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In situ polymerization synthesis and characterization of single wall nanotubes/poly(vinyl)triazole nanocomposites

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Abstract
The synthesis of single wall nanotubes (SWNT)/poly(vinyl)triazole (PVTri) composites by in situ emulsion polymerization method and its chemical and physical properties were investigated throughout this work. The surface modification of the SWNT by nitric acid treatment and air oxidation has improved the dispersion of the SWNT in the PVTri matrix. The SWNT/PVTri composite is obtained by covalent bonding of the carboxyl terminated SWNTs to PVTri. The effect of covalent bond formation between PVTri and SWNT on the thermal and electrical properties of the composite is also studied. The spectroscopic, thermal, and microscopic analysis has confirmed the structure, homogeneity, and the morphology of surface functionalized SWNT and SWNT/PVTri composites. SWNT/PVTri composites showed enhanced chemical stability in many common solvents and high electrical conductivity.

Keywords
poly(vinyl)triazole, carbon nanotubes, in situ polymerization, nanocomposites, thermal properties, electrical properties

Introduction
Since their discovery¹ numerous potential applications have been attributed to carbon nanotubes due to their homogeneous surface properties such as gas storage at high pressure.²,³ One can notice that none of the preceding material has shown the combination of superior thermal, mechanical, and electronic properties ascribed to carbon nanotubes (CNT).⁴⁻⁶ These properties make nanotubes ideal for a wide range of applications, especially in the domain of fundamental sciences and composites sciences.⁷,⁸ The resulting characteristics of reinforced composites have motivated a large number of investigations. Single wall nanotubes (SWNTs) exhibit remarkable properties for nanoscale devices and composite materials.⁹⁻¹⁸ CNT/polymer nanocomposites hold the promise of delivering exceptional mechanical properties and multi-functional characteristics depending upon the properties of the added material.¹⁹ Most publications on CNT/composites report the polymer-based matrices. Regarding chemical and thermal stability and mechanical strength, a great variety of polymer substances, could be chosen for appropriate applications. These advantages open many ways for selecting suitable materials for the composites. Recently, the use of polymer matrices for embedding the CNT has received increasing attention as strategy for membrane development. The thin polymeric membrane is the main component of the membrane electrode assembly of the polymer electrolyte membrane fuel cells. Poly(vinyl)triazole (PVTri), which is known for its thermal and proton conducting properties, with other polymers were used for complex polymer electrolyte fabrication.²⁰

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There is no work reported in the literature on SWNT/PVTri composites for membrane application. The challenge in the successful applications of such composite systems is hinged upon sufficiently well-dispersed SWNTs combined with good adhesion with the host matrix.\textsuperscript{21–23} The dispersion of SWNTs in polymer matrices without dilapidating p-p connections or lengths can exploit the merits of SWNTs. However, neat SWNTs are not dispersible in solvents or polymer matrices, because threads of SWNTs have strong interactions, that is p-p interactions or van der Waals forces. Therefore, the sidewalls of SWNTs need to be modified chemically or physically to improve dispersity or solubility in solvents or polymers.\textsuperscript{24–28} Both physical and chemical methods activate the CNTs at the open ends via the formation of functional groups. Different chemical functionalization techniques have been devised for enhancing the interfacial adhesion between the nanotubes and the matrix.\textsuperscript{29} One of these is the oxidative process utilizing strong acids such as HNO\textsubscript{3} or H\textsubscript{2}SO\textsubscript{4} in which carboxylic acid and hydroxyl moieties are created on nanotubes. These moieties at the defect sites can be used to link polymeric functional groups. This leads to an improvement in compatibility between the functional CNTs and polymer matrices of the nanocomposites.\textsuperscript{30,31} The silanization of functionalized nanotubes is another preferred method used to enhance the interfacial adhesion between nanotubes and the matrix. The silane coupling agents most commonly used are organosilanes. The organosilanes are represented by the following formula:\textsuperscript{32}

\[
R - (\text{CH}_2)_n - \text{Si} (\text{OR'})_3
\]

where \(n = 0 \cdots 3\), OR' is the hydrolyzable alkoxy group, and R is the functional organic group. R functional group of silane coupling agent reacts readily with the hydroxyl groups on the carbon nanotube surface produced through oxidation process.\textsuperscript{33}

