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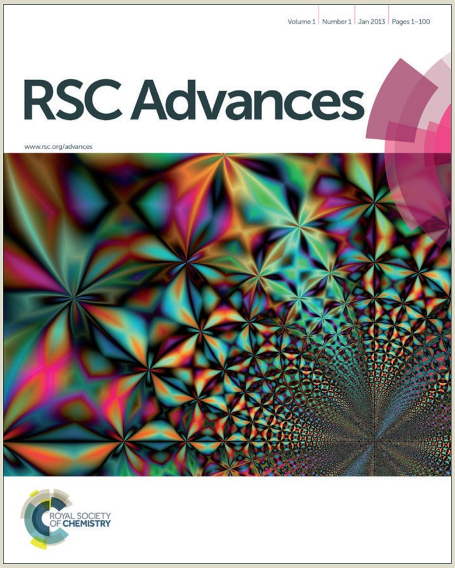

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Direct Functionalization of Multi–Walled Carbon Nanotube (MWCNT) via grafting of poly(furfuryl methacrylate) using Diels-Alder “Click Chemistry” and its thermoreversibility

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ABSTRACT

This investigation reports a simple and single step functionalization of multi-walled carbon nanotube (MWCNT) based upon the Diels-Alder (DA) reaction with poly(furfuryl methacrylate) (PFMA). In this case, at first tailor-made PFMA was synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization. This PFMA (M_n = 8500 g/mol, $Đ$ = 1.37) containing reactive furfuryl group as diene was covalently grafted onto the surface of pristine MWCNT via DA reaction under mild condition at room temperature (~ 30 °C) as well as 80 °C without any catalyst. The successful functionalization of PFMA onto MWCNT was confirmed by TGA, XPS spectra, FT-IR, Raman spectroscopy and HRTEM analyses. The average grafting density was calculated to be 0.012 $\text{mmol}\cdot\text{g}^{-1}$ (0.025 $\text{chain}\cdot\text{nm}^{-2}$) at room temperature and 0.025 $\text{mmol}\cdot\text{g}^{-1}$ (0.055 $\text{chain}\cdot\text{nm}^{-2}$) at 80 °C using TGA analysis. When heated at 160 °C for 5 h the DA polymer undergoes retro-DA (rDA) reaction and the polymer layer detached from the MWCNT surface. As a result the MWCNT precipitated in *N*-methyl-2-pyrrolidone (NMP) solvent. The rDA reaction was also analyzed by TEM analysis. HRTEM showed the presence of polymer layer of 23 nm around MWCNT surface after functionalization.

Keywords: MWCNT; RAFT polymerization; poly(furfuryl methacrylate); click chemistry; Diels-Alder reaction.

1. Introduction

Carbon nanotube[1,2] (CNT) is one of the most important class of nanoparticles widely used in different advanced materials. CNT have unique physical and chemical properties due to which CNT/polymer composites have large applications in sensors, EMI shielding, electric and electronic devices and in different strategic applications[3-6]. But to achieve a uniform and an efficient distribution of CNT into the polymer matrix, it needs suitable functionalization. When CNT is intermixed with polymer matrix, the phase separation and aggregation are observed. This leads to little or no physical effect in the polymeric compound. Thus efficient strategies are required for covalent modification of CNT with proper compound for better compatibility of CNT into the polymer matrix. The major disadvantage in the applications of CNT is its poor solubility and processibility. The organic functionalization of CNT improves its solubility in organic solvents, compatibility with organic polymers and processibility.[7-11] Different strategies have been used for the covalent functionalization of CNT; like oxidation[12,13], treatment with ozone,[14] fluorination,[15] free radical addition,[16]1,3 dipolar addition,[17] nucleophilic addition,[18] alkylation[19] and plasma modification.[20] But all these strategies usually need very harsh and drastic reaction condition. Many of these processes require several reaction steps. The chemicals and reagents used in these processes are highly sensitive to air, moisture etc. Those strategies can damage the sp^2 hybridized carbon atoms of nanotubes and thus they affect the optical, electrical and thermal properties of nanotubes. Among the different click reactions, Diels-Alder (DA) is the most interesting click reaction, as this is thermoreversible via retro-DA (rDA) reaction at higher temperature. During the last decade different click reactions; like Diels-Alder ([4+2] cycloaddition) reaction,[21] alkyne-azide reaction,[22] thiol-ene reaction[23] and thio-bromo click reaction[24] are being widely used in polymer chemistry to prepare new materials like smart materials, self-healing materials, biomaterials etc. The major advantages of click reaction are; they occur at mild reaction conditions and they offer quantitative yield without any by-product. The objective of this investigation is to modify CNT via DA reaction using tailor-made polymer with reactive pendant furfuryl group which can act as diene and CNT as dienophile. There are few reports in which CNT has been modified using furfuryl derivatives as well as by using maleimide derivatives using DA reaction[25-27]. Zydzik et al prepared polymers end-capped with cyclopentadiene which as diene reacted with SWCNTs as dienophile at room temperature as well as at higher temperature (80 °C).[28] By using high resolution TEM (HRTEM) analysis they observed that the surface of SWCNT was grafted with about 3 nm polymer layers.

