



Synthesis of thiol-glycol-functionalized carbon nanotubes and characterization with FTIR, TEM, TGA, and NMR technics

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Abstract

Carbon nanotube is one of the important topics of interest in the nanotechnology science. Many scientists have been interested in surface-modified nanotubes for decades. In this study, multi-walled carbon nanotubes (MWCNTs) were functionalized with polyethylene glycol and dithiols in esterification reactions. The MWNTs were first carboxylate-functionalized. The carboxylated MWCNTs were acyl chlorite substituted. The functionalized MWNTs were used as the precursor to esterification of polyethylene glycols and thiols. The reactions were performed catalysts or non-catalysts, solvent-free and solvent media, using microwave-assisted and classical methods. The synthesized compounds were characterized by FTIR, TGA, TEM and NMR techniques. We investigate the advantage of microwave synthesis method in terms of time and solvent in Green Chemistry. The obtained compounds exhibit very interesting results in their complexes with metals due to containing free hydroxyl and thiol groups.

Keywords MWCNT · Substituted MWCNT · Microwave-assisted synthesis · Esterification · Surface modification

Introduction

Carbon nanotubes have been the subject of considerable interest in the discovery of the fullerene. Carbon nanotubes (CNTs) find use in many areas, such as hydrogen storage, molecular electronics, biological sensors, high-resistant cables, metal sensors, gas sensors, and nanosensitive hand tools as quantum cables, emission imaging techniques, catalyst, information storage, intelligent sensors, protein-drug storage (Avilés-Barreto and Suleiman 2015; Lim et al. 2003; Jiang et al. 2005; Afrin et al. 2013; Hong et al. 2005; Dai et al. 2012; Hadavifar et al. 2014; Zang et al. 2009; Pandurangappa and Raghu 2008). With the modifications on CNTs with the functional groups, many features have

changed with the interest on covalent modification of CNTs (Avilés-Barreto and Suleiman 2015; Jiang et al. 2005; Hong et al. 2005; Lin et al. 2003; Chen et al. 1998; Hamon et al. 1999). Chemically modified CNTs provide specificity and selectivity (Pandurangappa and Raghu 2008). These chemical modifications are carried out by oxidations from the side surfaces of the carbon nanotubes, from the deformed portions on the surfaces, and generally from the more reactive end portions. These modifications are performed in colloidal forms due to their low solubility (Lim et al. 2003). Oxidants such as nitric acid, sulfuric acid/potassium dichromate, nitric acid/sulfuric acid, sulfuric acid/potassium permanganate, per chloric acid, hydrogen peroxide, and osmium tetroxide are used to form functional groups on CNTs such as –COOH, OH, etc. (Dillon et al. 1999; Dujardin et al. 1998; Nagasawa et al. 2000; Ng et al. 2002; Pan et al. 2006). Through these groups, CNTs are provided with functional groups via various reactions such as acylation, amidization, esterification, thioesterification, etherification (Zang et al. 2009; Li et al. 2011; Kim et al. 2012). Amidization derivatives synthesized by different groups are functionalized with amino, thiol groups (Te et al. 2010; Banerjee et al. 2005; Gabriel et al. 2006). Some of the synthesized amide derivatives have been used in the synthesis of compounds containing noble metals (Xing and Imae 2007). Santhosh

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et al. used long diamines such as 1,7-diaminoheptane, 1,10-diaminododecane, and 1,2-diaminododecane to explain that one side of the diamine was covalently attached to the glassy carbon surface and the other amine side not to bond with surface. They synthesized amines having free ends by binding to many polymers to obtain modified materials and identified that they interact with and adsorb the simple anions, metal ions and small organic compounds (Santhosh et al. 2007). Some functionalized MWCNTs have been used in metal enrichment of ions such as vanadium, copper, arsenic, gold, and lead due to complexes between MWCNTs containing free amine, thiol, and hydroxide groups and metal ions (Dai et al. 2012; Mormann et al. 2008; Xu et al. 2008; Wang et al. 2005; Tsai et al. 2005; Profumo et al. 2006; Xiao et al. 2008). With these modifications, Smally et al. were synthesized MWCNTs containing SH groups in tip dots and long-alkyl chains and tried to bind to metal surfaces. For this purpose, MWCNTs compounds containing 2-mercaptoethyl amine have been synthesized by amidation because of their large surface-to-surface distance between MWCNTs (Lim et al. 2003). Synthesis of dendritic structures with chitosan-containing Schiff bases was carried out with esterification (Jiang et al. 2005; Dai et al. 2012). Application of microwave technology in chemical syntheses has been popular in recent years. This is because microwave reactions are faster and more efficient than conventional reactions. In addition, microwave synthesis is quite advantageous with the instant adjustment function of pressure and temperature. Such reactions have become important in recent years due to the decrease in the volume of the solvent, the completeness of the reaction, high and well-increasing selectivity, reduced amount of reagent use, and increase the yield (Calisir and Çiçek 2017; Caddick and Fitzmaurice 2009; Cutress et al. 2009).

In this study, modified MWCNT derivatives containing free hydroxyl (–OH) and thiol (–SH) groups were synthesized under both classical and microwave-assisted reaction conditions using MWCNTs (D1–D7). The MWCNTs, which were purified from metal impurities, were subjected to oxidation and acylation, respectively. The targeted compounds were also reached by esterification and thioesterification reactions. Microwave-assisted reactions with classical methods have been compared in many respects. The products were characterized by FTIR, NMR techniques, TGA, and TEM.

Experimental

The MWCNTs used in this study were purchased commercially from Nanografi and Sigma Aldrich Company (product specifications, purity: 92%, outside diameter: 8–10 nm, average length: 1–3 µm). All other chemicals including

HPLC grade solvents and reagents, were purchased from Merck and Sigma-Aldrich. Milestone StartSYNTH-Microwave Synthesis Labstation system was used to perform some reactions. All reactions were sonicated with Bandelin Sonorex ultrasonic bath and were mixed and heated with IKA C-MAG HS 7 and Heidolph MR Hei-Standard FTIR magnetic stirrers. All reactions were performed in a fume hood. Vacuum-filter system was used to filtrate some products with 0.45-µm nylons net filter (HNWP). In some of the experiments, Thermo Scientific Heraeus Megafuge 16R centrifuge system was used to separate solid product (15 °C, 5500 rpm and 15 min). While in workup studies, Stuart Vorteks Mixer SA8 was used to mix vigorously. To wash some products, ultrapure water (conductivity: <0.2 µS/cm) was used produced from Thermo Scientific Smartpure2 pure water system. FTIR spectra were recorded on a Perkin Elmer BX 2 FTIR. ¹H-NMR (400 MHz) and ¹³C-NMR (100 MHz) spectra were obtained in CDCl₃ or DMSO-*d*₆ solvents using NMR spectrometer. TGA spectra were recorded on EXSTAR 6000 TG/DTA 6300 thermogravimetry/differential thermal analyzer. TEM images were recorded with Hitachi HT7700. The images were taken at 120 kV and in high-resolution mode.

