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Functionalization of Carbon Materials using Diels-Alder Reaction

Functionalization of Carbon Materials using Diels-Alder Reaction[a]

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A simple and efficient Diels-Alder (DA) reaction on carbon material has been demonstrated. The present work involves single and multiwall carbon nanotubes (CNT), as well as Herringbone carbon nanofiber. The CNTs show a dual nature of reactivity in DA reaction, i.e. they behave both as dienophile and diene with furfuryl groups and maleic anhydride derivatives, respectively. Various functional groups, including alcohol, amine, epoxy, carboxylic and ester have been introduced on the carbon materials. The results suggest that the reactivity of CNT in DA reaction may resemble the chemistry of small molecules.
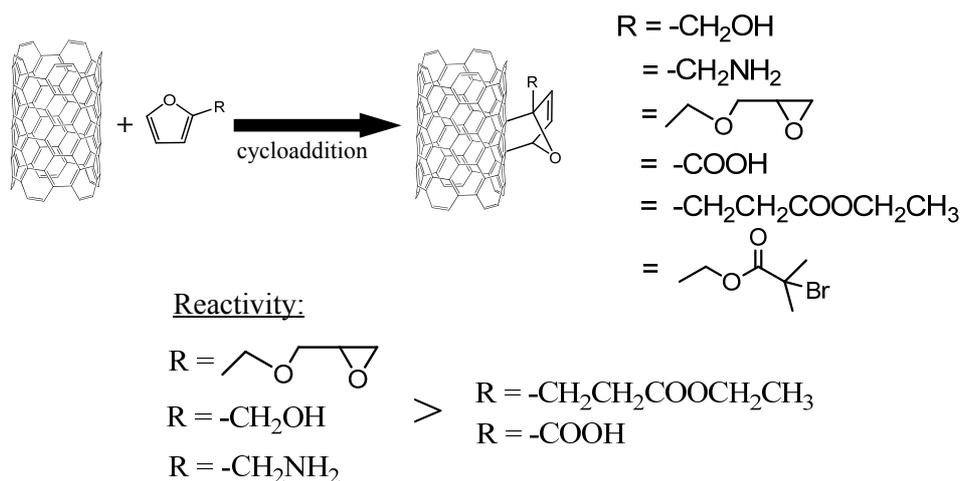
Introduction

The design of polymer nanocomposites based on carbonaceous based materials has been the focus of attention of several research groups during the last two decades.[1-4] Carbon nanofillers have shown outstanding mechanical, electrical and thermal properties due to their sp^2-hybridized carbon. However, these honeycomb structures tend to aggregate, which leads to sensible consequences on the properties of the polymer nanocomposites.

Different strategies have been used to improve the dispersion of carbon nanofillers in polymer matrices. Sonication,[5] high speed mixing[6-8] and calandering[9] improve the dispersion of carbon nanofillers in thermoset and thermoplastic polymers. Other approaches deal with the surface functionalization through noncovalent interactions (e.g. van der Waals forces, π-π stacking interactions) and the formation of covalent bonds at the nanoparticle. In the first case, the wrapping of carbon nanotubes using surfactants or polymer chains has shown stable dispersions of isolated nanoparticles in different solvents.[10] In the second case, the attachment of low molecular weight compounds or polymer chains directly at the surface of carbon nanofillers have lead to the reinforcement of different polymer nanocomposites.[11-13] The creation of covalent bonds destroys the sp^2-hybridized carbon, which decreases the opto-electrical properties of these nanoparticles.

The control on the functionalization of the carbon nanofillers with minor consequences on their properties is of primary importance for the preparation of high performance nanocomposites. There are two general methods for the covalent attachment of polymer chains at any substrate, known as "grafting to" and "grafting from". These methods have been extensively reviewed.[14] In most of the cases, a series of reactions is necessary for the final attachment of polymer chains on the carbon nanofiller surfaces[15-17] and harmful chemicals are required (e.g. thionyl chloride).[18-20]

Single step reactions like the in-situ polymerization in the presence of carbon nanofillers or the "grafting to" of functionalized polymers at the carbon nanofillers are the easiest alternatives for the preparation of nanocomposites, however, the control of the extent of functionalization of the nanofillers[21] and their dispersion in the polymer matrix are arduous.[22-24]

Therefore, the development of simple methods for the controlled functionalization of carbon nanofillers and the posterior compounding with polymer using conventional mixing methods (e.g. extrusion, injection molding and thermoforming, etc.) are realistic alternatives for the production of these materials.

