	affin	Paraffin + 10 wt	% Fe@MWCNTs	Paraffin + 20 wt	% Fe@MWCNTs
T	G'	G''	G'	$\widetilde{G}''$	G'	$\widetilde{G}''$
[K]	[Pa]	[Pa]	[Pa]	[Pa]	[Pa]	[Pa]
288,15	3181666,67	1257000	11650000	3446666,67	14763300	4641333,33
289,15	2798333,33	1167733,33	10624000	3270000	13280000	4341333,33
290.15	2374666.67	1065033.33	9463333.33	3078000	11175000	3936500
291.15	1919333.33	942433.33	8141333.33	2816666.67	10207300	3883666.67
292,15	1466333.33	804200	6949333.33	2568000	8127000	3343000
293 15	1110333 33	682466 67	5972000	2348666 67	6693333 33	2949000
294 15	780633 33	537400	4719000	1939333 33	5377000	2521333 33
295.15	551400	405000	3923666.67	1630000	4226000	2072000
296.15	454833.33	341066.67	3350666.67	1411000	3574000	1803666.67
297.15	390766.67	298866.67	3040333.33	1331000	3081000	1583000
298 15	337033 33	260433 33	2631333 33	1198000	2630666 67	1378333 33
299 15	292733 33	220833 33	1956000	1011500	2238666 67	1188666 67
300 15	256233 33	194733 33	2014000	1014333 33	1956333 33	1095533 33
301 15	217066.67	168900	1967333 33	883000	1640500	932750
302,15	184566.67	149966 67	1806666 67	801766 67	1510333 33	877333 33
302,15	172022 22	118300	1316000	700100	1327000	777133 33
304 15	142700	107500	1434300	676033 33	1160000	685200
205 15	172/00	01/80	127/722 22	614000	1020266 67	626600
305,15	112076.67	74526 67	1255466.67	567766 67	1029200,07	531000
300,13	111200	67360	1137066 67	506033 33	878433 33	185833 33
209.15	00500	52210	1072022.22	446966 67	977966 67	200422.22
200.15	67255	42020	710700	224750	877200,07	245700
210.15	60100	42930	054266.67	240200	813300,07	3 <del>4</del> 3700 286066 67
211 15	66656 67	27526.67	934200,07	207622 22	766000	250400
212.15	70606.67	21706.67	924333,33	307033,33	769000	239400
312,15	79000,07	31/90,0/	960000,07	208/00	700900	239200,07
313,13 214 1E	/3130,0/	2/9/0,0/	920600	255055,55	743330	213/00
314,15	/3213	21060	0/5155,55	244033,33	624200	109433,33
315,15	42870	21900	83/800,0/	220100,07	624200	10/000,0/
310,15	40820,07	25540,07	/85133,33	210033,33	508933,33	117500
31/,15	30150	19180	/2//33,33	19/300	529700	11/500
318,15	31490	19840	0/1833,33	190500	450833,33	123800
319,15	33825	1/300	058050	1//350	410050	98370
320,15	22210	124/2	5/5400	150/00,0/	345900	95530
321,15	21000,07	1282/,0/	543000,07	13/1/0	292200	80830
322,15	10280	5997	618450	155/50	245966,67	/0/56,6/
323,15	12//6,6/	/885,33	44/200	12/396,67	205866,67	55960
324,15	9542,33	4396,67	400800	105930	162200	52103,33
325,15	6490	3385,67	391250	104820	128850	37950
326,15	5485,67	2594,33	323133,33	89870	98370	32553,33
327,15	3534,67	1926	291166,67	72330	73860	26996,67
328,15	2152,33	961,33	263/33,33	66833,33	61600	17476,67
329,15	1252,33	493,6	242263,33	52390	49190	16556,67
330,15	720,33	294,63	228620	48856,67	42166,67	12223,33
331,15	525,9	202,45	2148/3,33	44176,67	37603,33	10959,33
332,15	435,55	135,2	208670	42000	40340	9624,33
333,15	345,05	108,12	203156,67	39990	39523,33	8913,67
334,15	285,55	81,04	199360	38300	39840	8387,67
335,15	224,45	62,48	203170	34916,67	37473,33	8100,33
336,15	165,8	45,36	231185	39140	38543,33	7313,67
337,15	117,35	32,45	194210	33453,33	36643,33	6883,67
338,15	91,2	23,84	191536,67	31572	35370	6633,33

## Shielding properties – gamma ray

Paraffin	Paraffin + 10 wt% Fe@MWCNTs	Paraffin + 20 wt% Fe@MWCNTs
1	1	1
0.942	0.921	0.919
0.827	0.823	0.822
0.769	0.734	0.724
0.704	0.656	0.666
0.631	0.623	0.601
0.569	0.561	0.541
0.521	0.483	0.472
0.490	0.465	0.443
0.451	0.413	0.395
0.406	0.359	0.333
0.375	0.341	0.321
0.325	0.319	0.287
0.293	0.282	0.260
	Paraffin 1 0.942 0.827 0.769 0.704 0.631 0.569 0.521 0.490 0.451 0.406 0.375 0.325 0.293	$\begin{tabular}{ c c c c c } \hline Paraffin & Paraffin + 10 wt\% Fe@MWCNTs \\ \hline 1 & 1 & 1 & \\ 0.942 & 0.921 & \\ 0.827 & 0.823 & \\ 0.769 & 0.734 & \\ 0.704 & 0.656 & \\ 0.631 & 0.623 & \\ 0.569 & 0.561 & \\ 0.521 & 0.483 & \\ 0.490 & 0.465 & \\ 0.451 & 0.413 & \\ 0.406 & 0.359 & \\ 0.375 & 0.341 & \\ 0.325 & 0.319 & \\ 0.293 & 0.282 & \\ \hline \end{tabular}$