In this investigation we report a single method of functionalization of MWCNT via DA reaction. In this case we first prepared tailor-made poly(furfuryl methacrylate) (PFMA) via RAFT polymerization. Later this PFMA was grafted onto MWCNT via DA reaction between the reactive furfuryl group in PFMA as diene and dienophile functionality in the MWCNT surface. The DA reaction was carried out without the presence of any catalyst. FT-IR and Raman analyses showed the successful DA reaction. TGA analysis was used to study the grafting density of FMA on MWCNT. XPS analysis also showed the grafting of PFMA onto the surface of MWCNT showing different peaks at different binding energies for different C 1s and O 1s transition of PFMA. Importantly, TEM analysis showed that the MWCNT surface was grafted with about 23 nm thick PFMA layer.

2. Experimental

2.1 Materials

Furfuryl methacrylate (FMA) (97%, Sigma-Aldrich) was passed through basic alumina column to make it inhibitor free. Tetrahydrofuran (THF, anhydrous, ≥ 99.9 %), 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTSPA) and 4,4′-azobis(4-cyanovaleric acid) (ABCVA) were used as received. N-Methylpyrrolidone (NMP, Merck) was distilled under vacuum before use. The MWCNT (diameter 110-170 nm, length 5-9 µm) with a purity of upto 90 wt % was purchased from Sigma-Aldrich and was used as received.

2.2 Characterizations

FT-IR spectra were recorded on a Perkin-Elmer (Inc. version 5.0.1 spectrometer) spectrum with the attenuated total reflection (ATR) mode. The FT-IR spectra of MWCNT were recorded in transmission mode in KBr pellets. TGA analysis was carried out on a TA (TGA Q50 V6.1 Build 181) instrument. In this case small amount (~ 6 mg) of sample was heated from 30 °C to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Raman Spectra were obtained using Jobin Yvon Horiba Raman Spectrometer employing an Ar-Kr laser operating at 514.5 nm. X-ray photo-electron spectroscopy (XPS) analysis was conducted on VersaProbe II instrument (Physical Electronics, USA). High Resolution Transmission Electron Microscopy (HRTEM) was carried out at a JEOL-2000 HRTEM operating at 200 kV. The samples were prepared by drop-casting a dilute suspension in $CHCl_3$ onto a carbon coated copper grid and allowing the solvent to evaporate. Scanning electron microscopy (SEM) analysis was carried out using ZEISS EVO 60 operating at 20 kV. The samples were prepared via drop casting onto a glass-wafer.

2.3 Synthesis of poly(furfuryl methacrylate) (PFMA) via RAFT polymerization

PFMA was prepared using CDTSPA as RAFT reagent and ABCVA as thermal initiator. In a typical polymerization reaction FMA (8 g, 4.814×10^{-2} mol) and toluene (9.2 ml) were taken in a 50 ml two neck round-bottom flask. The flask was closed by silicone septum in both the necks. RAFT agent, CDTSPA (0.3239 g, 8.023×10^{-4} mol) and ABCVA (0.0562 g, 2.005×10^{-4} mol), the thermal initiator were added into the flask. Oxygen was removed from the reaction mixture by passing N_2 through the round-bottom flask for 20 min. All manipulations for the polymerization reaction were carried out under N_2 atmosphere to make the system air free.[29,30] Polymerization was carried out at 90 °C. A conversion of 85% was obtained at 5 h. The viscous polymer was dissolved in THF and then was precipitated into n-hexane. The polymer was dried in a vacuum oven at 60 °C for 12 h. A part of the polymer sample was analyzed by GPC analysis to determine its molecular weight (M_n) and molecular weight distributions, $M_{n,GPC}$ = 8,500 g/mol, $Đ$ = 1.37, $M_{n,theo}$ = 8,900 g/mol.

2.4 Functionalization of MWCNT with PFMA by DA reaction (DA-MWCNT-PFMA)

MWCNT (45 mg) was dispersed in 90 mL NMP in ultrasonic bath in a 250 mL round bottom flask for 1 h. After dispersion of MWCNT, 450 mg PFMA was added to the mixture. Then the mixture was stirred for 48 h at room temperature under open atmosphere. The dispersion was subsequently filtered and washed several times with 200 mL THF to remove unreacted polymer and dried under vacuum. The same reaction condition was used for another sample, but in that case the mixture was heated at 80 °C.

3. Results and Discussion

Tailor-made PFMA was prepared via RAFT polymerization using CDTSPA as CTA. PFMA had a molecular weight of 8500 g/mol and dispersity (*Đ*) of 1.37, as analyzed by GPC analysis. This PFMA was grafted onto the MWCNT surface via DA reaction as shown in Figure 1.