One facile method for the functionalization of the graphene based structure of the carbon nanofillers is the Diels-Alder (DA) cycloaddition reaction, because it does not generate byproducts and can be performed under mild conditions. The possibility of the DA reaction has been studied theoretically since 2002.[25] It has been proved experimentally that the DA reaction can be performed on CNT either assisted by microwaves[26] or by using fluorinated CNT[27] or by metal complex catalyzed high pressure reactions.[28] However, these methods are performed using reactants without further functional groups. The benzocyclobutane based compounds have also been used for the DA with CNT.[29] However, this method involves complicated synthetic procedures and unknown side reactions during the DA with CNT may occur. More recently, DA reactions on multiwall carbon nanotubes (MWCNTs) have been reported.[30, 31] However, the DA reaction is delicate and vulnerable to temperature and dienophiles like oxygen.

In this communication we show, for the first time, the application of the DA reaction on a variety of different carbonaceous materials, namely single and multi walled carbon nanotube

and Herringbone carbon nanofiber using various diene and dienophile functional groups. The reactivity of the carbonaceous materials as diene or dienophile with suitable opponent partners has been studied and compared with the chemistry of the small molecule DA reactions for the first time. Finally, we show the usage of simple and novel furfuryl based ATRP initiator as an example for the surface initiated "grafting from" polymerization of styrene at MWCNT.

Experimental Part

Materials and methods

All the reagents were purchased from Sigma-Aldrich and used as received. The MWCNT (carbon content >99 %) and Herringbone carbon nanofiber were kindly gifted by FutureCarbon®. SWCNT was purchased from He Ji Ltd (China), with a purity of singlewall > 90% and the overall carbon content was > 95 %. Fourier transform infrared spectra were performed on a Bruker Equinox 55 using KBr pellet method. Thermal gravimetric analyses (TGA) were carried out on a Netzsch TG209 F1 Iris. The experiments were conducted under argon flow from 25 °C to 900 °C (10 °C/min). The weight loss was estimated from 100 °C to 600 °C in this study. Transmission electron microscopy (TEM) analysis was done using a FEI Tecnai G^2 F20 operated at 200 kV. The modified CNT were dispersed in $CHCl_3$, homogenized for 5 minutes by sonication and a drop was placed on a copper TEM grid. Scanning electron microscopy (SEM) was done using a Zeiss LEO Gemini 1550VP operated at 1 kV. The sample was prepared by drop casting on a Si-wafer fitted on carbon tab.

Diels-Alder reaction between furfuryl moiety and carbonaceous materials

In a typical Diels-Alder reaction, 50 mg of CNT were taken in a Schlenk tube. To this, 0.5 mL of furfuryl alcohol followed by 5 mL of anisole were charged. The reaction tube was

purged with argon for 30 min and closed tightly using a septum. Then the reaction tube was kept in an oil bath at 150 °C for 24 h. After the stipulated reaction time, the CNT were washed thoroughly using THF in order to remove the excess of furfuryl alcohol.

Synthesis and Anchoring of ATRP initiator "furfuryl-2-bromoisobutyrate" on MWCNT

The synthesis of furfuryl-2-bromoisobutyrate has been performed by utilizing typical esterification reaction between alcohol and acid bromide. Triethylamine was used as catalyst and acid scavenger (See SI for the experimental procedure and ^{1}H-NMR characterization). The ATRP initiator immobilization was done as in the case of furfuryl alcohol. The only difference is that furfuryl-2-bromoisobutyrate was used in place of furfuryl alcohol.

Synthesis of maleimidoethanol

The synthesis of maleimidoethanol was done using a slightly modified reported procedure.[32]

Surface initiated "grafting from" polymerization of styrene on MWCNT:[33, 34]

40 mg of furfuryl-2-bromo-isobutyrate modified MWCNT (0.18 mmol/g of ATRP initiator) was charged in a clean dry Schlenk tube. To this, 6.5 mg of CuBr, 1.5 mg of $CuBr_2$-PMDETA complex[35] and 3 mL of styrene were added. The reaction tube was subjected to three times freeze-pump-thaw cycles. At room temperature, under argon flow 9.5 μL of PMDETA was added and the reaction tube was sealed. It was kept in oil bath for 24 hours at 90 °C. It was cooled to room temperature and repeatedly washed with THF in order to remove any free polymer.