Synthesis of MWCNTs–COOH

MWCNT were purified with 10% HCl for 20 h to remove the metal and other impurities such as amorphous carbon in an ultrasonic bath. MWCNTs were washed with ultrapure water and dried in the oven at 60 °C for 48 h. Then 1.00 g MWCNTs were added to a 100 mL round bottom flask containing 20 mL mixture of concentrated H₂SO₄:HNO₃ (3:1, v/v). The mixture was sonicated in an ultrasonic bath 30 min and then refluxed 24 h in an oil bath with stirrer, then cooled to room temperature. After that ultrapure water was added, mixed with vortex mixer and centrifuged until pH of solution was neutral value (7.0). The product was dried in the oven 65 °C for 48 h (Lim et al. 2003; Jiang et al. 2005; Li et al. 2011; Xu et al. 2008; Jeong et al. 2006; Qiu et al. 2013).

Synthesis of MWCNTs–COCl

MWCNTs–COOH (0.60 g) was added in a 50-ml flask containing 20.0 mL thionyl chloride. The reaction mixture was stirred and refluxed 24 h at 65 °C. Excess thionyl chloride was removed by evaporation under vacuum in an ice-water trapped system at low temperature. And washed three times with anhydrous THF to remove impurities. Dried in the oven 12 h at 60 °C. Synthesized acyl-modified MWCNTs were used directly in the next reaction without waiting (Avilés-Barreto and Suleiman 2015; Dai et al. 2012; Jeong et al. 2006; Qiu et al. 2013).

Synthesis of thiol-functionalized MWCNTs, D1–D3

General procedure-1 (classic)

MWCNTs–COCl (0.10 g) was added in a reaction bottle with cap (100 mL) containing 50.0 mL ethanol absolute and dispersed 30 min in an ultrasonic bath. Pyridine (5.0 mL) and a dithiol (10.0 mL) were added into the reaction bottle. The reaction mixture was sonicated 20 h in an ultrasonic bath at 55 °C. Then left to cool to room temperature.

General procedure-2 (microwave-assisted)

MWCNTs–COCl (0.10 g), pyridine (5.0 mL), and a dithiol (5.0 mL) were added in a microwave glass reactor (30 mL) and closed with reactors cap. The reaction mixture was refluxed in microwave synthesis system ($E = 1000$ W) for 2 h at 150 °C and 1 h at 120 °C. Then left to cool to room temperature.

General workup procedure

The resultant mixture was suspended with ethanol, mixed with vortex, and filtered by 0.45- μ m HNWP filter under vacuum. Washed three times ethanol and diethyl ether. Dried in an oven at 65 °C.

Synthesis of MWCNT–CO–S–CH₂CH₂SH (D1)

Synthesized from 1,2-ethanedithiol to the general procedure-1 and general procedure-2. Purified by general workup procedure. FTIR (γ cm⁻¹) 1721 (O=C–S stretch), 2920–2850 (asymmetric and symmetric stretch of CH₂ groups), 2614 (–SH stretch), 1534–1243 (S–C(O)–C stretching), 1058 (CH₂–CH₂–O– bending); ¹H NMR (DMSO-*d*₆, 400 MHz) δ 1.53 (H), 3.35 (2H), 4.64 (2H); ¹³C{¹H} NMR (DMSO-*d*₆, 100 MHz) δ 36.00, 44.00, 170.88; TGA (TG %) MWCNT–COCl: 70.64 (595 °C) and D1: 85.20 (575 °C).

Synthesis of MWCNT–CO–S–CH₂CH₂–O–CH₂CH₂SH (D2)

Synthesized from diethylene glycol dithiol to the general procedure-1 and general procedure-2. Purified by general workup procedure. FTIR (γ cm⁻¹) 1716 (O=C–S stretch), 2915–2848 (asymmetric and symmetric stretch of CH₂ groups), 2616 (–SH stretch), 1535–1241 (S–C(O)–C stretching), 1052 (C–O–C bending); ¹H NMR (DMSO-*d*₆, 400 MHz) δ 1.51 (H), 3.36 (2H), 3.66 (2H), 4.00 (2H),

4.67 (2H); ¹³C{¹H} NMR (DMSO-*d*₆, 100 MHz) δ 30.61, 36.14, 69.99, 74.55, 168.8; TGA (TG %) MWCNT–COCl: 70.64 (595 °C) and D2: 83.90 (577 °C).

Synthesis of MWCNT–CO–S–CH₂CH₂–O–CH₂CH₂–O–CH₂CH₂SH (D3)

Synthesized from triethylene glycol dithiol to the general procedure and general procedure-2. Purified by general workup procedure. FTIR (γ cm⁻¹) 1719 (O=C–S stretch), 2920–2845 (asymmetric and symmetric stretch of CH₂ groups), 2616 (–SH stretch), 1535–1263 (S–C(O)–C stretching), 1070 (C–O–C bending), 1052 (S–C(O)–C bending); ¹H NMR (CDCl₃, 400 MHz) δ 1.27 (H), 1.58(2H), 2.65 (2H), 3.64 (2H); ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 22.00, 27.14, 29.99, 31.25, 69.25 168.75; TGA (TG %) MWCNT–COCl: 70.64 (595 °C) and D3: 82.61 (595 °C).

Synthesis of glycol-functionalized MWCNTs, D4–D7

General procedure-A (classic)

MWCNTs–COCl (0.10 g) and glycol (5–10 mL) were added in a reaction flask (100 mL) containing 30.0 mL toluene and dispersed 15 min in an ultrasonic bath. The black suspension was refluxed 42 h at 110 °C. Then left to cool to room temperature.