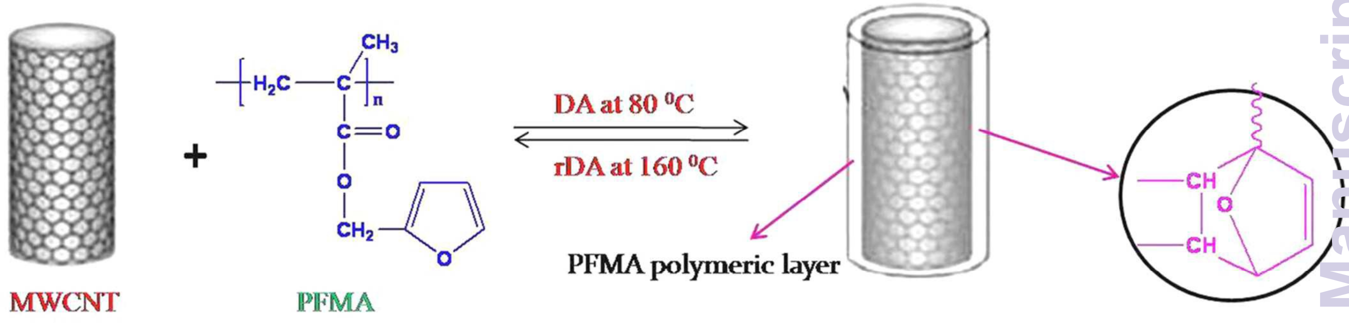


Figure 1. Schematic representation of direct functionalization of MWCNT via Diels-Alder reaction between MWCNT and poly(furfuryl methacrylate) (PFMA).

Grafting of PFMA was carried out at room temperature (~ 30 °C) as well as at 80 °C. Figure 2 shows the ATR-FT-IR spectra of MWCNT, DA adduct of MWCNT-PFMA and rDA adduct of MWCNT-PFMA. The material prepared via DA reaction at 80 °C shows different absorption bands due to presence of organic moieties; at 2918 cm^{-1} for –C–H stretching, 1748 cm^{-1} for >C=O group, 1636 cm^{-1} for –C=C– group, 1110 cm^{-1} for –C–O– group and 1024 cm^{-1} for characteristic absorption band for furan ring. So, appearance of these bands in MWCNT-PFMA with respect to the ATR spectra of MWCNT (Figure 1A) indicates that the MWCNT was functionalized by PFMA through DA reaction. When this DA polymer was heated at 160 °C for 5 hrs the above absorption bands in its FT-IR spectrum (Figure 1C) disappeared indicating the retro-DA (rDA) reaction on the MWCNT surface. In this case >C=C< group in MWCNT surface as dienophile reacted with the furfuryl group in PFMA as diene via DA reaction to obtain organo-modified MWCNT.[25]

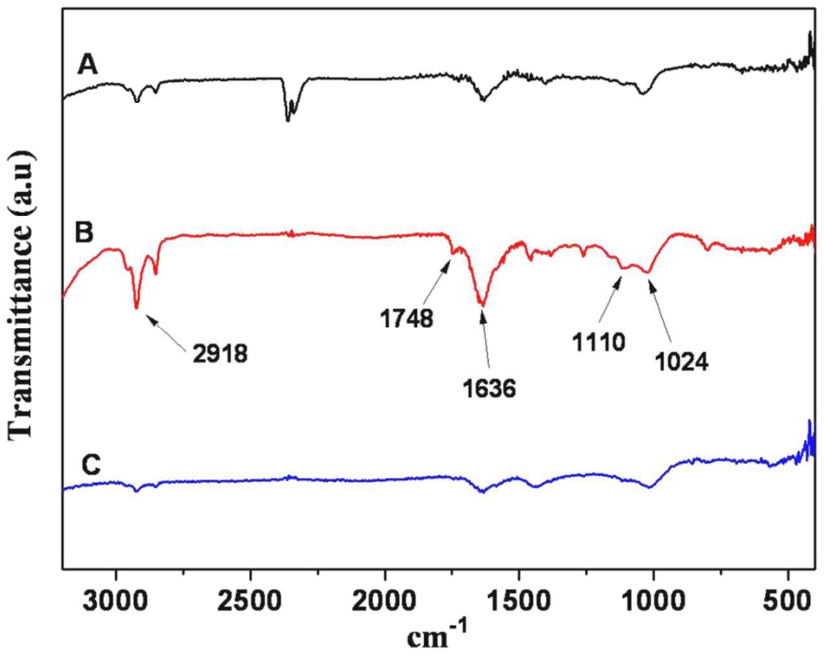
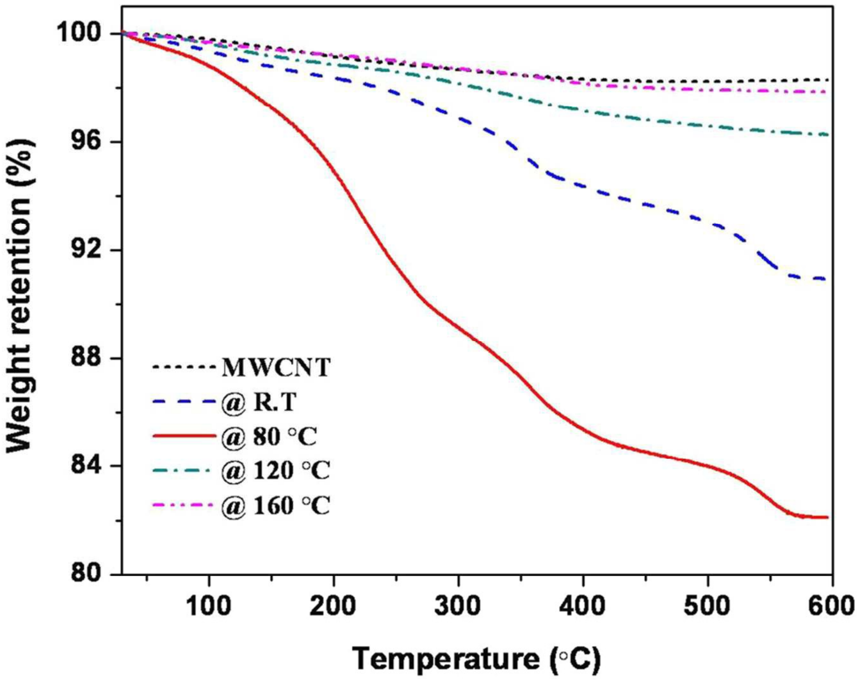