Table S3: The summary of experimental data for the pure paraffin and manufactured composites with 10 and 20 wt.% of Fe@MWCNT addition presented in the form of the ratio of the number of counts for a given layer thickness ( $N_{reduced layer}$ ) to the number of counts coming from the <sup>60</sup>Co source ( $N_{reduced source}$ ) as the average of three measurement series for each composite sample

### Shielding properties - X-ray

Table S4: The data summary of X-ray shielding ability for the composites with 10 and 20 wt.% addition of Fe@MWCNTs and for the pure paraffin presented in the form of the ratio of the signal intensity of given material layer thickness ( $I_{layer sample}$ ) to the signal intensity for aired field ( $I_{air}$ ) at 70 kV voltage

<i>x</i> (cm)	Paraffin	Paraffin + 10 wt% Fe@MWCNTs	Paraffin + 20 wt% Fe@MWCNTs
0	1	1	1
2	0.685	0.678	0.670
4	0.489	0.453	0.425
6	0.346	0.298	0.266
8	0.240	0.197	0.168

Table S5: The data summary of X-ray shielding ability for the composites with 10 and 20 wt.% addition of Fe@MWCNTs and for the pure paraffin presented in the form of the ratio of the signal intensity of given material layer thickness ( $I_{layer sample}$ ) to the signal intensity for aired field ( $I_{air}$ ) at 80 kV voltage

<i>x</i> (cm)	Paraffin	Paraffin + 10 wt% Fe@MWCNTs	Paraffin + 20 wt% Fe@MWCNTs
0	1	1	1
2	0.892	0.855	0.854
4	0.654	0.594	0.565
6	0.468	0.398	0.363
8	0.333	0.269	0.235

Table S6: The data summary of X-ray shielding ability for the composites with 10 and 20 wt.% addition of Fe@MWCNTs and for the pure paraffin presented in the form of the ratio of the signal intensity of given material layer thickness ( $I_{layer sample}$ ) to the signal intensity for aired field ( $I_{air}$ ) at 90 kV voltage

x (cm)	Paraffin	Paraffin + 10 wt% Fe@MWCNTs	Paraffin + 20 wt% Fe@MWCNTs
0	1	1	1
2	0.999	0.999	0.999
4	0.936	0.867	0.832
6	0.687	0.596	0.549
8	0.495	0.411	0.363

Table S7: The data summary of X-ray shielding ability for the composites with 10 and 20 wt.% addition of Fe@MWCNTs and for the pure paraffin presented in the form of the ratio of the signal intensity of given material layer thickness ( $I_{\text{layer sample}}$ ) to the signal intensity for aired field ( $I_{\text{air}}$ ) at 100 kV voltage

x (cm)	Paraffin	Paraffin + 10 wt% Fe@MWCNTs	Paraffin + 20 wt% Fe@MWCNTs
0	1	1	1
2	0.999	0.999	0.999
4	0.999	0.999	0.999
6	0.915	0.808	0.751
8	0.673	0.567	0.505

Table S8: The data summary of X-ray shielding ability for the composites with 10 and 20 wt.% addition of Fe@MWCNTs and for the pure paraffin presented in the form of the ratio of the signal intensity of given material layer thickness ( $I_{layer sample}$ ) to the signal intensity for aired field ( $I_{air}$ ) at 110 kV voltage

<i>x</i> (cm)	Paraffin	Paraffin + 10 wt% Fe@MWCNTs	Paraffin + 20 wt% Fe@MWCNTs
0	1	1	1
2	0.999	0.999	0.999
4	0.999	0.999	0.999
6	0.999	0.999	0.973
8	0.865	0.741	0.666

Table S9: The data summary of X-ray shielding ability for the composites with 10 and 20 wt.% addition of Fe@MWCNTs and for the pure paraffin presented in the form of the ratio of the signal intensity of given material layer thickness ( $I_{layer sample}$ ) to the signal intensity for aired field ( $I_{air}$ ) at 120 kV voltage

x (cm)	Paraffin	Paraffin + 10 wt% Fe@MWCNTs	Paraffin + 20 wt% Fe@MWCNTs
0	1	1	1
2	0.999	0.999	0.999
4	0.999	0.999	0.999
6	0.999	0.999	0.999
8	0.999	0.922	0.836

Table S10: The data summary of X-ray shielding ability for the composites with 10 and 20 wt.% addition of Fe@MWCNTs and for the pure paraffin presented in the form of the ratio of the signal intensity of given material layer thickness ( $I_{layer sample}$ ) to the signal intensity for aired field ( $I_{air}$ ) at 130 kV voltage

x (cm)	Paraffin	Paraffin + 10 wt% Fe@MWCNTs	Paraffin + 20 wt% Fe@MWCNTs
0	1	1	1
2	0.999	0.999	0.999
4	0.999	0.999	0.999
6	0.999	0.999	0.999
8	0.999	0.999	0.986



Fig. S3: The dependence of X-ray<sub>attenuation factor</sub>  $^{-1}$  for the manufactured composites with 10 wt.% and 20 wt.% of Fe@MWCNTs addition and for the pure paraffin at 80, 90, 100, 110, 120 and 130 kV voltage.