Results and Discussion

The main advantage of Diels-Alder reaction is that it does not require any catalyst and, most importantly, it does not produce any byproducts. Hence all the reactions for this study were

performed either in bulk or with solvents as diluents. However, the thermal stability of furan based compounds is problematic and this is especially true in the presence of oxygen.[36] So, the reaction was thoroughly argon purged at least 30 minutes before the commencement of the reaction. Our preliminary work suggested, in the absence of oxygen, most of the furfuryl compounds are stable up to 100-150 °C for time periods of 24-48 hours.[37] For a typical reaction, 200 mg MWCNT and 200 mL of furfuryl alcohol were taken in a Schlenk tube and argon was purged for 30 minutes (table 1, entry 1). The reaction tube was kept in oil bath at 75 °C for 24 hours. After the stipulated reaction time, it was diluted with a copious amount of THF and repeatedly washed until constant weight loss was observed in TGA. After drying, the TGA analysis showed a weight loss of approximately 3 %. This corresponds to approximately 0.32 mmol/g of –OH group on MWCNT. The SWCNT can also be modified using identical reaction condition (table 1, entry 2). However, compared to MWCNT, the SWCNT showed noticeably higher reactivity under identical reaction condition. In the case of SWCNT, 0.56 mmol/g of –OH were observed. This might be due to the high ring strain in SWCNT which makes it more reactive compared to MWCNT.[38] Like CNT, the Herringbone carbon nanofiber also showed considerable reactivity towards furfuryl alcohol (table 1, entry 3). The reaction was carried out in anisole at 150 °C for 24 hours. The calculation based on TGA showed 0.23 mmol/g of –OH group on Herringbone nanofiber. From these initial results, it is evident that the reactions of furfuryl alcohol on various carbonaceous materials were successful. Hence it can be inferred that the furfuryl alcohol acts as a diene and CNT act as a dienophile.

It is well recognized in Diels-Alder reaction that electron rich dienes are more reactive with dienophiles and vice versa.[39] Apart from electron rich diene furfuryl alcohol, several other functional groups attached to furan moiety are commercially available. We have selected the compounds based on approximate electron donating/withdrawing ability of the substituent

group on the furan. The chemical structures of the compounds used in this study are shown in table 2. The compounds are furfuryl alcohol, furfurylglycidyl ether, furfuryl amine, ethyl 3-(2-furyl)propanoate and 2-furoic acid, respectively. The first three compounds are electron rich dienes whereas the last one has the electron withdrawing group attached to the furan. Ethyl 3-(2-furyl)propanoate can be considered as electronegatively similar to furan. The Diels-Alder reactions of these functionalities on MWCNT are carried out in anisole at 150 °C for 24 hours. The results of the reaction between these compounds and MWCNT are shown in table 2. The electron donating substituent like –OH, –NH$_2$ and epoxy ether show higher reactivity compared to electron withdrawing groups like –COOH. The electronegatively neutral ethyl 3-(2-furyl)propanoate showed reactivity in between these two classes of functional groups. From these results, one can reasonably infer that the Diels-Alder reaction of the furan group on CNT shows similar behavior reminiscent of chemistry of small molecules.[40] For all the electron donating groups examined for these given reaction conditions, more than 0.3 mmol/g of functional groups can be anchored on MWCNT, whereas an electron withdrawing group like carboxyl substituted furan show less reactivity (table 2).

In order to perform "grafting from" surface initiated atom transfer radical polymerization, furfuryl-2-bromoisobutyrate was synthesized (see SI for synthesis and characterization). The ATRP initiator was anchored on MWCNT in anisole medium at 80 °C (table 1, entry 4). The IR and TGA showed the successful chemical modification of MWCNT. The IR peaks corresponding to the ATRP initiator can be seen around 1750 cm^{-1} and 1560 cm^{-1} (figures 1b and 2b). The TGA measurement showed 4.8 % wt loss which may probably correspond to 0.20 mmol/g of ATRP initiator on MWCNT. The ATRP of styrene was carried out at 90 °C for 24 hours. The polystyrene grafted-MWCNT was washed thoroughly in order to remove free polymer adsorbed (if there is any). The polymer modified MWCNT showed weight loss of 48 % in TGA under argon atmosphere (Figure 1(c)). The IR spectroscopy also confirmed