Figure 2. FT-IR spectra of MWCNT (A), MWCNT-PFMA after DA reaction at 80°C (B) and MWCNT-PFMA after rDA reaction at 160 °C (C).

TGA analysis was carried out to study the amount of PFMA grafted onto the surface of MWCNT. Figure 3A and 3B show the TGA and DTG plots of the MWCNT and PFMA grafted with MWCNT respectively. In TGA analysis, the samples were heated from 30 °C to 600 °C under N_2 atmosphere. Pristine MWCNT did not show any significant weight loss in this temperature range. TGA as well as DTG plots of DA adduct of MWCNT and PFMA prepared at room temperature and 80 °C show that there are three stages of weight loss at 210 °C, 355 °C and 540 °C. PFMA prepared by RAFT polymerization also showed the same three stages degradation pattern shown in Figure S1 (supporting information). This indicates grafting of PFMA onto the surface of MWCNT.



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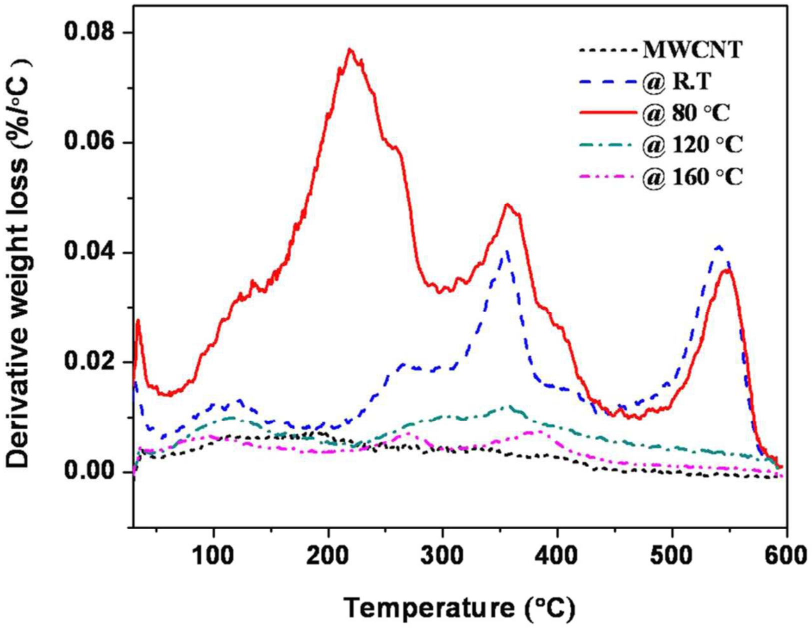
147 **Figure 3A. TGA thermograms of MWCNT, DA-MWCNT-PFMA prepared at room**

148 **temperature, 80 °C, 120 °C for 48 h and rDA product at 160 °C for 5 h.**



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150 **Figure 3B. DTG thermograms of MWCNT, DA-MWCNT-PFMA at room temperature, 80**

151 **°C, 120 °C for 48 h and rDA product at 160 °C for 5 h.**

TGA analysis showed the weight loss of 9% and 18% in MWCNT-PFMA prepared at room temperature and 80 °C respectively. So the extent of grafting of PFMA onto the MWCNT surface was more at 80 °C than the same at room temperature. For better understanding the maximum functionalization of MWCNT, the reaction between MWCNT and PFMA was carried out at 120 °C, an intermediate temperature between 80 °C and 160 °C. The reaction was run for 48 h and the TGA analysis of this reaction product was carried out. There was only 4 % weight loss. So, the above study indicates that the retro-DA reaction was initiated at 120 °C but was not completed. But when the DA-MWCNT-PFMA was heated at 160 °C for 5 hrs the rDA reaction completed fully, as it is observed from the TGA thermograms (Figure 3A). Few research articles also reported the use of similar reaction temperature range to study the DA and rDA reaction in the MWCNT system.[31-33] According to the % of wt loss for PFMA unit in TGA, the grafting density of polymer onto the MWCNT surface was calculated following the procedure reported by Barner-Kowollik et al.[28] The molecular weight of polymer and the specific surface area of the MWCNT were taken into account to determine the grafting density using the following equations;

$$\alpha_1 = \frac{w_{\text{polymer}}}{M_n\,(100 - w_{\text{polymer}})} \quad \text{mol}\cdot\text{g}^{-1} \qquad \text{Eq-1}$$

$$\alpha_2 = \frac{\alpha 1 \cdot N_A}{280} \ \text{chain}\cdot\ \text{nm}^{-2} \qquad \text{Eq-2}$$

