



## Multi-Walled Carbon Nanotube Reinforced Polyimide Composites

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**Abstract :** Polyimides have a wide range of uses such as aeronautical applications of fuel cells, optics and electronic materials industry due to their outstanding thermal, mechanical and chemical properties. In this study, it was aimed to prepare composite polyimide films with amine-tethered multi-walled-carbon nanotubes (MWCNT). Firstly, to produce amine functional groups onto the surface of MWCNTs, MWCNTs were reacted with H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>, thionyl chloride and ethylenediamine. Then polyamic acid solution was prepared from 3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and, 4'-oxydianiline (ODA). The functionalized carbon nanotube was added to the PAA solutions with certain amounts (1, 3, 4, 5 and 6 wt. % followed by stepwise thermal imidization. The thermal stability of the composite polyimide films were enhanced with addition of modified-carbon nanotube due to covalent interaction between polyimide based matrix and modified-carbon nanotube as a result of the imidization reaction. The addition of MWCNT increased the T<sub>g</sub> of the BTDA-ODA-6% MWCNTs polyimide film from 275 to 304 °C with respect to the BTDA-ODA polyimide film. In addition, the mechanical properties of the films were improved. While the modulus of BTDA-ODA film was found as 743 MPa, with the introduction of MWCNT the modulus of BTDA-ODA-6% MWCNTs was increased up to 1119 MPa.

**Keywords:** Polyimide, carbon nanotube, nanocomposite.

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## INTRODUCTION

Multi-walled and single-walled carbon nanotubes (MWCNTs and SWCNTs) have superior chemical, electrical, and thermal performance (1). Despite their extraordinary properties, dispersion of carbon nanotubes into a polymer matrix is limited because of their hydrophobic character. To overcome this problem, the covalent and non-covalent chemical modifications of carbon nanotubes should be carried out (2).

Covalent chemical modification of CNTs allows a fine dispersion within a polymer matrix. Generally, the carboxylic acid or hydroxyl groups are created on the CNT surface by treatment with sulfuric and nitric acid. The functional groups make further reactions of carbon nanotubes possible (3,4).

Polyimides are a class of organic compounds that have received much attention owing to their excellent properties, such as superior thermal stability, mechanical properties and good chemical resistance (5). In addition, the composites can be used in advanced microelectronics and aerospace technologies due to their flexibility and radiation resistant properties (6). In recent years, a great amount of research has focused on the carbon nanotube/polyimide nanocomposites, to improve the properties of the polyimides. Incorporation of carbon nanotubes in polyimides has been shown to remarkably improve the mechanical and thermal properties of the resulting composites. Park *et al.* prepared carbon nanotube containing polyimide composites by in situ polymerization (7). Zhu *et al.* investigated the effect of carbon nanotubes on mechanical and electrical properties of the composites. The results showed that the composites containing carbon nanotubes had a higher tensile strength with good electrical properties (8). So *et al.* investigated the effect of carbon nanotubes on the morphological, mechanical, and electrical properties of MWNT-reinforced polyimides (9).

Non-covalent and covalent surface modifications have been used for functionalization of CNTs. Although, covalent surface modification can be better controlled to produce more stable nanomaterials (10). Commonly, the first step in this method is to incorporate carboxylic acid groups. In a second step, the carboxylic acid groups activated with thionyl chloride ( $\text{SOCl}_2$ ) and then covalently attaching any molecule that contains a free-amine group such as ethylene diamine (11-14).