the presence of polystyrene on MWCNT (Figure 2(c)). The peaks at 2800-3000 cm^{-1} correspond to the polystyrene backbone and 700 cm^{-1} corresponds to pendent aromatic C-H out of plane deformation. From TGA and IR spectra one can corroborate that the MWCNT was effectively grafted with polystyrene. The SEM and TEM analysis of polymer grafted MWCNT is shown in figure 3. The SEM image of polymer modified MWCNT shows homogeneous modification in large area whereas the high magnified TEM assists to clearly see the MWCNT coated with polymer. From SEM/TEM, TGA and IR results, we can substantiate that the MWCNT was decorated with polystyrene uniformly with a thickness of about 3 nm.

It is well-known in Diels-Alder reaction chemistry that anthracene is one of the excellent dienes.[40] An interesting facet of CNT is its extended aromatic π–system which resembles anthracene. Therefore we attempted to use CNT as diene and maleic anhydride and maleimidoethanol as dienophile. The reaction between maleic anhydride and maleimidoethanol with SWCNT and MWCNT has been studied (table 1, entries 5-7). The successful reaction has been confirmed by TGA measurements. Therefore, from these results it can be inferred that CNT act as diene with strong dienophiles like maleimido derivates. By using various strong dienophiles under appropriate reaction conditions one can control the concentration of functional groups on various CNTs.

The so far discussed DA reactions, including other dienes and dienophiles, have been used for carbon platelets and graphite surfaces (data not shown here). Also the initial results using water as reaction medium are promising which opens the way to a very useful green method for the up-scaling industrial process.

Conclusion

We have shown clean, simple and robust Diels-Alder reactions on carbonaceous materials like carbon nanotubes, including single and multiwall, and carbon fiber. We also showed that the carbon materials behave both as diene and dienophile, depending on the reaction partner. Preliminary results indicate that single walled carbon nanotubes are more reactive than corresponding multiwall tubes, and in terms of reactivity, the CNT show similar behavior reminiscent of small molecule chemistry. Other carbon materials like carbon nanofibers show relatively less reactivity presumably due to the less available surface area. Although the reactions mentioned here are straightforward, it should be stressed that the removal of oxygen is important in order to obtain reproducible results. The mechanistic aspect of this robust normal and retro DA reaction requires a detailed study in order to be understood thoroughly. This will be reported elsewhere. [41]

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[37] *It can be seen visibly after the reaction. The color of the filtrate becomes brownish to dark brown when the reaction was done in the presence of oxygen.*