Where w_{polymer} = amount of polymer degraded upto 600 °C;
M_n = molecular weight of the polymer chain;
N_A = Avogadro No. ; α_1 = Grafting density in mol g^{-1}
α_2 = Grafting density in chain nm^{-2}

Based on the above equations the grafting density (α_1) for the sample reacted at 80 °C and for the sample reacted at room temperature were calculated to be 0.025 mmol·g^{-1} and 0.012 mmol·g^{-1} respectively. Based on the above procedure the grafting density (α_2) in chain·nm^{-2} was also calculated using the theoretical specific surface area of MWCNT as 280 $m^2 \cdot g^{-1}$.[31] The grafting density (α_2) for the sample reacted at 80 °C and the sample reacted at room temperature were calculated to be 0.055 $chain \cdot nm^{-2}$ and 0.025 $chain \cdot nm^{-2}$ respectively.

Raman spectroscopy was carried out to study the grafting of PFMA onto the surface of MWCNT. Figure 4 shows the Raman spectra of MWCNT, DA-MWCNT-PFMA and its retro-DA product. Raman spectra of MWCNT show a tangential band (G-band) at about 1571 cm^{-1} and a disorder band (D-band) at about 1350 cm^{-1}. The DA reaction of PFMA with MWCNT transforms some sp^2 hybridized carbons of MWCNT bundles to sp^3 hybridized carbons. This transformation from sp^2 to sp^3 increases the disorder band and thus increases the peak intensity ratio of D and G band (I_D/I_G) in Raman spectra. In rDA reaction the MWCNT-PFMA adduct breaks down and gives back MWCNT and PFMA, the starting materials of DA reaction. Due to this rDA reaction some sp^3 carbons of MWCNT are transformed back to sp^2 carbons as a result the intensity ratio of D and G band (I_D/I_G) of rDA-MWCNT-PFMA product decreases w.r.t. the same in its DA product. This DA product of MWCNT-PFMA shows more solubility at room temperature in NMP after sonication compared to its rDA product. When this DA product was heated at 160 °C for 5 h, MWCNT precipitated from its dispersion in NMP solvent. This suggests that the PFMA was cleaved from MWCNT, because of rDA reaction. This feature shows temperature responsive characteristics of the MWCNT functionalized with PFMA i.e. the DA product is soluble in NMP at room temperature but insoluble on heating. In Raman spectrum pure MWCNT shows an I_D/I_G value of 0.63 and the functionalized MWCNT shows an increase in I_D/I_G value of 0.76. This indicates that MWCNT is successfully functionalized by DA reaction between MWCNT and PFMA. Again after heating this DA product at 160 °C for 5 h shows an I_D/I_G value of 0.63 indicating the rDA reaction.

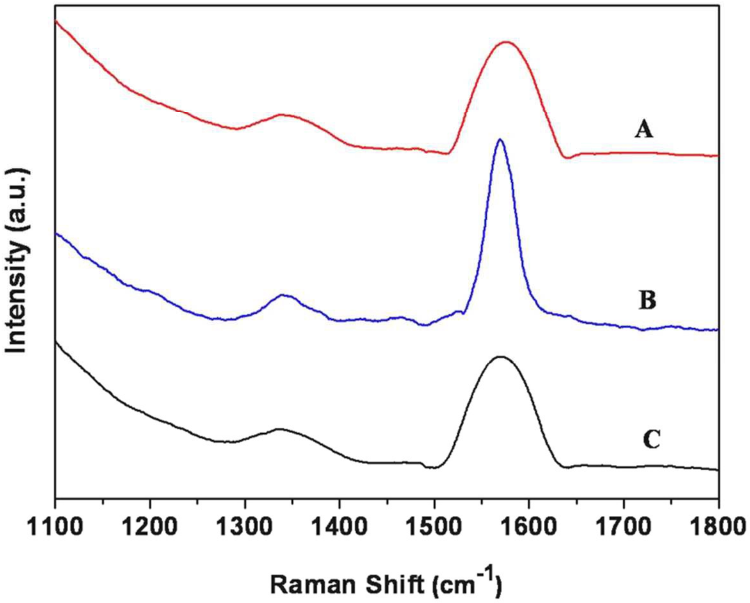

Figure 4. Raman spectra of MWCNT (A), DA-MWCNT-PFMA at 80°C (B) and rDA-MWCNT-PFMA (C).