There have been a number of papers concerning the attachment of synthetic polymers onto CNTs, which might be used in the development of materials with new optical, magnetic, and electrical properties.\textsuperscript{34–37} However, to consolidate covalent functionalized CNT/heterocyclic polymer through simple free radical polymerization is hardly reported and papers on SWNT/PVTri composites are not reported. The aim of this work is to study CNT dispersion in a polymer matrix, which is known and investigated as proton transport facilitator for membranes for high temperature fuel cell applications. Chemically functionalized SWNT/PVTri composites were produced using an in situ process. The functionalized SWNT and the final composites have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier transform infrared (FTIR) spectroscopy. Differential scanning calorimetry (DSC) technique was used for the thermal analysis of the PVTri and SWNT/PVTri composites. Moreover, the electrical measurement of the composite material is determined at room temperature. The improved physical and chemical behavior of the as synthesized material was discussed in the light of the structural and morphological characterization results.

**Experimental session**

**SWNT synthesis**

The chemical vapor deposition method was used for the synthesis of SWNT materials. The flow of the reducing (H\textsubscript{2}), inert (He), and reactive (C\textsubscript{2}H\textsubscript{2}) gases was controlled by electronic mass flow controllers (Brooks Smart Mass Flow- 0.5 V/dc). A quartz tube was inserted coaxially inside the high temperature tubular furnace (Protherm PTF 12/38/450), which is equipped with a Honeywell 1010 temperature controller. The crucible bearing the MgO impregnated by the catalysts was fabricated from quartz and was placed inside the quartz tube in a position that corresponds to the center of the furnace. Prior to the CVD synthesis, the support containing the catalyst was prepared by impregnation of MgO (Sigma) in an aqueous 1% Ni(NO\textsubscript{3})\textsubscript{2}6H\textsubscript{2}O solution for 24 h and leave it to dry in an oven at 373 K. The dried support was further purged with He at room temperature in the tubular furnace. The deposited nickel (II) ions were reduced to metallic nickel nanoparticles under a He/H\textsubscript{2} flow of 60 mL/min (H\textsubscript{2} 99.998%), at 853 K for 3 h. Then the furnace temperature was increased at a rate of 10°C/min up to 973 K and CVD took place for 20 min by replacing H\textsubscript{2} with C\textsubscript{2}H\textsubscript{2} (20 mL/min C\textsubscript{2}H\textsubscript{2} %99.8, 300 mL/min He).

The temperature was increased at a rate of 10°C/min and CVD took place isothermally at 1073 K for 3 h under C\textsubscript{2}H\textsubscript{2}/He flow (10 mL/min C\textsubscript{2}H\textsubscript{2} 600 mL/min He). Then the temperature of the tubular furnace was decreased to room temperature under He flow.

**Chemical modification of SWNT**

SWNT were sonicated in a mixture of concentrated sulfuric and nitric acid (3:1 by volume) for 24 h at 200 rpm and at 40°C. The obtained carboxylterminated SWNT (0.5 g) were then dispersed into 25 mL anhydrous ethanol. 3-(trimethoxy)-propylmethacrylate-silane (KH-570) (0.5 mmol), diluted in 25 mL anhydrous ethanol, was added dropwise into the mentioned solution for 10 h. The resulting mixture was maintained for 36 h at the same temperature and mixing speed, and
the chemical modifications of SWNT were realized. After centrifuged at 5000 rpm for 60 min, the formed chemical modifications were dispersed in anhydrous ethanol, repeated five times. Dried for 48 h at 40°C, chemical modifications of SWNT were finally obtained.