General procedure-B (microwave-assisted)

MWCNTs–COCl (0.10 g), and a glycol (5.0 mL) were added in a flask (100 mL) containing 30.0 mL toluene and linked a condenser. The reaction mixture was refluxed in microwave synthesis system ($E = 1000$ W) for 2 h at 120 °C. Then left to cool to room temperature.

Synthesis of MWCNT–CO–O–CH₂CH₂OH (D4)

Synthesized from ethylene glycol to the general procedure-A and general procedure-B. Purified by general workup procedure. FTIR (γ cm⁻¹) 3200 (–OH stretch), 1704 (O=C–O stretch), 2918–2845 (asymmetric and symmetric stretch of CH₂ groups), 1536–1242 (O–C(O)–C stretching), 1142 (O–C(O)–C bending); ¹H NMR (DMSO-*d*₆, 400 MHz) δ 2.56 (2H), 3.44 (2H); ¹³C{¹H} NMR (DMSO-*d*₆, 100 MHz) δ 61.72, 65.23, 167.17; TGA (TG %) MWCNT–COCl: 70.64 (595 °C) and D4: 81.73 (574 °C).

Synthesis of MWCNT–CO–O–CH₂CH₂–O–CH₂CH₂OH (D5)

Synthesized from diethylene glycol to the general procedure-A and general procedure-B. Purified by general

workup procedure. FTIR ($\gamma \text{ cm}^{-1}$) 3200 (–OH stretch), 1704 (O=C–O stretch), 2915–2847 (asymmetric and symmetric stretch of CH_2 groups), 1536–1242 (O–C(O)–C stretching), 1148 (O–C(O)–C bending), 1096 (C–O–C bending); ^1H NMR (DMSO- d_6 , 400 MHz) δ 3.39 (2H), 3.48 (2H), 3.54 (2H), 4.62 (2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 100 MHz) δ 56.40, 57.25, 72.94, 72.94, 167.06; TGA (TG %) MWCNT–COCl: 70.64 (595 °C) and D5: 73.90 (577 °C).

Synthesis of MWCNT–CO–O–CH₂CH₂–O–CH₂CH₂–O–CH₂CH₂–OH (D6)

Synthesized from triethylene glycol to the general procedure-A and general procedure-B. Purified by general workup procedure. FTIR ($\gamma \text{ cm}^{-1}$) 3200 (–OH stretch), 1702 (O=C–O stretch), 2916–2844 (asymmetric and symmetric stretch of CH_2 groups), 1535–1243 (O–C(O)–C stretching), 1147 (O–C(O)–C bending), 1025 (C–O–C bending); ^1H NMR (CDCl_3 , 400 MHz) δ 1.47 (1), 1.73 (2H), 1.87 (2H), 2.10 (2H), 2.58 (2H) 3.44 (2H), 3.57 (2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 45.42, 55.22, 60.84, 72.54, 165.15; TGA (TG %) MWCNT–COCl: 70.64 (595 °C) and D6: 81.33 (595 °C).

Synthesis of MWCNT–CO–O–CH₂CH₂–O–CH₂CH₂–O–CH₂CH₂–O–CH₂CH₂OH (D7)

Synthesized from tetraethylene glycol to the general procedure-A and general procedure-B. Purified by general workup procedure. FTIR ($\gamma \text{ cm}^{-1}$) 3200 (–OH stretch), 1702

(O=C–O stretch), 2918–2847 (asymmetric and symmetric stretch of CH_2 groups), 1539–1243 (O–C(O)–C stretching), 1162 (O–C(O)–C bending), 1083 (C–O–C bending); ^1H NMR (DMSO- d_6 , 400 MHz) δ 3.40 (2H), 3.50 (8H), 3.89 (2H), 4.56 (2H), 4.00 (H); $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 100 MHz) δ 60.66, 63.25, 67.19, 70.23, 70.28, 72.79, 165.00; TGA (TG %) MWCNT–COCl: 70.64 (595 °C) and D7: 67.90 (576 °C).

Results and discussion

MWCNTs were reacted with acid mixture for synthesis of the precursor compound carboxylated MWCNTs. The compound MWCNTs–COOH was checked with FTIR; 3297 cm^{-1} , and carboxylic acid stretch was observed. Carboxylated MWCNTs were treated with thionyl chloride to handle acyl-substituted MWCNTs. After disposing the excess of thionyl chloride, in order to verify the product, a few pieces of silver nitrate were added into some MWCNTs–COCl. At the end of the experiment, white cloudiness in acyl chloride was observed while no turbidity was observed in the carboxylic acid. And also the precursor compound was evaluated with FTIR spectra; 3297 cm^{-1} carboxylic acid stretch was disappeared.

Mono/di/triethylene glycol dithiol- and mono/di/tri/tetraethylene glycol-substituted MWCNTs were synthesized with esterification reaction. The reaction scheme is given in Scheme 1 and the best reaction conditions are given in Table 1. MWCNTs–COCl reacted with excess of dithiol

Scheme 1 Synthesis of glycol- and thiol-substituted MWCNTs (D1–D7) with microwave-assisted method