The grafting of the poly(furfuryl methacrylate) (PFMA) onto the surface of MWCNT was further confirmed by XPS analysis. Figure 5 shows the XPS spectra of non-modified MWCNT and the MWCNT functionalized with PFMA. XPS analysis of unmodified MWCNT was carried out as reference sample in order to facilitate the interpretation of XPS spectra obtained for the PFMA modified MWCNT. The presence of O 1s peak attributed to PFMA indicates the functionalization of MWCNT with PFMA via DA reaction. Unmodified MWCNT shows C 1s binding energy at 284.4 eV for the sp^2 C–C structure which is good agreement with the previously reported literature.[28,34-39] Additionally, the binding energy at 290.5 eV for π-π* transition is well-known for the graphitic and aromatic compounds (sp^2 hybridization). The PFMA modified with MWCNTs i.e. DA-MWCNT-PFMA show few new peaks at different binding energies along with two major peaks at 284.4 eV and 290.5 eV attributed to MWCNT. In case of DA-MWCNT-PFMA, the C 1s spectrum shows peak at 284.6 eV for $-\underline{C}H_2$, $-\underline{C}H_3$

aliphatic carbon, at 286.5 eV for $-O\underline{C}H_2$ carbon and at 288.4 eV for carboxylic carbon $O{=}\underline{C}{-}OCH_2$. The corresponding O 1s components show peak at 533.6 eV for $-\underline{O}CH_2$ and at 532.1 eV for $\underline{O}{=}C{-}OCH_2$ which are good agreement with the literature. An additional peak was observed at 535.4 eV which is due to furan group of PFMA. These different peaks for the different C 1s and O 1s components of PFMA confirm the successful functionalization of MWCNT with PFMA via DA reaction.

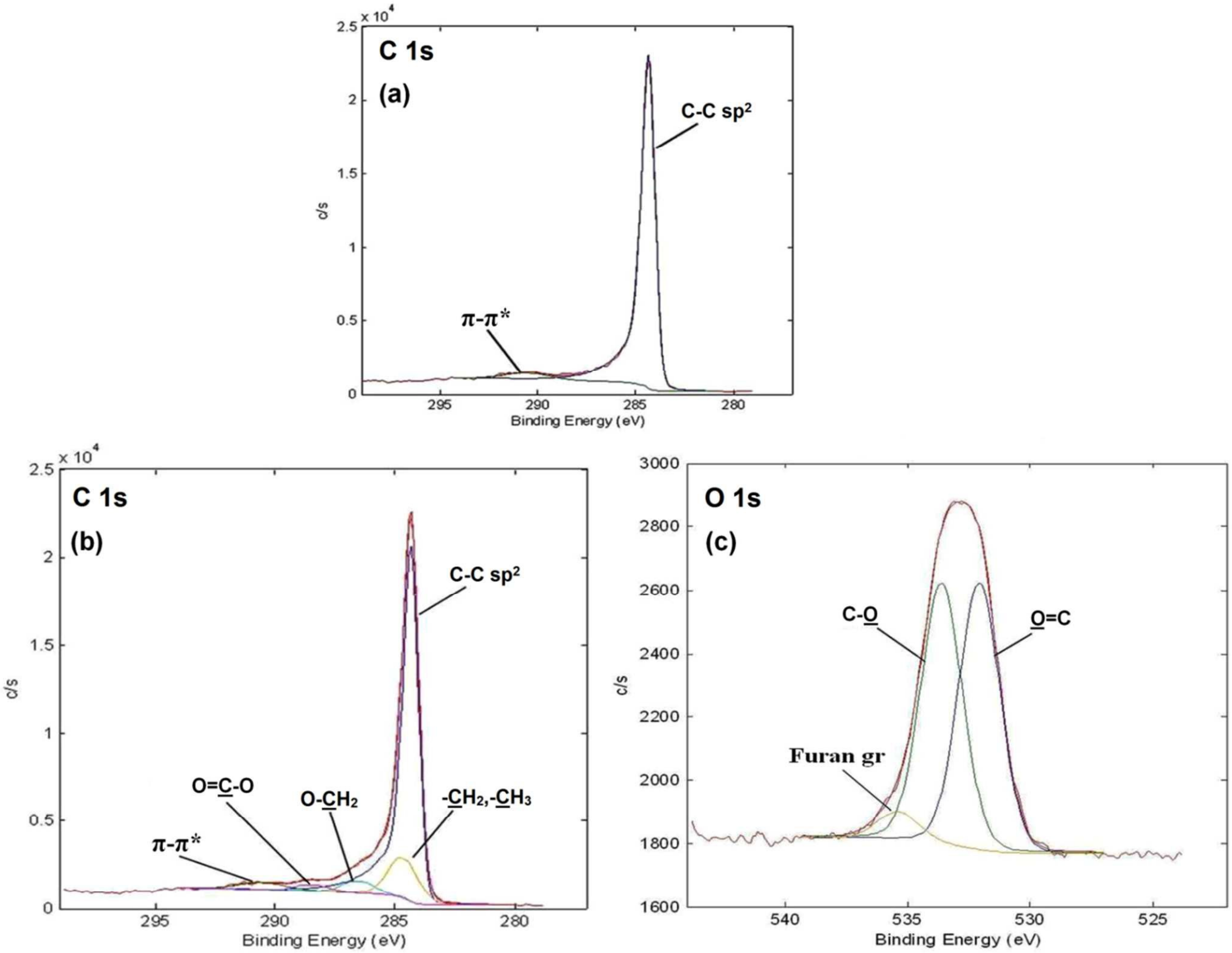

Figure 5. XPS spectra of C 1s signal of pristine MWCNT (a), C 1s signal of MWCNT modified with PFMA via DA reaction at 80 °C (b) and corresponding O 1s signal of MWCNT modified with PFMA (DA-MWCNT-PFMA) (c).