**In situ polymerization of PVTri with SWNT**

Chemical modified SWNT synthesized before (0.12 g, 10 mmol), lauryl sodium sulfate (0.05 g, 1.4 mmol), and sodium bicarbonate (0.25 g, 3.0 mmol), were added into 150 mL water under stirring and mixed uniformly at 40°C. 1-Viny-1,2,4-triazole (2.85 g, 30 mmol) was then added into the solution under the nitrogen atmosphere and was pre-emulsified for 12 h. Then ammonium persulfate (0.15 g, 0.7 mmol) dissolved in 20 mL water was added dropwise into the mixture flask and kept for 10 h at 80°C (notice: ammonium persulfate is an explosive compound). Monomers and surfactants in the suspension were then removed under centrifugation at 3000 rpm to give stable SWNT/PVTri composite. The obtained SWNT/PVTri composite was centrifuged several times, washed with 50 mL methanol to remove the excess free polyvinyltriazole, monomer, and surfactants completely. After this, they were annealed at 65°C in vacuum for 24 h.

**Characterization techniques**

The structure of PVTri and SWNT/PVTri materials were characterized by Infrared spectroscopy and XRD. Infrared spectra were recorded on a Bruker Tensor 27 spectrophotometer in the range 4000–400 cm\(^{-1}\), with a 2 cm\(^{-1}\) resolution over 30 scans, using Ge ATR. X-ray diffraction diagrams were obtained on a Bruker AXS Diffractometer D8, rotating anode X-ray generator working at 40 kV, 40 mA, with CuK\(\alpha\) (\(\lambda = 1.54\) Å) monochromatic radiation device. The powdered samples were pressed onto suitable holders. The scanning range of 20 was from 20° to 90°. Textural analysis of the SWNT/PVTri composite was characterized using a Philips XL30 SFEG SEM and Philips 200KV Field Emission TEM. DSC measurements were carried out on a NETZSCH DSC 404C under argon atmosphere and heating curves were recorded at a rate of 10°C/min until 500°C. The sample size of the PVTri polymer was 5.80 mg and the sample size of the SWNT/PVTri composite was 1.30 mg.

**Electrical measurements**

The dielectrical measurements were performed between 20 Hz and 1 MHz at room temperature with LCR Meter (Agilent 4284 A). A picoampermeter (Keithley 6487) instrument was employed for current-voltage measurements.

The samples were cold-pressed into disks that were 8 mm in diameter, 0.99 mm and 1.21 mm in thickness for dielectrical measurements and I-V measurements, respectively. The MIM (metal–insulator–metal) structure is created by placing the pressed samples between two disk-shaped electrodes.

**Results and discussions**

**Preparation and characterization of SWNT/PVTri composite**

Modified CNTs can enhance the adhesion between CNTs and polymer matrix. Acid modification is one of the most common methods of CNT modification. CNT can be modified by refluxing with nitric acid or a mixture of nitric acid and sulfuric acid. Carboxyl and hydroxyl functional groups are formed on the CNT surface during acid modification. Acid-modified MWCNT can be modified with silane coupling agent. The silane will react with the hydroxyl groups (—OH) on the surface of SWNTs. In the present study, 3-(trimethoxy)-propylmethacrylate-silane (KH-570) was used as the silane agent to treat SWNTs. SWNTs was functionalized by oxidation with a mixture of concentrated nitric acid and sulfuric acid. The functionalized SWNTs were chemically modified by covalent bonding of the 3-(trimethoxy)-propylmethacrylate-silane molecule with oxidized carbon nanotubes, in an aim to improve their compatibility with PVTri for application in SWNT/PVTri composite.