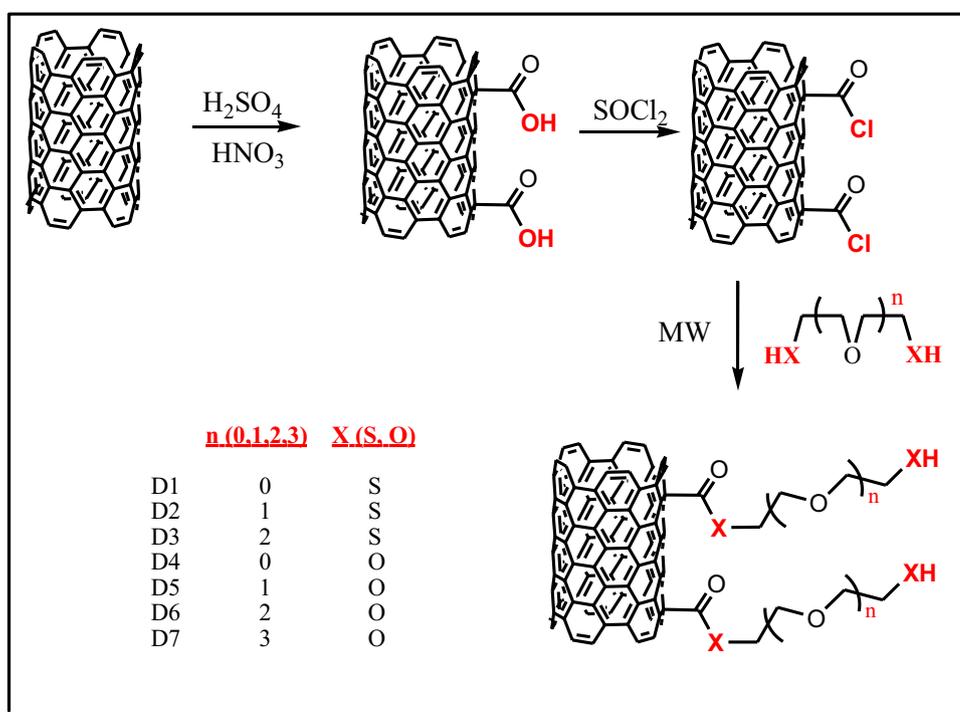


Table 1 Microwave-assisted reaction and ordinary reaction conditions for thiol- and glycol-substituted MWCNTs

Ligand	Classic synthesis method				Microwave-assisted synthesis method			
	Reaction time (h)	Solvent	Catalysis	Temperature (°C)	Reaction time (h)	Solvent	Catalysis	Temperature (°C)
D1	20	Ethanol	Pyridine	55	3	No solvent	Pyridine	120
D2	20	Ethanol	Pyridine	55	3	No solvent	Pyridine	120
D3	20	Ethanol	Pyridine	55	3	No solvent	Pyridine	120
D4	42	Toluene	No catalysis	110	2	Toluene	No catalysis	120
D5	42	Toluene	No catalysis	110	2	Toluene	No catalysis	120
D6	42	Toluene	No catalysis	110	2	Toluene	No catalysis	120
D7	42	Toluene	No catalysis	110	2	Toluene	No catalysis	120

and glycol derivatives in an esterification reaction. Classic method and microwave-assisted synthesis method were compared for reaction conditions (reaction times, solvents, heating system) between methods. In the classic method, the reaction performed in an oil bath to reflux reaction system (conventional heating). Microwave-assisted method needs shorter time, less solvent usage, etc. In spite of the fact that pyridine was used as a catalysis to synthesis of dithiol-functionalized MWCNTs, no catalyst was used to synthesize glycol-substituted MWCNTs. While absolute ethanol was used as a solvent in classical method, there was no solvent used in microwave-assisted synthesis method to synthesize dithiol derivatives.

FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, TGA spectra and TEM images were collected for the target compounds. Figure 1 shows FTIR spectra for the mono/di/tri-ethylene glycol dithiol-substituted MWCNTs and MWCNT-COCl. In the FTIR spectra of MWCNT-COCl, carbonyl stretch at 1683 cm^{-1} , Cl-C(O)-C stretch at 1241 cm^{-1} were observed. In the FTIR spectra of the D1 compound is examined, while carbonyl (C=O) stretch observed at 1683 cm^{-1} in the MWCNT-COCl compound; the carbonyl (C=O) stretch shifted to 1721 cm^{-1} after the thio-esterification reaction. In addition, asymmetric and symmetrical CH_2 stretching at $2920\text{--}2850\text{ cm}^{-1}$, -SH stretching at 2614 cm^{-1} , S-C(O)-C stretching at $1534\text{--}1243\text{ cm}^{-1}$, $\text{CH}_2\text{CH}_2\text{-O}$ bending was observed at

1058 cm^{-1} . A similar situation exists for the compound D2; the carbonyl (C=O) stretch shifted to 1716 cm^{-1} after the thio-esterification reaction. Also asymmetric and symmetrical stretches of CH_2 groups at $2915\text{--}2848\text{ cm}^{-1}$, -SH stretching at 2616 cm^{-1} , S-C(O)-C stretching at $1535\text{--}1241\text{ cm}^{-1}$, $\text{CH}_2\text{CH}_2\text{-O}$ bending at 1052 cm^{-1} were observed in the FTIR spectra. The FTIR spectra of the D3 compound is examined, the carbonyl (C=O) stretch shifted to 1719 cm^{-1} after the thio-esterification reaction. The asymmetric and symmetrical CH_2 stretching at $2920\text{--}2845\text{ cm}^{-1}$, -SH stretching at 2616 cm^{-1} , S-C(O)-C stretching at $1535\text{--}1263\text{ cm}^{-1}$, C-O-C bending at $1070\text{--}1052\text{ cm}^{-1}$ were observed.

Figure 2 shows FTIR spectra for the mono/di/tri/tetra-ethylene glycol-substituted MWCNTs. In the FTIR spectra of the D4 compound is examined, while carbonyl (C=O) stretch observed at 1683 cm^{-1} in the MWCNT-COCl compound; the shift of carbonyl (Cl-C=O) stretch at 1683 cm^{-1} to carbonyl (O=C-O) stretch at 1705 cm^{-1} after the esterification reaction. Also -OH stretch at 3200 cm^{-1} , asymmetric and symmetrical stretch of CH_2 group at $2918\text{--}2845\text{ cm}^{-1}$, O=C-O- CH_2 bending at $1536\text{--}1242\text{ cm}^{-1}$, O-C(O)-C bending at 1142 cm^{-1} were observed. In the FT-IR spectra of the compound D5, -OH stretching at 3200 cm^{-1} , carbonyl (O=C-O) stretch at 1704 cm^{-1} , asymmetric and symmetrical CH_2 stretching at $2915\text{--}2847\text{ cm}^{-1}$, O-C(O)-C stretching at $1536\text{--}1242\text{ cm}^{-1}$, O-C(O)-C bending at 1148 cm^{-1} ,