Figure 6 shows high resolution TEM (HRTEM) micrograph of pristine MWCNT, DA product of MWCNT-PFMA, rDA product of MWCNT-PFMA. Modified MWCNT i.e. DA product of MWCNT-PFMA shows an amorphous layer of PFMA polymer (approximately 23 nm) in the surface of MWCNT. Again when this DA product is heated at 160 °C for 5 hrs, PFMA was peeled off from the surface of MWCNT which indicates the successful rDA reaction.

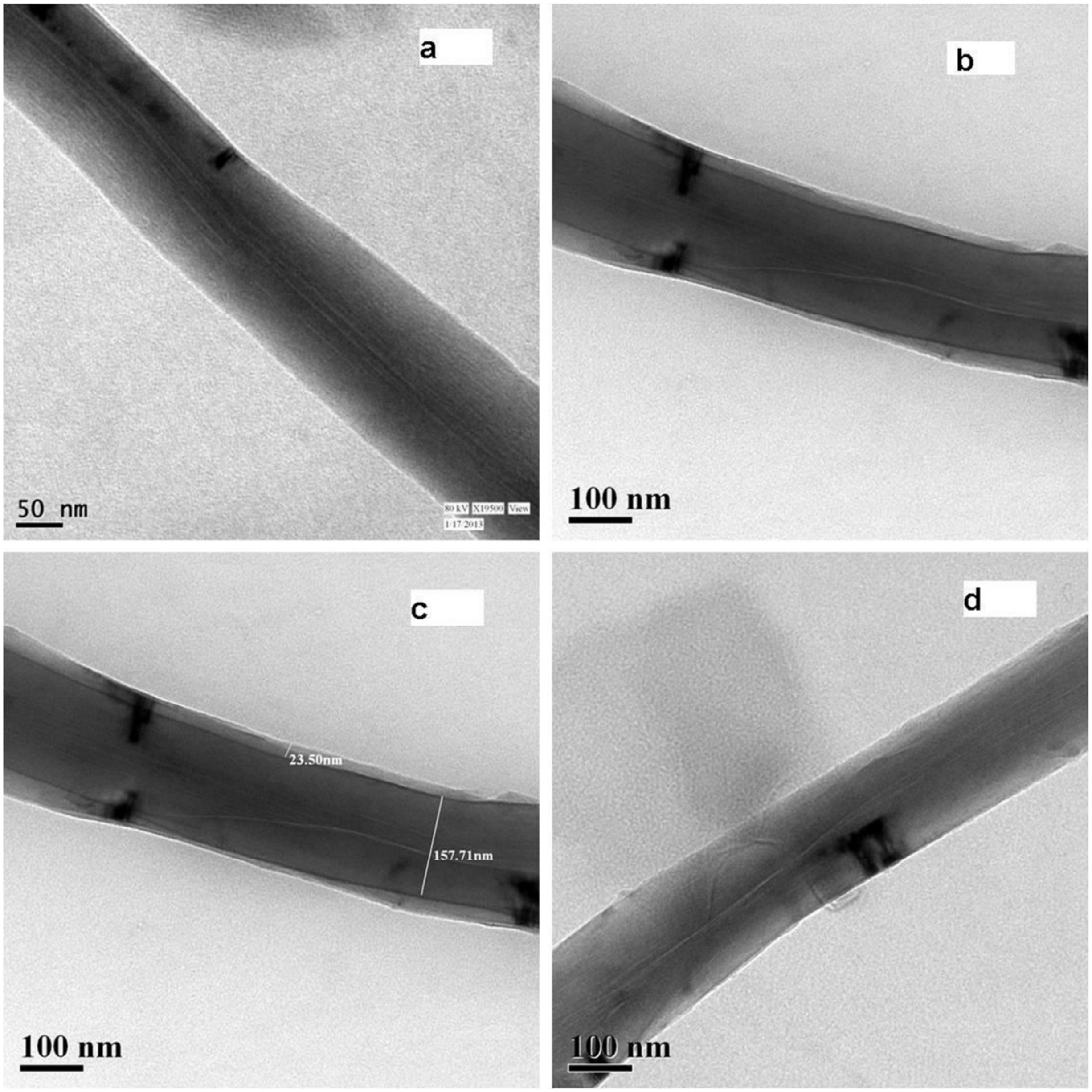

Figure 6. HRTEM micrographs of Pristine MWCNT (a), DA-MWCNT-PFMA at 80 °C (b) & (c) and its rDA product (d).