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Figure 1. Thermogravimetric analysis of (a) unmodified, (b) Furfuryl-2-bromoisobutyrate modified and (c) polystyrene grafted MWCNT.
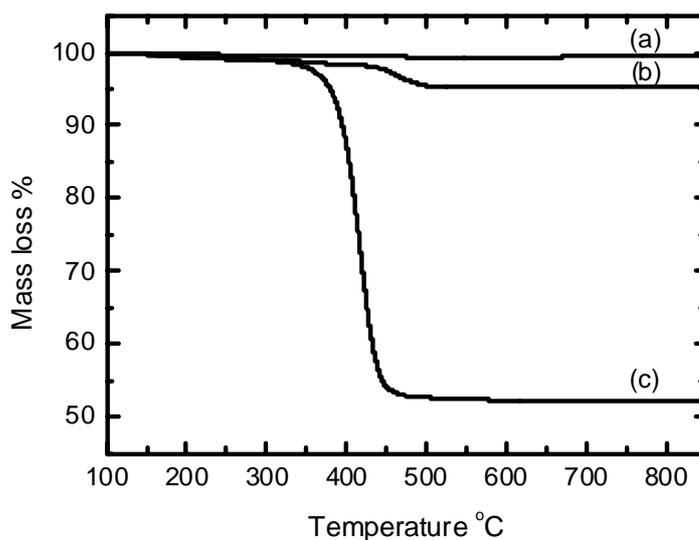
Figure 2. Infrared spectra of (a) unmodified, (b) furfuryl-2-bromoisobutyrate modified and (c) polystyrene grafted MWCNT
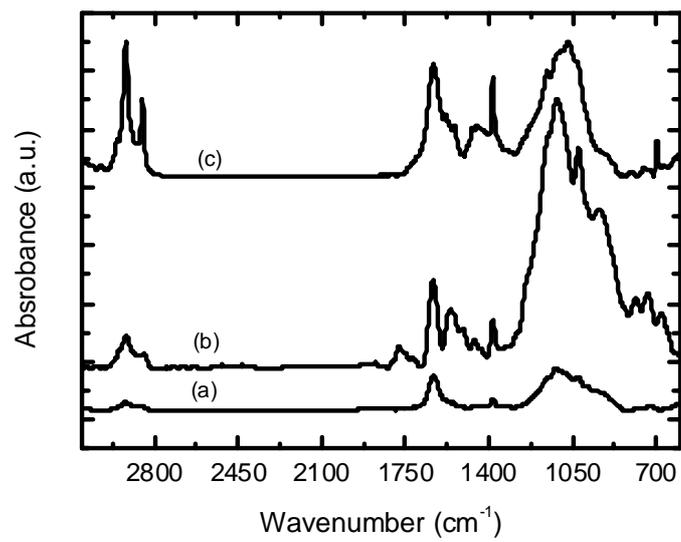
Figure 3. SEM image of polystyrene grafted MWCMT. Inset: High resolution TEM image of a single MWCNT with grafted polystyrene.
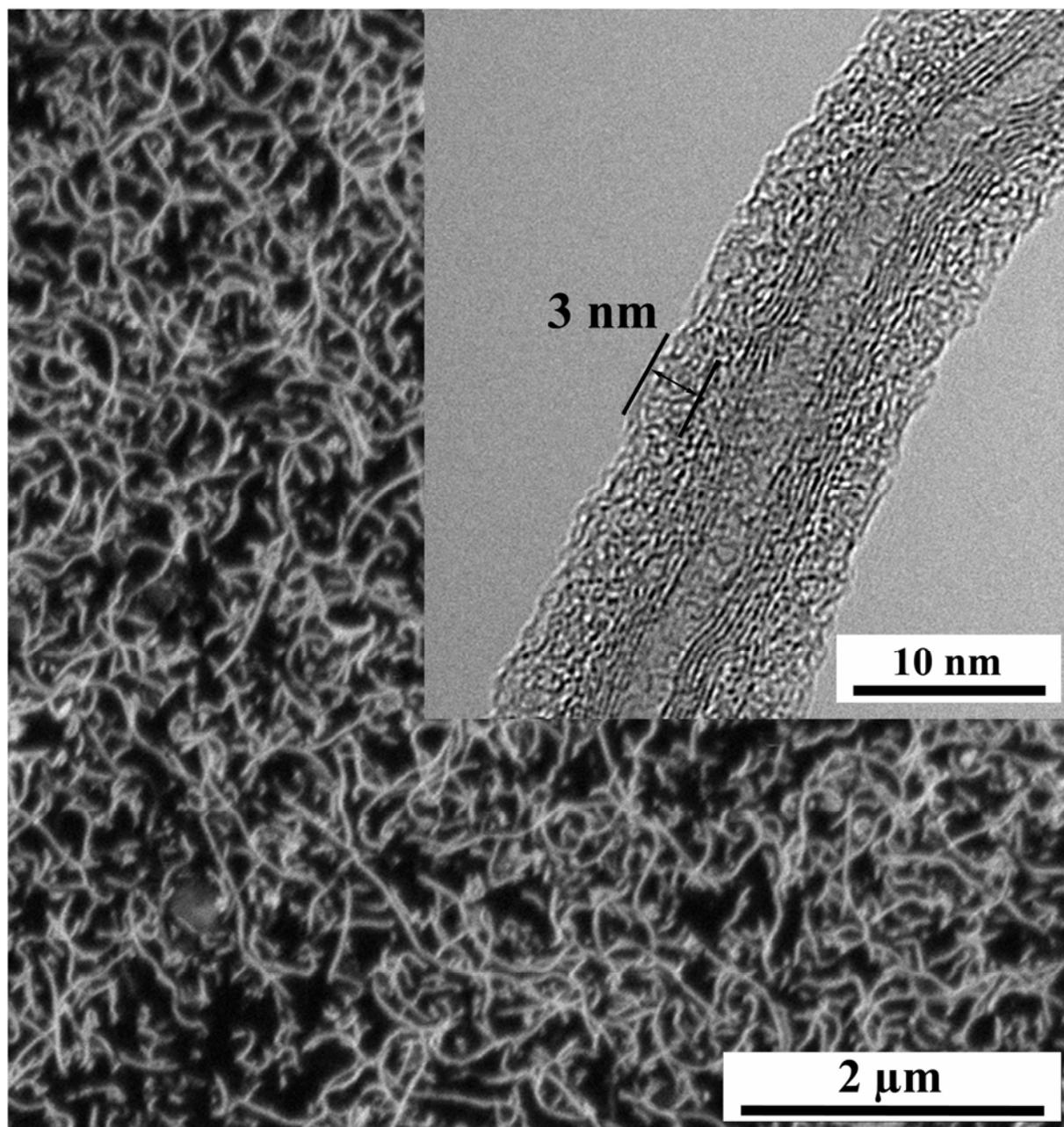
Table 1. The reaction of carbon material SWCNT, MWCNT and nano fiber with diene and dienophile