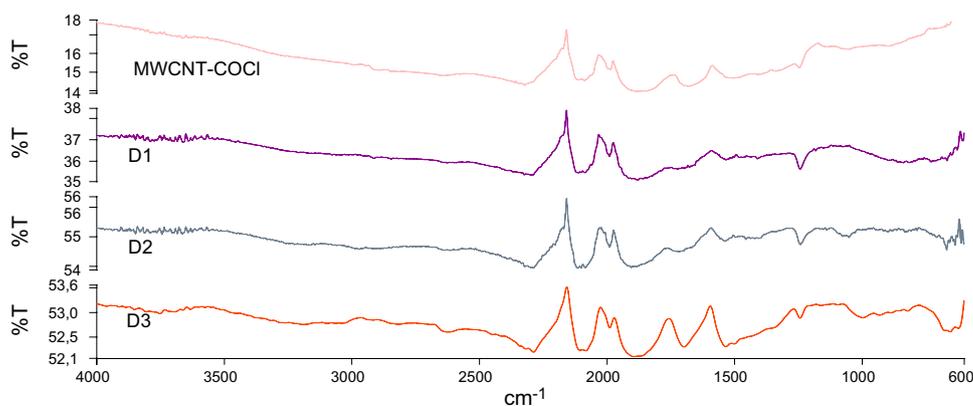
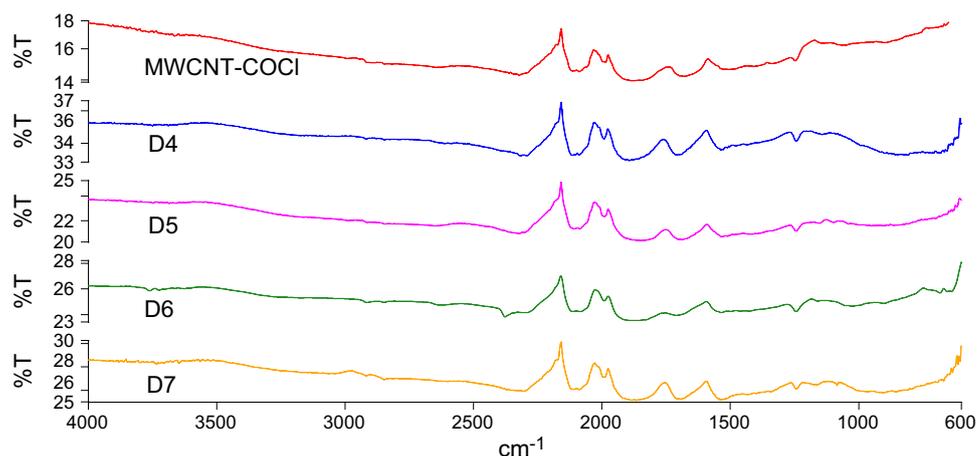
Fig. 1 FTIR spectra for the mono/di/triethylene glycol thiol-substituted MWCNTs

Fig. 2 FTIR spectra for the mono/di/tri/tetraethylene glycol-substituted MWCNTs



$\text{CH}_2\text{CH}_2\text{-O}$ bending in 1096 cm^{-1} were observed. In the spectra of *D6* compound, -OH stretching at 3200 cm^{-1} , carbonyl ($\text{O}=\text{C}-\text{O}$) stretch at 1702 cm^{-1} , asymmetric and symmetrical CH_2 stretching at $2916\text{--}2844\text{ cm}^{-1}$, $\text{O}-\text{C}(\text{O})-\text{C}$ stretching at $1535\text{--}1243\text{ cm}^{-1}$, $\text{O}-\text{C}(\text{O})-\text{C}$ bending at 1147 cm^{-1} , $\text{C}-\text{O}-\text{C}$ bending in 1025 cm^{-1} were observed. Similarly, *D7* compound characterized with FTIR. In the FTIR spectra of *D7* compound, -OH stretching at 3200 cm^{-1} , carbonyl ($\text{O}=\text{C}-\text{O}$) stretching at 1702 cm^{-1} , asymmetric and symmetrical CH_2 stretching at $2918\text{--}2847\text{ cm}^{-1}$, $\text{O}-\text{C}(\text{O})-\text{C}$ stretching at $1539\text{--}1243\text{ cm}^{-1}$, $\text{O}-\text{C}(\text{O})-\text{C}$ bending at 1162 cm^{-1} , $\text{C}-\text{O}-\text{C}$ bending at 1083 cm^{-1} were observed. According to these results, it was observed that carbonyl vibration shifted to low frequency values with the effect of high volume groups in line with the literature (Kaya et al. 2012). Also proton NMR and carbon NMR spectra show that the success on synthesis of esterification and thioesterification products.

The compounds were characterized with $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ in $\text{DMSO-}d_6$ and CDCl_3 solvents. For this purpose, all synthesized compounds were dispersed in some of solvents (Fig. 5) to find the NMR solvent. As a result of stability and solubility test CDCl_3 and $\text{DMSO-}d_6$ were chosen for NMR solvents. While proton NMR spectra showed that no peak was observed on the proton NMR spectrum of acylated MWCNTs and some peaks were observed on the products' spectra. These new peaks comes from bridges of ethylene glycol and ethylene glycol dithiol which bound by strong chemical bonds. In the $^1\text{H-NMR}$ spectra of *D1*, $\text{HS}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 1.53 ppm, $\text{HS}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 3.35 ppm, 4.64 ppm $\text{HS}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shifts were observed. In $^{13}\text{C-NMR}$ spectrum, $\text{HS}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 36.00 ppm, $\text{CH}_2-\text{S}-\text{C}=\text{O}$ chemical shift at 44.00 ppm, $\text{O}=\text{C}-\text{S}$ chemical shift at 170.88 ppm were observed. For *D2* compound, $\text{HS}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 1.51 ppm, $\text{HS}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 3.36 ppm,