We report on a procedure that the reactions for preparation of SWNT/PVTri of chemical modification and emulsion polymerization were carried out in Figure 1. The methoxy groups of KH-570 are hydrolyzed with hydroxyl groups in the surface of SWNT under the influence of base. Chemical-bond linkage is formed between the KH-570 and SWNT and the KH-570 is chemically bonded to the SWNT surface. Methacrylate group of the KH-570 is reacted with C=C group of 1-vinyl-1,2,4-triazole monomer via free radical polymerization. Finally, SWNT/PVTri composite is formed. The separation of the free monomer, polyvinyltriazole, and surfactant from the SWNT/PVTri composite was achieved by centrifugation several times to remove the nonreactive compounds.

The infrared spectra of the chemical groups on surface of SWNT were investigated by FTIR spectra shown in Figure 2. After H\(_2\)SO\(_4\)/HNO\(_3\) treatment SWNT show an IR peak at 1705 cm\(^{-1}\) (Figure 2(a)), indicative of the C=O stretching vibration of carboxylic acid groups. The broad peak between 3200 and 3600 cm\(^{-1}\) is assigned to the O–H stretches, while the
peak at 1565 cm\(^{-1}\) is attributed to the SWNT C=C stretching mode associated with sidewall attachment.\(^{43}\) SWNT/PVTri composite showed a new absorption band at 1504 cm\(^{-1}\) (Figure 2(b)), associating with the C=N stretching band, while pristine PVTri\(^{44}\) showed one absorption weak band at 1508 cm\(^{-1}\) (Figure 2(c)). Two another bands at 1268 cm\(^{-1}\) 949 cm\(^{-1}\) were assigned to the ring vibration (N-N stretching) and the nitrogenous penta-heterocyclic compound stretching bands from SWNT/PVTri composite, respectively (Figure 2(b)). In PVTri (Figure 2(c)), the triazole units show several medium or strong peaks in the 1430–1650 cm\(^{-1}\) range due to ring stretching (C=N, C=N) vibrations.

The XRD patterns of the functionalized SWNT, SWNT/PVTri composite and PVTri polymer are shown in Figure 3. The peaks occurring at 20 = 26.04°, and 42.661°, and 51.839° can be attributed to the graphitic structure of SWNT with (0 0 2), (1 0 1), and (0 0 4) graphitic planes. The peaks appeared at 34.400°, 35.698°, and 61.098° correspond to NO\(_2\)-C bond formed on the SWNT surface after acid reaction (Figure 3(a)). The PVTri sample is not a crystalline material and it shows only one large peak centered at around 22° (Figure 3(b)). The comparison between the XRD powder pattern of SWNT/PVTri composite and SWNT shows that nitrogen oxide peaks were disappeared. The peaks of SWNT sample appearing at 26.041° and 42.661° are shifted to 26.460°and 42.518°, respectively, on the SWNT/PVTri XRD spectra (Figure 3(c)). New peaks have appeared on composite spectra such as the peak situated at 20 49.258°, which is assigned to carbon nitride bond. The crystallization degree of the polymer has increased
with the introduction of the SWNT. The combination of structural and morphologic characterizations shows that the composite SWNT/PVTri is obtained.

**Morphological properties**

TEM images (Figure 4(a)) show SWNT bundles, which have 20–40 nm of diameter and several microns of length. The black dots may be the catalyst particles covered by graphite layer. The nickel particles appear as dark spots dispersed in the MgO support (light grey) with a wide size distribution. The particles appear spherical in shape. Figure 4(b) presents a SWNT bundle covered by a thin layer of PVTri, as shown on the little square (Figure 4(b)).

The surface morphology of the materials was also analyzed by SEM. Figure 5(a) shows the SWNT/PVTri composite texture. The tubes covered by the polymer appear like the wires weaved between them. They have formed a SWNT/PVTri tube network. The tubes are well-dispersed in the polymer matrix. Figure 5(b) presents the SWNT/PVTri composite at a magnification of 500 nm. Polymer covered tubes have connected the polymer aggregates between them.