In this study, we focused on the modification of MWCNTs and the preparation of functionalized MWCNTs/polyimide composite films. Amine-tethered MWCNTs (MWCNTs-NH<sub>2</sub>) were prepared by three step reactions. Firstly, MWCNTs were oxidized by a mixture

of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, to produce surface carboxyl groups. Then, the COOH groups of MWCNTs were substituted with thionyl chloride and the resulting product was further reacted with ethylenediamine. Polyamic acid solutions were prepared by an *in situ* polymerization reaction from 3,3',4,4'-benzophenone tetracarboxylic dianhydride" (BTDA), 4,4'-oxydianiline (ODA) and various ratios of MWCNTs-NH<sub>2</sub> and followed by thermal imidization. The prepared composite films were characterized by scanning electron microscopy (SEM), Fourier transform-infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA), differential scanning calorimeter (DSC), and tensile and elongation tests.

## MATERIALS AND METHODS

### Reagents and Apparatus

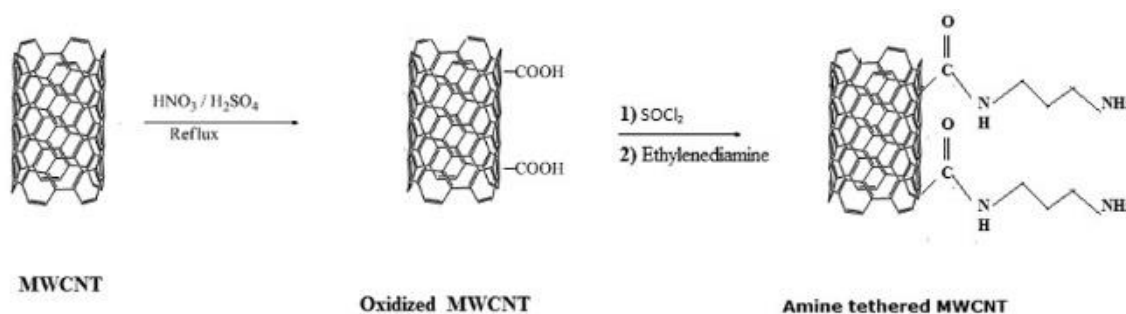
Carbon nanotube (multi-walled, purity 95%, diameter: 10–15 nm, length: 0.1–10 µm, density: 1.7–2.1 g/cm<sup>3</sup>) was purchased from Alfa Aesar. 4,4'-oxydianiline (ODA), thionyl chloride (SOCl<sub>2</sub>) (≥99%), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), (3-aminopropyl)trimethoxysilane (97%), ethylenediamine and dimethylacetamide (DMAc) were purchased from Sigma Chem. Co. (St Louis, MO).

The structures of MWCNTs, in oxidized and amine-tethered forms, as well as polyamic acid and composite polyimides were investigated by Perkin Elmer ATR-FTIR spectrometer. The spectra were recorded in the frequency range of 4000-380 cm<sup>-1</sup>. The morphology of the composite polyimide films were investigated by scanning electron microscopy (SEM) on Phillips XL 30 ESEM-FEG/EDAX. Thermogravimetric analysis (TGA) was carried out on Perkin-Elmer Thermogravimetric analyzer STA 6000 at heating rate of 10 °C/min from 30 to 750 °C in inert atmosphere. Differential scanning calorimeter studies were carried out on Pyris Diamond DSC (Perkin Elmer at a heating rate of 5 °C/min under N<sub>2</sub>). Mechanical properties of the composite films were analyzed by standard tensile stress-strain tests using a Zwick Z010 universal tensile tester (Istanbul, Turkey).

### Synthesis of amine-tethered MWCNTs (MWCNT-NH<sub>2</sub>)

The modification of MWNCTs was carried out in three steps. At first, 1 g MWCNTs was refluxed in a mixture of sulfuric acid/nitric acid (3:1 v/v) at 120 °C for 4 h. The mixture was diluted with deionized water (2 L) and filtered. The oxidized product was dried at 50 °C. Then, the COOH groups of the oxidized MWCNTs were converted to acyl chloride (-COCl) groups with thionyl chloride at 70 °C for 24 h. The unreacted thionyl chloride was removed by heating at 80 °C. The product was dried in vacuum. Finally, 0.5 g of acyl

chloride functionalized MWCNTs was refluxed at 90 °C for 24 h with ethylene diamine to prepare amine-tethered MWCNTs (15). The reaction pathway is shown in Figure 1.