$\text{O}=\text{C}-\text{S}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 4.00 ppm, $\text{O}=\text{C}-\text{S}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 4.67 ppm were observed. When $^{13}\text{C-NMR}$ spectrum is examined, $\text{HS}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 30.6 ppm, $\text{CH}_2-\text{S}-\text{C}=\text{O}$ chemical shift at 36.14 ppm, $\text{O}=\text{C}-\text{S}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 69.99 ppm, $\text{HS}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 74.55 ppm, $\text{O}=\text{C}-\text{S}$ chemical shift at 168.8 ppm were observed. The last thiol-substituted compound *D3* showed that $\text{HS}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 1.27 ppm, $\text{O}=\text{C}-\text{S}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 1.58 ppm, at 2.65 ppm $\text{O}=\text{C}-\text{S}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift, $\text{S}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 3.64 ppm in NMR spectra. When $^{13}\text{C-NMR}$ spectrum is examined, $\text{HS}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 22.00 ppm, $\text{O}=\text{C}-\text{S}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 27.14 ppm, $\text{O}=\text{C}-\text{S}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 29.99 ppm, $\text{HS}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 31.25 ppm, $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$ chemical shift at 69.25 ppm, $\text{O}=\text{C}-\text{O}$ chemical shift at 168.75 ppm were observed. In the $^1\text{H-NMR}$ spectrum of *D4*, $\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$ chemical shift at 2.56 ppm, $\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$ chemical shift at 3.44 ppm were observed. In $^{13}\text{C-NMR}$ spectrum, $\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$ chemical shift at 61.72 ppm, $\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$ chemical shift at 65.23 ppm, $\text{O}-\text{C}=\text{O}$ chemical shift at 167.17 ppm were observed. In the $^1\text{H-NMR}$ spectra of the *D5* compound, $\text{-O}-\text{CH}_2-\text{CH}_2-\text{OH}$ chemical shift at 3.39 ppm, $\text{-O}-\text{CH}_2-\text{CH}_2-\text{OH}$ chemical shift at 3.48 ppm, $\text{-O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}=\text{O}$ chemical shift at 3.54 ppm, $\text{-O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}=\text{O}$ chemical shift at 4.62 ppm were observed. In the $^{13}\text{C-NMR}$ spectrum, $\text{-O}-\text{CH}_2-\text{CH}_2-\text{OH}$ chemical shift at 56.40 ppm, $\text{-O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}=\text{O}$ chemical shift at 57.25 ppm, $\text{-O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}=\text{O}$ chemical shift and $\text{-O}-\text{CH}_2-\text{CH}_2-\text{OH}$ chemical shift at 72.94 ppm, $\text{O}=\text{C}-\text{O}$ chemical shift at 167.06 ppm were observed. When $^1\text{H-NMR}$ spectra of *D6* compound were examined, $\text{-O}-\text{CH}_2-\text{CH}_2-\text{O}-$ chemical shift at 1.73 ppm, $\text{-O}-\text{CH}_2-\text{CH}_2-\text{O}-$ chemical shift at 2.87 ppm, $\text{-O}-\text{CH}_2-\text{CH}_2-\text{OH}$ chemical shift at 2.10 ppm, $\text{-O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}=\text{O}$ chemical shift at 2.58 ppm,

–O–CH₂–CH₂–O–C=O chemical shift at 3.44 ppm, HO–CH₂–CH₂–O– chemical shift at 3.57 ppm, chemical shift of HO–CH₂–CH₂–O– at 4.26 ppm were observed. In ¹³C-NMR spectrum, O–CH₂–CH₂–O– chemical shift at 45.42 ppm, O–CH₂–CH₂–O–C=O chemical shift at 55.22 ppm, O–CH₂–CH₂–O–C=O chemical shift at 60.84 ppm, –CH₂–OH chemical shift at 72.54 ppm, O=C–O chemical shift at 165.15 ppm were observed. In the ¹H-NMR spectra of D7 compound, –CH₂–OH chemical shift at 3.40 ppm, –O–CH₂–CH₂–O– chemical shift at 3.50 ppm, –O–CH₂–CH₂–O–C=O chemical shift at 3.89 ppm, –O–CH₂–CH₂–O–C=O chemical shift at 4.56 ppm, –OH chemical shift at 4.00 ppm were observed. In the ¹³C-NMR spectrum, –CH₂–OH chemical shift at 60.66 ppm, –O–CH₂–CH₂–O–C=O chemical shift at 63.25 ppm, –O–CH₂–CH₂–O–C=O chemical shift at 67.19 ppm, HO–CH₂–CH₂– chemical shift at 70.23 ppm, –O–CH₂–CH₂–O–CH₂–CH₂– chemical shift at 70.28 ppm, of –O–CH₂–CH₂–O–CH₂–CH₂–, chemical shift at 72.79 ppm, O=C–O chemical shift at 165.00 ppm were observed. That can be seen clearly in proton NMR spectra between 1.47 and 4.64 ppm (–SH, –OH, and –CH₂) and in the carbon NMR spectra 165–168 ppm (C=O) indicates synthesis of target compounds (see in Supp. Supp. Matt.).

Additionally, TGA curves of MWCNT, MWCNT–COCl, and triethylene glycol dithiol-substituted MWCNT (D3) are given in Fig. 3 (the TGA curves of all synthesized compounds are given in Supp. Matt.). That can be clearly understood from MWCNTs, MWCNTs–COOH, MWCNTs–COCl and compounds curves. Although a mass loss of 29.36% at 595 °C was observed for MWCNT–COCl in the TGA (TG %) spectrum, it was observed that 14.8% was degraded at 575 °C because the D1 product obtained was more stable than the acyl chloride compound. ~2% deterioration in temperatures below 171 °C is caused by impurities that are attached to the structure or trapped. There was a mass loss of about 2% at 203 °C. This is the separation of the ethylene bridge. A maximum mass loss of 0.61% dTG/min and 0.51% dTG/min was observed at 272 and 290 °C. In the 5% mass loss up to 350 °C, both of the thiol groups

