Polybenzoxazine/carbon nanotube nanocomposites as a polymeric sensing material for volatile organic compounds

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Abstract
The emissions of volatile organic compounds (VOCs) have hazardous effects on humans and the environment, and hence they should be detected and reduced. In this study, polybenzoxazine (PBZ) and amine-functionalized multiwall carbon nanotube (MWCNT) composites were synthesized as a sensor for VOCs. MWCNT were functionalized with two types of diamines, namely, 1,6-hexanediamine (HDA) and phenylenediamine (PDA). HDA or PDA treated MWCNTs were loaded into the benzoxazine matrix with different weight percentages (0.1, 0.3, 0.5, and 1%). FTIR analysis confirmed the chemical attachment of the two types of diamines on MWCNT. XRD diffraction and scanning electron microscopy (SEM) were used to investigate the nanofillers morphology and clarify the differences between pristine and amine-functionalized MWCNT. Thermal gravimetric analysis (TGA) was used to study the composites’ thermal stability and degradation behavior. It was found that, in contrast to neat PBZ, the major degradation temperature of PBZ/0.5%MWCNT-PDA nanocomposites were enhanced by 10%. The electrical conductivity of PBZ was $6.32 \times 10^{-9}$, which was enhanced to $6.11 \times 10^{-7}$ in the composites with 1% MWCNT-PDA. This material was tested as a VOCs sensor for methanol, acetone, and toluene and showed that PBZ/1% MWCNT-PDA composite responded to all the vapors.

Keywords Carbon nanotube · Polybenzoxazine · Electrical conductivity · Vapor sensor · Volatile organic compound

Introduction
Ignition of fuel in vehicles, chemical derivatives, industrial effluents, burning of coal, and fertilizers is considered a source that triggers environmental pollution. Many chemicals that have low boiling points and evaporate at room temperature are called volatile organic compounds (VOC) [1]. These (VOCs) severely affect the atmospheric environment and organic life; thus, VOCs should be detected rapidly in the air. When humans are exposed to VOCs, they will gain many infections and diseases [1]. Benzene, toluene, xylene, ethylbenzene (BTEX), and aldehydes are the major components of VOCs [2]. Moreover, VOCs resulting from the degradation and cracking of different types of polymers such as polypropylene (PP) (VOCs) affect severely the environment and can limit their uses [3].

Many materials have been reported for monitoring VOCs such as ZnO, methylammonium lead iodide perovskit and tungsten disulfide [4–6]. ZnO, a typical metal oxide semiconductor (MOS), has potential uses in the detection of hazardous gases because of its wide bandgap, n-type transport characteristic, and high electrical performance. Meanwhile, doping ZnO materials is an efficient approach to increase their sensing capability [7, 8].

Polymers play an important role when used as the sensing material. However, these polymeric sensing materials have great advantages such as working at low temperatures (less than 100 °C), and low cost [9]. Thin films are the main shape of polymeric sensors due to the high relation between their surface area and volume ratio as well as their active porous surface. These features augment the sensing process for the target gases. Polymeric sensors have many applications, such as optical sensors, mechanical sensors, and resistive sensors [9].

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Polymer composites exhibit superior properties over neat polymers, and thus, they have also been reported for monitoring VOCs [10]. Carbon nanotubes (CNTs) were utilized with different polymers as sensing composites [11–13]. Electrically conductive aerogels consisting of carbon nanotubes and cellulose were used before as vapor sensors. To test their vapor sensing capabilities, the electrical resistance of these aerogels was measured after exposure to vapors such as methanol, ethanol, toluene, and others. The results revealed that CNT–cellulose composite aerogels exhibit rapid response, high sensitivity, and good reproducibility to both polar and nonpolar vapors [14].

Polybenzoxazines (PBZ), as a kind of phenolics, are high-performance thermosets with a range of features and overcome some drawbacks of resole and novolac type phenolics. The easy processability of benzoxazine can explain development of benzoxazine chemistry. Benzoxazine have the simple preparation method of amine, phenol, and formaldehyde in one pot [15–20]. PBZ also has characteristics that are unusual for many resins, such as low water adsorption, which appears to contradict the phenolic nature of the resin, and limited or no shrinkage upon curing [21–23]. Hence, PBZ was recommended as promising polymer networks for different applications [24]. For instance, PBZ was utilized along with various materials in coating applications on steel [25–27]. High performance cashew nut shell carbon reinforced thiourea based biophenolic benzoxazine-epoxy composites were as biobased coating materials [28]. PBZ thermoset/clay nanocomposites were reported for metal coating applications [29]. Carbon nanotube was used as filler in PBZ matrix as a coating material [30]. When PBZ is reinforced with carbon derivatives such as aerogel [31], excellent marine antifouling [32], carbon balls [33], graphene oxide [34, 35], mesoporous silica [36], polyphosphazene microspheres [37], and metal oxides the conductivity is increased compared to neat polymers [38].