**Figure 1:** Modification of multi-walled carbon nanotube.

### Preparation of BTDA-ODA Polyamic acid Solution

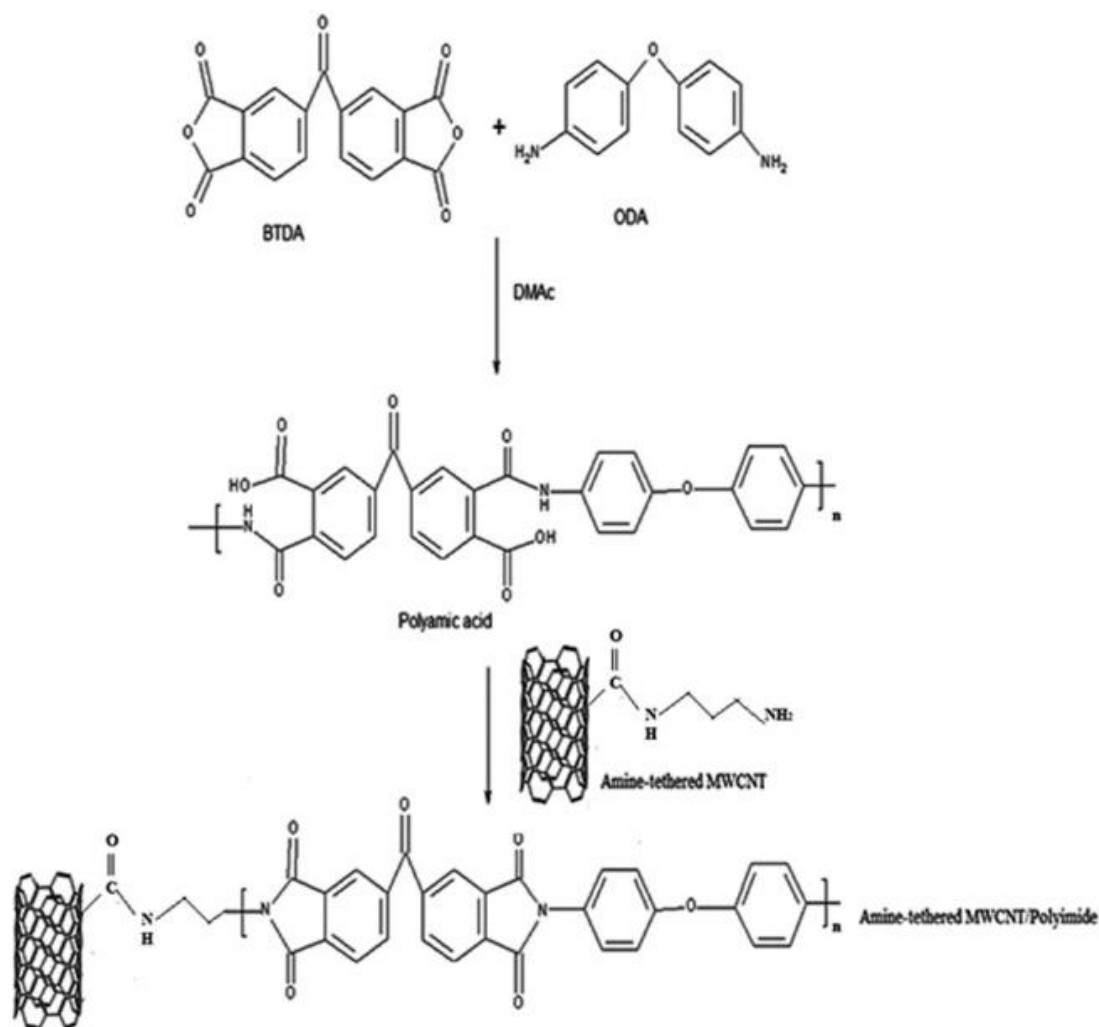
The synthesis of the polyamic acid (PAA) precursor was followed according to literature (16). The solid concentration was afforded as a 20% (wt/v). Briefly, 9.011 g (0.045 mol) of ODA was dissolved in 80 mL DMAc until obtaining a clear solution. Then, 9.815 g (0.045 mol) of BTDA was partially added and the mixture was stirred for 24 h at room temperature. Table 1 summarizes the preparation method of PAA solutions.