were removed from the structure. With a 0.58% dTG/min degradation at 380 °C and a 0.36% dTG/min degradation at 450 °C, there was a mass loss of 2.5% structure. This corresponds to the separation of the carbonyl group. For the second compound, D2, despite a 29.36% mass loss at 595 °C for MWCNT–COCl in the TGA (TG %) spectrum, 16.1% was degraded at 577 °C, due to the D2 product obtained was more stable than the acyl chloride compound. In the spectrum, there is a mass loss of approximately 2%, resulting from impurities trapped in the structure and up to 155 °C. A total loss of 9% mass with a maximum distortion of 0.70% dTG/min in the 220–380 °C range corresponds to the separation of the diethylene glycol dithiol group. The 3% mass loss in the 400–580 °C range belongs to the separation of the carbonyl group. Despite a 29.36% mass loss at 595 °C for MWCNT–COCl in the TGA (TG %) spectrum, it was observed that 17.39% at 595 °C deteriorated because the D3 product obtained was more stable than the acyl chloride compound. In the TGA spectrum, a mass loss of 1.15% was observed as a result of the removal of impurities below 100 °C. The mass loss of approximately 16.28% in the range of 217–355 °C corresponds to the degradation of the triethylene glycol dithiol group. Although a mass loss of 29.36% at 595 °C was observed for MWCNT–COCl in the TGA (TG %) spectrum, it was observed that 18.27% of the D4 product was degraded at 574 °C as it was more stable than the acyl chloride compound. The first mass loss of the D4 compound in the TGA spectrum has been observed up to 108 °C and indicates the separation of impurities trapped in the structure. The mass loss of approximately 4% in the 190–413 °C range belongs to the group C=O. Although a mass loss of 29.36% at 595 °C was observed for MWCNT–COCl in the TGA (% TG) spectrum, it was observed that 26.10% of the D5 product was degraded at 577 °C as it was relatively more stable than the acyl chloride compound. At 140 °C, approximately 3% mass loss belongs to the separation of some impurities. A mass loss of approximately 11% with a distortion of 1.08% per minute in the range of 140–250 °C corresponds to the separation of the

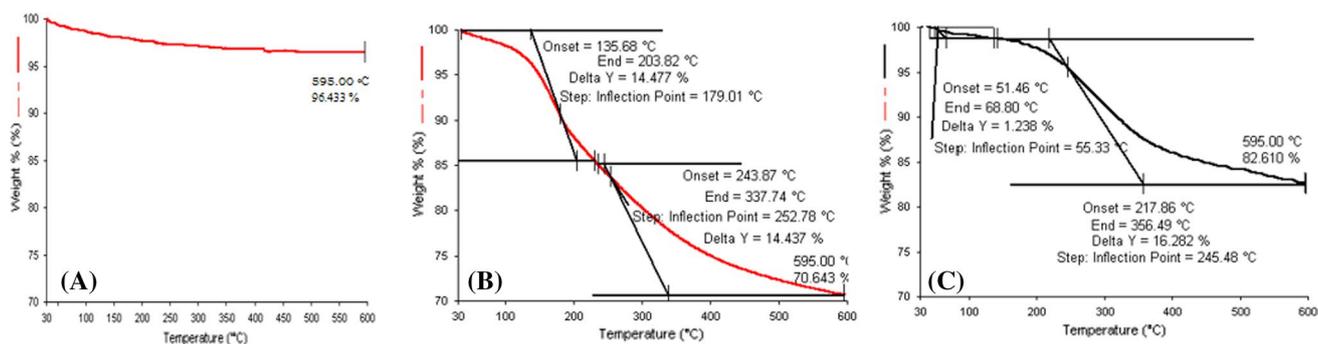


Fig. 3 TGA spectra for the MWCNT (a), MWCNT–COCl (b), and triethylene glycol dithiol-substituted MWCNT (c)

first ethylene glycol bridge. 8% mass loss (maximum 0.84% dTG/min) in the range of 271–380 °C indicates the separation of the second ethylene glycol bridge. Finally, 4% mass loss in the 400–580 °C range belongs to the C=O group. Despite a 29.36% mass loss at 595 °C for MWCNT–COCl in the TGA (TG %) spectrum, it was observed that 18.67% of the *D6* product was degraded at 595 °C because it was more stable than the acyl chloride compound. 1.48% mass loss up to 140 °C was observed in TGA spectrum because of some nanostructures. 17% mass loss in the range of 266–375 °C occurs by separating the triethylene glycol group. Despite a 29.36% mass loss at 595 °C for MWCNT–COCl in the TGA (TG %) spectrum, the *D7* product obtained was 32.10% at 576 °C due to its bulky structure and less stability than the acyl chloride compound due to its long glycol chains. In the TGA spectrum, a mass loss of 2% by mass was observed up to 140 °C. A 20% mass loss (2% dTG/min) in the 200–413 °C range results from the separation of the tetraethylene glycol group. The 5% mass loss observed in the 410–576 °C range is due to the separation of the C=O group.

The surface morphology of the substituted MWCNTs were characterized by TEM. TEM images of compound MWCNTs, MWCNTs–COOH and *D1–D7* are given in Table 2 (detailed TEM images are given in Supp. Matt.). When the TEM image of MWCNTs is examined, it is seen that it is composed of very complex long and pure nanotubes (Table 2a). It is clear that nanotubes overlap because

the modifications on the surface change the interactions between the nanotubes. In addition, the nanotubes are shortened with modifications on the nanotubes, which is also seen in Table 2. The thickness and fluctuations on the nanotubes indicate modifications on the surface. When Table 2b is examined, the breaks in the structure and the narrowing and shortening of the carbon nanotube cavity show that the structure is oxidized, that is, carboxylated. Table 2b–f shows that the thickening points indicated by arrow signs show that the surface morphology changes in the desired direction. The thickening of the *D1* compound in Table 2c also shows that it is functionalized with