Nevertheless, it is hard to homogeneously disperse the CNTs in the PBZ polymer because the CNTs are insoluble in many solvents. In addition, because of the great surface energy and Van der Waals force, the CNTs tend to agglomerate into strict packages. The covalent connection between the reactive chemical groups of PBZ and CNTs, or modification of the CNT surface with functional groups that will further react with the polymer matrix, can be used to improve interactions between the PBZ and CNT nanofillers. Yang et al. synthesized a high dispersible pyrene-functionalized benzoxazine (Py-PBZ)/ single-walled carbon nanotube composite materials. The novel material showed high thermal stability after thermal curing [39]. Wang et al. [40] synthesized PFBZ-MWCNTs hybrid material that achieved good mechanical strength and high electrical conductivities ($7 \times 10^{-5}$ S/cm$^{-1}$) as a result of the good compatibility occurred between the matrix and filler.

This work focused on the preparation of nanocomposites from PBZ and amine-functionalized MWCNTs for sensing VOCs. MWCNTs were oxidized to provide the surface with carboxyl groups for the interactions with the diamines. Functionalization of carboxylated MWCNTs (MWCNTs-COOH) was carried out using two different diamines, namely; 1,6-hexanediame (HDA) and phenylenediamine (PDA). It was thought that the surface functionalization of MWCNTs by amines could increase the sensing properties of the composite. The characteristics of the composites were analyzed by different techniques, including FT-IR, XRD, SEM, thermal properties, and electrical conductivity. The PBZ/ PDA functionalized MWCNTs nanocomposite showed the highest electrical conductivity. Moreover, the new composite materials were tested as VOCs sensors for different solvents such as methanol, acetone, and toluene. This is the first time that such a novel composite was tested as a VOCs sensing material.

**Experimental**

**Materials**

Dodecyl amine, Bisphenol-A, and paraformaldehyde were obtained from Kishida Co., Japan. Ethyl acetate, nitric acid, and sulfuric acid were obtained from El-Naser Co., Egypt. 1,6-hexanediame (HDA), and phenylenediamine (PDA) were obtained from Fluka, Switzerland Multi-walled carbon nanotube with a diameter of 10–20 nm and length of 0.1–10 μm was acquired from EPRI (>90% pure). All reagents were obtained from Sigma Aldrich and used without further purifications.

**Preparation of amine functionalization MWCNTs**

Two consecutive steps were carried out for the functionalization of MWCNTs: oxidation followed by treatment with HDA or PDA. For oxidative processing, 3 g of pristine MWCNT was charged to a 150 mL water solution of nitric acid and sulfuric acid (5 M HNO$_3$ /5 M H$_2$SO$_4$) with a volume ratio of (1:3) in the refluxed system. The mixture was placed in a beaker and heated to 90 °C for 3 h. The mixture was then refined and cleaned many times with distilled water till the estimated pH becomes neutral. Finally, the carboxylated MWCNTs (MWCNTs-COOH) were dried in an oven at 90 °C for 4 h.

The process of amine functionalization of MWCNTs was carried out as follows. A specific weight of carboxylated MWCNTs (2.5 g) was introduced to the HDA solution (15 g HDA/35 g ethanol). The mixture was agitated for 14 h at 50 °C before being filtered. The membrane used in the filtration process was composed of a 0.2-m mixed cellulose
ester (MCE). The sample was then dehydrated at 80 °C for 3 h. The name of the obtained materials was abbreviated as MWCNT-HDA.

In the case of MWCNT-PDA, carboxylated MWCNTs (2.5 g) was introduced to PDA solution (15 g PDA/35 g ethanol). MWCNTs were functionalized with PDA according to a previous producer [39].