Entry No.	Type of Carbon Material (mg)	Reactant		Reaction Conditions			Weight loss (%)[a]	[X] (mmol/g)[b]
		Chemical structure X	Quantity	Medium (mL)	T (°C)	Time (hours)		
1	MWCNT (200)		200 mL	Bulk	75	24	3.1	0.32
2	SWCNT (200)		200 mL	Bulk	75	24	5.5	0.56
3	CNF-HB[c] (50)		0.5 mL	Anisole (5)	150	24	2.2	0.23
4	MWCNT (50)		0.25 mL	Anisole (5)	80	48	4.8	0.20
5	MWCNT (50)		1 g	Benzyl ether (5)	75	48	6.1	0.62
6	MWCNT (50)		0.5 g	Toluene (5)	75	24	3.2	0.23
7	SWCNT (200)		3.5 g	THF (20)	75	24	5.9	0.42
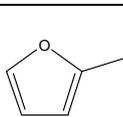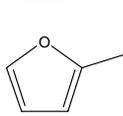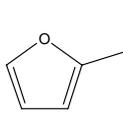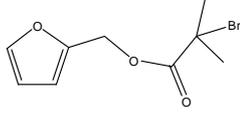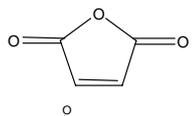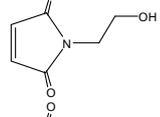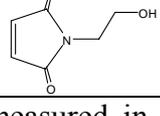
a. Weight Loss measured in TGA between 100 °C and 600 °C; b. Concentration of functional groups on carbon material; c. CNF-HB = Herringbone carbon nanofiber.

Table 2. Reaction between MWCNT as diene and various substituted furan as dienophile.[a]

Entry No.	Reactant		Weight loss (%)[b]	[X] (mmol/g)[c]
	Diene group X	Quantity		
1		0.5 mL	3.2	0.33
2		0.75 mL	6.5	0.42
3		0.5 mL	3.8	0.39
4		0.75 mL	4.1	0.25
5		0.75 g	2.6	0.23
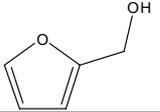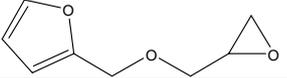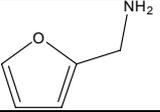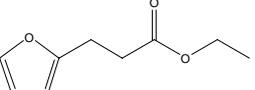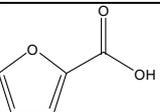
a. 50 mg of MWCNT in 5 mL of anisole at 150 °C for 24 hours; b. Weight Loss measured in TGA between 100 °C and 600 °C; c. Concentration of functional groups on carbon material.

Text for the table of content:

Well known classical Diels-Alder (DA) reactions have been applied to modify the surfaces of carbonaceous materials including carbon nanotubes. The carbon materials behave both as diene and dienophile and the reactivity resembles similar to small molecular chemistry. By applying DA reaction to anchor the initiator, the "grafting from" surface initiated ATR polymerization on carbon nanotube has been demonstrated.

Reactivity:

R = (furfuryl glycidyl ether structure)

-CH$_2$OH

-CH$_2$NH$_2$

$>$

-CH$_2$CH$_2$COOCH$_2$CH$_3$

-COOH