**Table 1:** Composition of polyamic acid solutions.

Codes	ODA (g)	BTDA (g)	Amine-tethered MWCNTs (%)
BTDA-ODA	9.0108	9.8154	-
BTDA-ODA-1%MWCNTs	9.0108	9.8154	1
BTDA-ODA-3% MWCNTs	9.0108	9.8154	3
BTDA-ODA-4% MWCNTs	9.0108	9.8154	4
BTDA-ODA-5% MWCNTs	9.0108	9.8154	5
BTDA-ODA-6% MWCNTs	9.0108	9.8154	6

### Preparation of Amine-Tethered MWCNTs/Polyimide Films

One of the following (1, 3, 4, 5 or 6 wt%) amine-tethered MWCNTs were added to the PAA solution. The mixtures were sonicated for 10 min at room temperature and were cast on a glass substrate. Then, the glass substrate were dried stepwise at 80 °C, 100 °C, 150 °C, 200 °C and 300 °C for 1 h at each temperature. The schematic fabrication process of amine-tethered MWCNTs/polyimide films is shown in Figure 2. The polyimides were obtained in 89–95% yield. The strong chemical bond between amino groups of CNTs-ODA and PI matrix. During the polymerization and thermal imidization process, amine-tethered MWCNT tended to form strong chemical bond with BTDA-ODA polyimide (17). The prepared products were washed with ethanol and dried under vacuum.