**Preparation of polybenzoxazine hybrid materials**

**Preparation of polybenzoxazine hybrid based on aliphatic amine (PBZ/ MWCNT-HDA)**

Benzoxazine was synthesized from dodecylamine (100 mmol), Bisphenol A (50 mmol), and paraformaldehyde (200 mmol) solventless method according to reported work [20]. After that 0.1% of MWCNT-HDA was added to the benzoxazine monomer. The prepared mixture was sonicated for 30 min. The hybrid material was poured into a Petri dish and left at 120 °C for 2 h. The complete polymerization was done at 140, 160, 180, 200, and 220 °C for 1 h. The preparations were repeated starting with different weight % of MWCNT-HDA (0.3, 0.5, 1%).

**Preparation of polybenzoxazine hybrid based on aromatic amine (PBZ/ MWCNT-PDA)**

Nanocomposites of polybenzoxazine with MWCNT-PDA were synthesized following the same procedure used for preparing (PBZ/ MWCNT-HDA).

**Preparation of sensing sample**

To test the selection of MWCNT-PDA concentration in the PBZ matrix for developing an efficient sensor, amounts from the solvent with varying concentrations for each component were collected.

From a sensing standpoint, the findings of gas sensing for these samples revealed that the percolation theory agrees with the concentricity of nanotubes [41]. The sensor was placed in the vapor cell and subjected to 100 ppm of solvents. The gas combination was created, and the air was used to make the gas in low concentration and change the amount of solvent in the vapor cell to change the concentration of solvent. A micro-pipette was used to inject a specific amount of solvent into the unit for vapor detection. In the unit detecting vapor, the sensor was exposed to the solvent vapor after being completely mixed with the diluting gas (in. air). The resistance of the sensor began to increase because of exposure, and then at a constant value of resistance, the sensor was removed to recuperate in the open area. A 6517 Keithley Source meter was used to test the conductivity and responsiveness of the MWCNT-PDA/PBZ nanocomposite films in the presence of solvent fumes [41].

**Characterization**

The Perkin Elmer-1430 was used to perform FTIR analysis in the wavenumber range of 4000–400 cm⁻¹. Thermogravimetric analysis (TGA) was performed using a Shimadzu TGA-50H using 8–10 gm samples at a heating rate of 10 °C/min⁻¹. The samples were heated from room temperature to 800 °C under a nitrogen atmosphere. The morphology of the nanocomposite was measured using X-ray diffraction (XRD) pattern on a contemporary PAN analytical diffract meter, the Xpert PRO model. At room temperature and under continuous operating circumstances, all the diffraction patterns were studied (40 kV & 40 m A). Shore D hardness of the test specimens was determined using an ASTM-D2240-05 durometer. All these experiments were carried out at room temperature (25 °C+1 °C). A Keithley electrometer type 6517 A was used to test the conductivity using a four-probe method. The pellets are put between two copper electrodes and linked to the Keithley electrometer’s two terminals.

**Result and discussion**

**FT-IR analysis**

The FT-IR spectra of MWCNT-COOH, MWCNT-HAD, and MWCNT-PAD is shown in Fig. 1. The FT-IR spectra of MWCNT-COOH were utilized to assess the impact of acid pretreatment on carbon nanotubes (Fig. 1a). The H-C-O band vibration is associated with the peak at 1380 cm⁻¹.
demonstrated by the identified top at 1740 cm\(^{-1}\). The carboxylic groups which loaded on the carbon nanotubes by the oxidation process, as seen by these bands. In addition to providing the surface with carboxyl groups, the acid pretreatment was reported to disturb the hexagonal shape of MWCNTs making it easier to functionalize nanotubes with amines [40].

The peaks occurring at 1052 and 1083 cm\(^{-1}\) in MWCNT-HDA and MWCNT-PDA spectra (Fig. 1b and c, respectively) are attributed to the C–N stretching vibration peak. In addition, the bands at 1457 and 1453 cm\(^{-1}\) peaks are related to the amide group (CO-NHR). Furthermore, the bands at 1516 and 1509 cm\(^{-1}\) showed the development of secondary amine groups on the MWCNT design [40].

The spectra of PBZ/0.3% MWCNT-HDA and PBZ/0.3% MWCNT-PDA are shown in Fig. 2a and b. The spectra exhibit the distinctive bands related to PBZ structure; peak at 1465 cm\(^{-1}\) corresponding to tri-substituted phenyl group, band at 1361 cm\(^{-1}\) corresponding to oxazine ring, peaks at 1225 and 1206 cm\(^{-1}\) corresponding to (C–O–C), bands at 1011 and 1143 cm\(^{-1}\) attributed to (Ar–O), and bands at 970 and 910 cm\(^{-1}\) corresponding to oxazine ring. These peaks assert the formation of functionalized PBZ-MWCNT nanocomposites.