The SEM images (in Figure 7) indicate that in case of DA-MWCNT-PFMA (Figure 7B) at 80 °C, the MWCNT was embedded by PFMA polymeric layer. The DA-MWCNT-PFMA showed the homogeneous modification of MWCNT by PFMA over large area. Due to the attachment of organic moieties with the MWCNT, the PFMA modified MWCNT showed better solubility and compatibility in NMP as solvent. But in case of the rDA-MWCNT-PFMA (Figure 7C) at 160 °C, no polymeric layer was observed on the surface of MWCNT and it looked almost similar with the unmodified MWCNT (Figure 7A). Due to lack of organic moieties it was readily precipitated in NMP.

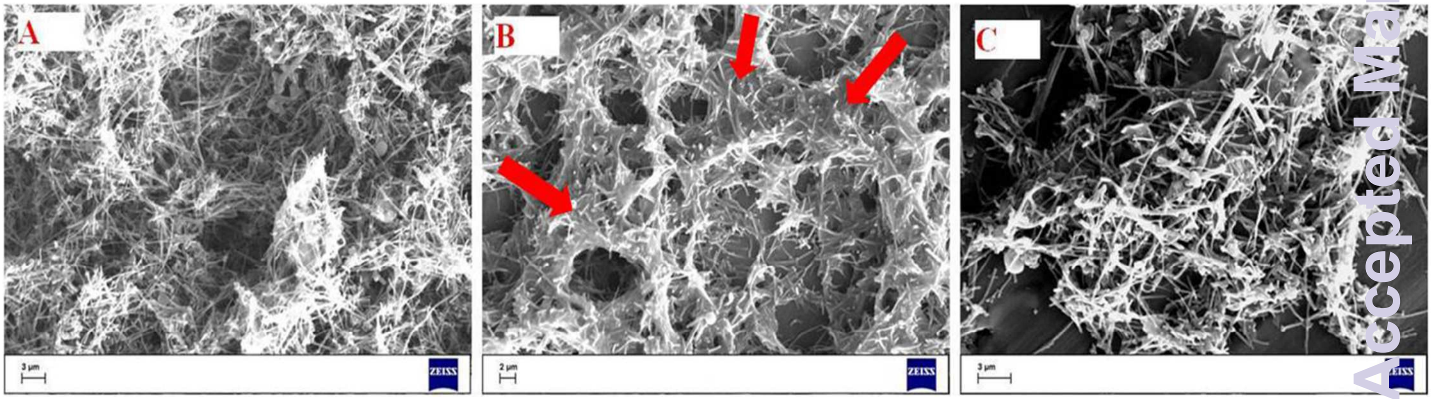

Figure 7: SEM images of Pristine MWCNT (A), DA-MWCNT-PFMA at 80 °C (B) and its rDA product at 160 °C (C).

Figure 8. Solubility of DA product of MWCNT-PFMA (A) and its corresponding retro-DA product (B) in NMP.

The DA adducts between MWCNT and PFMA in DA-MWCNT-PFMA were broken down by thermally induced retro-DA reaction. So, the defunctionalization of MWCNT and PFMA took place when the DA product was heated at 160 °C for 5 h. The defunctionalization of MWCNT, i.e successful retro-DA reaction of MWCNT-PFMA was characterized by FT-IR and Raman spectroscopy, as shown in Figure 2 and Figure 4 respectively. HRTEM analysis also showed the removal of organic moieties from MWCNT, when it was heated at 160 °C for 5 h. The thermally treated MWCNT-PFMA loses its organic moieties via retro-DA reaction. As a result the MWCNT-PFMA sample became insoluble and was precipitated in NMP after retro-DA reaction. Figure 8 shows the solubility image of modified MWCNT with PFMA via DA reaction and its retro-DA product in NMP solvent. In the first case the MWCNT-PFMA product is fully dispersed in NMP solvent at room temperature after sonication and remains same for several days in dispersion condition (Figure 8A). This DA-MWCNT-PFMA precipitates from its dispersion in NMP when heated for 5 h at 160 °C via retro-DA reaction due to detachment of

PFMA moieties from MWCNT surface (Figure 8B). These features show the thermo-responsive characteristics of PFMA modified MWCNT. Because of thermoreversible characteristics this material can have potential application in self-healing composites based upon materials have furfuryl functionality DA click reaction.[21, 40-42]

4. Conclusions

In summary, the tailor-made poly(furfuryl methacrylate) bearing pendent reactive furfuryl group was successfully grafted onto the surface of MWCNT chemically via a simple and single-step method of Diels-Alder [4 + 2] cycloaddition reaction without using of any catalysts. The grafting of PFMA was successfully confirmed by using various spectroscopic analyses like FT-IR, Raman, XPS and HRTEM analysis. The grafting of PFMA onto MWCNT surface was quantified by TGA analysis. In this direct functionalization process we achieved very high grafting density onto the CNT surface. Importantly, the DA product CNT-PFMA got precipitated in NMP when heated at 160 °C for 5 h due to retro-DA reaction. This single step and facile modification of MWCNT via DA reaction can open an innovative strategy for easy and direct modification of carbon nanotubes making them potential composite material for applications in energy storage, sensors, field emission transistors, supercapacitors and self healing materials.

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Direct Functionalization of Multi–Walled Carbon Nanotube (MWCNT) via grafting of poly(furfuryl methacrylate) using Diels-Alder "Click Chemistry" and its thermoreversibility

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Graphical Abstract