![XRD powder pattern of: (a) functionalized SWNT, (b) PVTri, and (c) SWNT/PVTri composite.](image-url)
Solubility properties

Figure 6 shows the solubility of SWNT and SWNT/PVTri in ethanol, dimethyl formamide (DMF), and chloroform. The obtained polymer attached SWNT samples can dissolve in common organic solvents such as ethanol, DMF, and chloroform. When they were dispersed in these solvents by sonication, a well-dispersed suspension formed and remained stable for days. The stability of the dispersion for
2 weeks after ultrasonication of samples is compared. The SWNT has presented poor dispersion in ethanol (Figure 6(a)), DMF (Figure 6(c)), and chloroform (Figure 6(e)). The SWNT/PVTri composites were dissolved well in ethanol (Figure 6(b)), DMF (Figure 6(d)), and chloroform (Figure 6(f)) and formed homogenous solution, which was very stable even after prolonged standing for 3 weeks. Neither sedimentation nor aggregation of nanotube bundles was observed. The obvious improvement of the solubility for the obtained samples proved that the in situ reaction was successful, and the PVTri chains did covalently link to the surface of SWNT.

**Thermal analysis**

The glass transition temperature ($T_g$) of the PVTri pure was measured at TUBITAK center (Turkey) as 165°C. The incorporation of the tubes in polymer has increased the $T_g$ value by showing that a strong interaction was formed between the tubes and the matrix. The DSC thermal analysis method was performed on PVTri and SWNT/PVTri composite in argon atmosphere until 500°C. The DSC thermograms of PVTri and SWNT/PVTri are presented in Figure 7(a) and (b), respectively. The curves are very different from each other. The glass transition temperature of PVTri was located around 165°C, whereas the $T_g$ value of SWNT/PVTri composite was measured at a higher temperature, which is situated roughly at 300°C. DSC results illustrate that SWNT are strongly bonded to polymer PVTri as seen on SEM and TEM images and on structural analysis results.

**Electrical properties**

I-V characteristics of pure PVTri have been studied up to 450 V, however current could not be measured in the polymer matrix. The sample has behaved like a good insulator. Figure 8 shows the graphic of dielectric constant vs. frequency of pure PVTri. As seen from Figure 8, the pure PVTri has exhibited a dielectric constant higher than 8 at low frequencies.

Figure 9 shows the current density vs. electrical field of SWNT/PVTri sample at room temperature. The J-E curve of the composite has showed ohmic behavior. The conductivity of SWNT/PVTri composite was obtained as 1.25 S/m.

By using in situ polymerization method PVTri are attached to SWNT. Although PVTri is an
insulator, the composite of SWNT/PVTri has shown ohmic conductive behavior. This behavior is due to SWNT which created conductive transmission lines without directly contacting with each other in the medium. This high degree of conductivity has indicated that the structure of composite does not only consist of physical contact between SWNT and PVTri, but also chemical bonds were created between PVTri and SWNT. This result confirms the morphologic, thermal, and structural characterization results.

Conclusion

This work permits to synthesize a composite material by using SWNT having exceptional physical and chemical properties and a polymer which is a proton conductor facilitator having an important affinity to metals. The SWNT/PVTri composite was successfully obtained via the methods of chemical modification and emulsion polymerization. The thermal analysis, microstructure, and morphology of aggregated structures of obtained SWNT covalently bonded by PVTri were studied. The formation of a homogeneous material is confirmed by FTIR, SEM, TEM, and DSC characterization methods. The DSC analysis shows the high thermal stability of the resulting composite material. Due to a formation of a nanotube network in polymer media, the resultant composite material shows high electrical conductivity behavior. The development of polymer electrolyte membrane fuel cells is one of the striking alternative energy resource systems that can be used in many applications such as electric vehicles, mobile phones, and on-site power generators. This work could thus constitute a beginning for future investigations on CNT-based bipolar plates for fuel cell application.

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