**SEM analysis**

SEM micrographs of the WCNT-HDA, MWCNT-PAD, PBZ/0.1%MWCNT-HDA, PBZ/0.3%MWCNT-HDA, PBZ/0.1% MWCNT-PDA, and PBZ/0.3%MWCNT-PDA samples are shown in Fig. 3a–f, respectively. The image of modified MWCNT is entirely different from the others in the matrix, as the tube of MWCNT did not degrade when handled with an oxidative agent and amine-functionalized (Fig. 3a and b). This indicates that MWCNT has a high level...
Fig. 4 XRD patterns of a pristine CNT-HDA, 0.5% CNT-HDA/PBZ, and 1% CNT-HDA/PBZ; b pristine CNT-PDA, 0.5% CNT-PDA/PBZ, and 1% CNT-PDA/PBZ.
Fig. 5  TGA curves (a) and (c) and DTG curves (b) and (d) of neat PBZ and PBZ nanocomposites.
of stability and resistivity in acid and amine media. The acid pretreatment was reported to disturb the hexagonal shape of MWCNTs facilitating the functionalization of nanotubes with amines. The surface of PBZ/MWCNT-HDA/ (0.1% and 0.3%) showed great homogeneity and order of MWCNT in the polybenzoxazine resin (Fig. 3c and d). Figure 3e and f showed that the PAD does not cover the MWCNT surface in the PBZ/0.1% and 0.3% MWCNT-PDA samples.

**X-ray diffraction**

Figure 4a and b show the XRD pattern of pristine MWCNT-HDA and PBZ composites. Figure 4a shows that MWCNT-HDA differs from the two other samples due to the development of a peak at 2θ = 18.5 and 24°, suggesting that the HDA reagent is present in the filler. This peak appeared at 2θ = 24 and 18 degrees for 0.5 percent MWCNT-HDA and 1%MWCNT-HDA, respectively [35].

The remarkable variation in sites of peak indicates that MWCNT-HDA penetrates the benzoxazine matrix extremely well and exfoliates the structures. Figure 4b shows the XRD patterns of MWCNT-PAD, 0.5%MWCNT-PDA, and 1% MWCNT-PDA. Because of the extreme PDA surfactant, two peaks at 2θ = 18.5 and 24° appeared. However, in hybrid materials, 0.5%MWCNT-PDA and 1% MWCNT-PDA had a peak at 2θ = 18° for both ratios which corresponding to the PAD reagent [40].

**Thermal properties of nanocomposites**

Thermogravimetric (TGA) curves a & c and their derivatives DTG b & d of virgin PBZ, MWCNT-HDA/PBZ, and MWCNT-PDA/PBZ nanocomposites are shown in Fig. 5a–d. Under nitrogen conditions, there are usually three stages of weight loss. The first weight loss was due to the volatilization of amines (under 300 °C) and phenolic moieties (300–400 °C) which were assigned to the initial weight reduction phases. The second weight loss was identified with the degradation of the char (over 400 °C) [42]. In contrast, the thermal stability of the PBZ/MWCNT hybrid complexes was higher than those of the pure PBZ due to the strong π-π interactions between PBZ and the MWCNT [43].

However, in the derivative of TGA curves, MWCNT-HDA/PBZ and MWCNT-PDA/PBZ with higher thermal stability only displayed two overlapping peaks, indicating that bisphenol-A backbone degradation occurs shortly after Mannich bridge cleavage. Because of the increased thermal stability of bridge structures, the initial peak was delayed until 350 °C [44].

Because of its greater aromaticity, the MWCNT-PDA/PBZ has better thermal stability than the MWCNT-HDA/PBZ. It was observed that adding MWCNTs to MWCNT-PDA/PBZ and MWCNT-HDA/PBZ enhanced their thermal characteristics. Indeed, adding MWCNTs causes a positive shift to higher temperatures in the decomposition temperatures of PBZ/0.5% MWCNT-HDA (T1%,) and (T10%), which were (226 and 336 °C, respectively. In contrast to neat PBZ, the major degradation temperature of PBZ/0.5% MWCNT-PDA nanocomposites was enhanced by 10%. In addition, it was seen that MWCNTs were reduction the rate of decomposition of the nanocomposites if compared with neat PBZ. The char residue demonstrated more significance especially with the sample of PBZ/ MWCNT-PDA resins due to the aromatic structures.