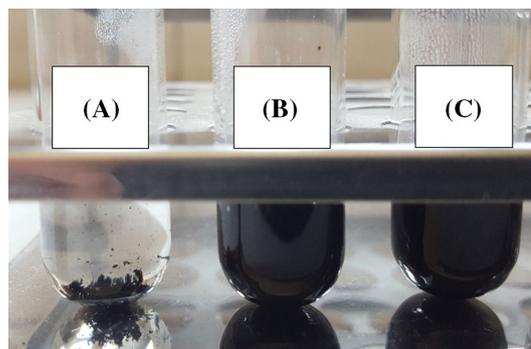
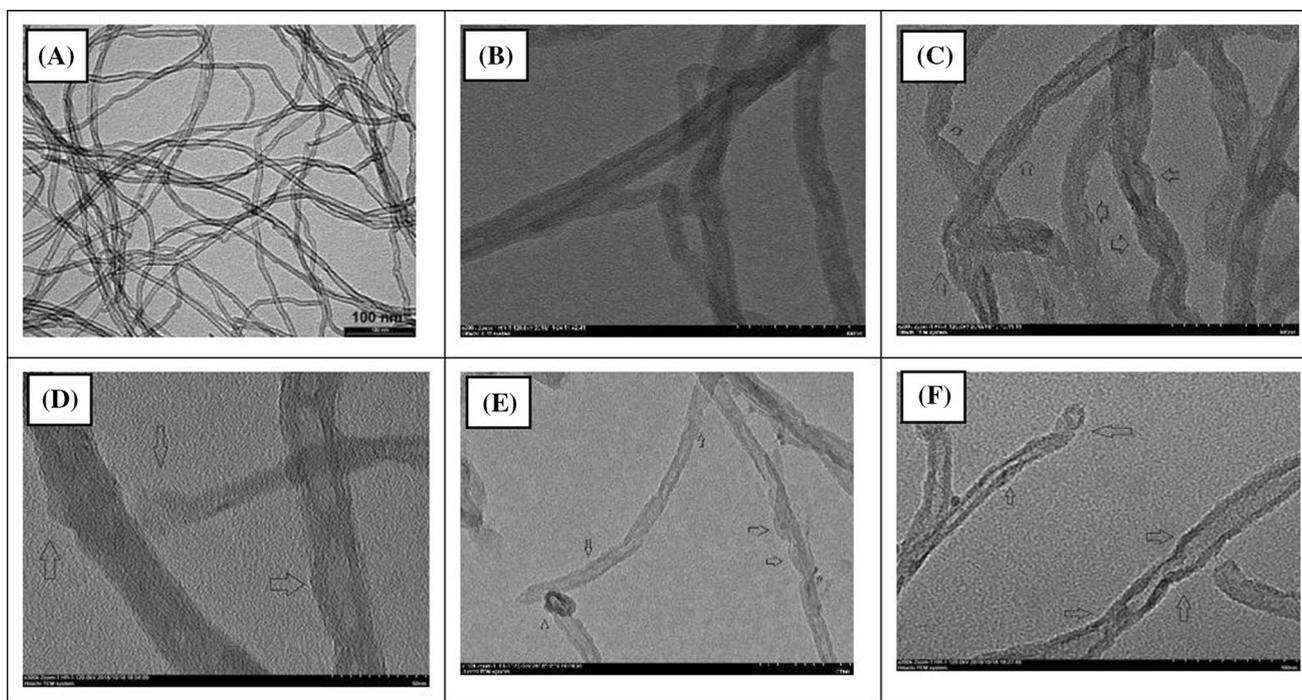


Fig. 4 The solubility test in water after 3 h ultrasonic bath for MWCNT (a), MWCNT–COOH (b), *D7* (c)

Table 2 TEM images of MWCNTs (100 nm) (a), MWCNTs–COOH ($\times 200.0$ k Zoom-1 HR-1 120.0 kV and 100 nm) (b), *D1* ($\times 200.0$ k Zoom-1 HR-1 120.0 kV and 100 nm) (c), *D5* ($\times 200.0$ k

Zoom-1 HR-1 120.0 kV and 100 nm) (d), *D6* ($\times 200.0$ k Zoom-1 HR-1 120.0 kV and 100 nm) (e), *D7* ($\times 200.0$ k Zoom-1 HR-1 120.0 kV and 100 nm) (f)



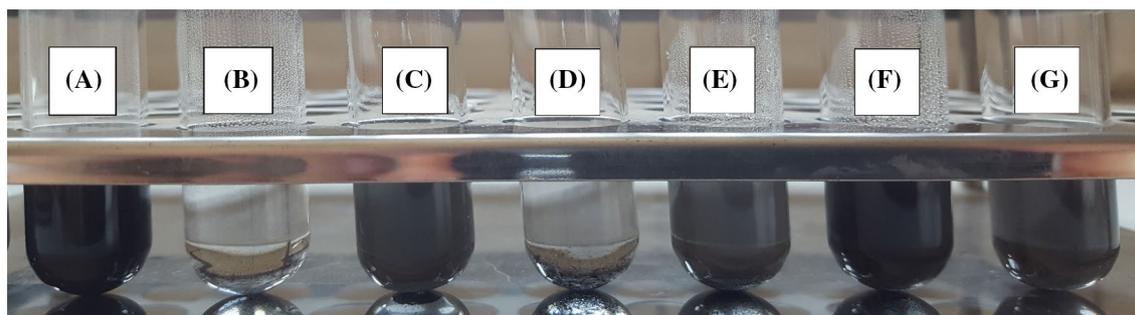


Fig. 5 The solubility of *D7* in different solvents after 3 h ultrasonic bath; in water (a), in THF (b), in ethanol (c), in diethyl ether (d), in dichloromethane (e), in chloroform (f), in DMSO (g)

ethylene glycol dithiol. Likewise, when TEM images of *D5*, *D6*, *D7* molecules are characterized, modification of CNTs with diethylene glycol, triethylene glycol, and tetraethylene glycol, respectively, led to thickening.

Furthermore, solubility experiments of the synthesized compounds play an important role in the characterization of the compounds. For this reason, MWCNTs, MWCNTs–COOH, and *D1–D7*-substituted MWCNTs were assayed. Figure 4 shows that multi-walled carbon nanotube is not soluble in water (A). However, it is readily dispersible in water after substitution.

In Fig. 5, water, ethanol, dichloromethane, chloroform and DMSO are the best solvents. However, the best solubility in tertiary solvents used in NMR studies was observed in DMSO. In addition, trichloroacetic acid (TCA) was added to DMSO in some studies to increase the solubility.

Conclusions

In this study, three dithiol-substituted MWCNTs and four glycol-substituted MWCNTs were successfully synthesized. For this purpose, commercially available MWCNTs were transformed into MWCNTs–COOH and MWCNTs–COCl, which are the precursor of target-substituted MWCNTs. These precursor compounds were reacted with ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol and ethylene glycol dithiol, diethylene glycol dithiol, triethylene glycol dithiol compounds which were linked to the acyl groups on MWCNTs by esterification–thioesterification reaction. These reactions were synthesized by applying conventional synthesis techniques and eco-friendly syntheses technic called green chemistry in the history of science. Solvent, temperature, use of the microwave synthesizer, and catalyst were examined to determine the optimum reaction conditions. The resulting substituted MWCNTs were characterized in terms of structure and morphology by FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, TGA and TEM techniques. The

synthesis of these compounds is essential. In metal enrichment studies, it is aimed to apply metal to environment and water technologies by selectively removing metal ions from metal mixtures. It is also aimed to investigate their use in cytotoxicology studies.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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