**Nanocomposites’ electrical conductivity**

All the prepared materials exhibited a nanostructured solid network (specific surface areas). These features make them ideal candidates for portable chemical sensors [14]. It has previously been established that rheological percolation which requires particle contact, occurs at a very low concentration of MWCNT in PBZ/MWCNT-HDA and BZ/MWCNT-PDA hybrids. The excellent dispersion of MWCNTs throughout the matrices was further shown by SEM studies (shown in Fig. 5). Electrical measurements of MWCNT filled with polybenzoxazine matrices agree well with these findings. From Fig. 6a and b, it was found that even with an MWCNT concentration of 0.1 wt%, substantial improvements in electrical conductivity were achieved which reached 1.04 × 10⁻⁸ Ω⁻¹ cm⁻¹. Increasing the quantities of
MWCNT only marginally enhanced the electrical conductivity. This indicates the presence of a percolation threshold at lower MWCNT concentrations (0.1 wt%) [42]. In comparison to MWCNT-HDA nanocomposites, MWCNT-PDA based nanocomposites have a somewhat higher electrical conductivity of $6.32 \times 10^{-9}$ and $6.11 \times 10^{-8} \ \Omega^{-1} \ \text{cm}^{-1}$. The differentiation of morphologies seen for nanocomposites might be a possible clarification based on our experimental data. To better clarify these results, another presupposition might be offered. It was also linked to a larger amount of crosslinking in the PBZ network, resulting in a higher and more positive immobilization of the MWCNT in the polymer framework to aid electron transport.

**Sensing properties**

The prepared sample (1%MWCNT-PDA) was tested as a sensing material for methanol, acetone, and toluene. This method was used with all solvents. The gas combination was created, and the air was used to make the gas in low concentration and changing the amount of methanol in the vapor cell to change the concentration of methanol. The resistance of the sensor began to increase as a result of exposure, and then at a constant value of resistance, the sensor was removed to recuperate in the open area. Source meter was used to test the conductivity and responsiveness of the MWCNT-PDA/PBZ nanocomposite films in the presence of methanol fumes [41].

PBZ/ 1%MWCNT-PDA at the percolation threshold was selected as sensing material for VOC vapor due to its good electrical performance resulted from the doping content of MWCNT which was functionalized by PDA. This functionalization raises the concentration of sp2 linked carbon atoms on the nanotube surface, which can adsorb VOCs [41]. Figure 7a–c showed the sensing behavior of PBZ/1%MWCNT-PDA towards toluene, acetone, and methanol. It was found that the electrical conductivity of films changes with temperature which can be attributed to the increment in the number of electron pathways of aromatic structures [45]. It was observed that there are changes in values of electrical conductivities of PBZ/MWCNT-PDA films which exposer to VOC. This

![Fig. 7 Conductivity of 1%CNT-PDA/PBZ nanocomposites sensor for a Toluene, b Methanol and c Acetone](https://example.com/figure7.png)
is attributed to little damage to the CNT surface [41]. PBZ/MWCNT-PDA sensor showed some differences in case acetone and methanol that appears clearly in Fig. 6. The temperature has a severe effect on the movement of electrons which is responsible for electrical conductivity. Therefore, the increase of temperature caused a decrease in values of conductivity that attributed to a change in the physical properties of these solvents. However, in the case of toluene (Fig. 6a) high values of conductivity can be attained at high temperatures up to 120 °C.

**Conclusion**

In this study polybenzoxazine/modified carbon nanotubes were prepared for sensing VOCs. Functionalization of carbon nanotubes with amines after acidic pretreatment enhanced the compatibility with benzoxazine matrix. The nanocomposites of polybenzoxazine and modified carbon nanotube with aromatic and aliphatic amine were evaluated with XRD, SEM, thermogravimetric analysis, and electrical conductivity. The nanomaterial based on carbon nanotube functionalized with aromatic diamine (p-phenylenediamine) has higher thermal stability and electrical conductivity than the other functionalized with aliphatic diamine (1,6 hexyl diamine). The composite based on 1% polybenzoxazine and phenylenediamine-functionalized carbon nanotube (PBZ/1%MWCNT-PDA) showed a higher conductivity than the neat resin and other composites based on HDA. Accordingly, the PBZ/1%MWCNT-PDA sample was tested as a sensing sheet for VOCs including methanol, acetone, and toluene. This sample introduced a good sensing for these solvents with high sensitivity and a long-life sheet used in most environmental conditions.

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**Declarations**

**Conflict of interest** The authors declare that they have no conflict of interest.

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