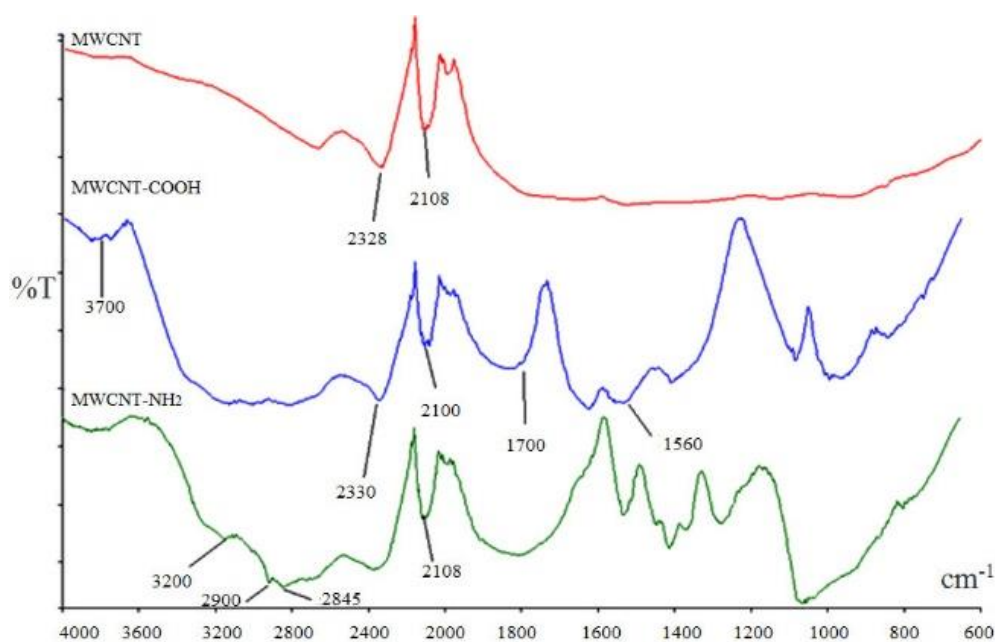


**Figure 2:** Preparation of amine-tethered MWCNTs/polyimide films.

## RESULTS

### Characterization of MWCNTs-NH<sub>2</sub>

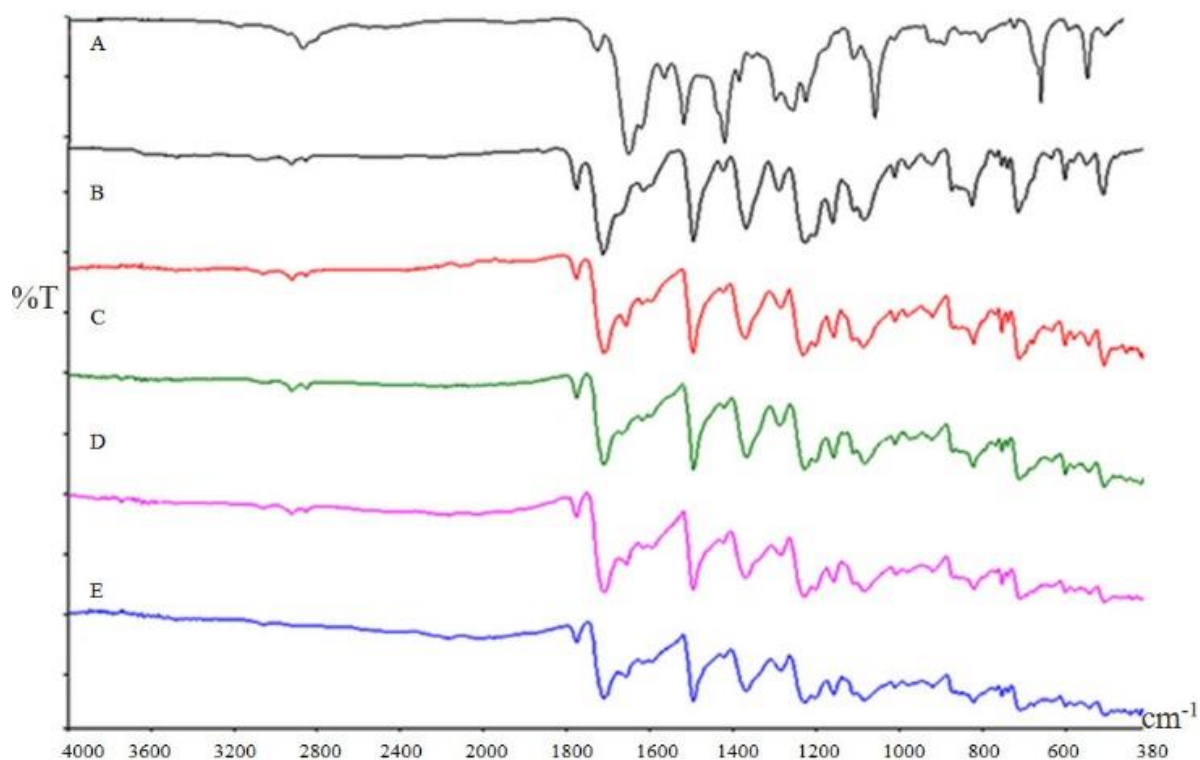
Figure 3 shows the FTIR spectra of MWCNT, MWCNTs-COOH and MWCNTs-NH<sub>2</sub>. The band at 3700 cm<sup>-1</sup> corresponds to free hydroxyl groups. The broad band in the range of 3400-2800 cm<sup>-1</sup> is associated to the characteristic O-H stretching from carboxyl groups in the oxidized MWCNTs (O=C-OH and C-OH). The peak at 1560 cm<sup>-1</sup> is related to the carboxylate anion stretch mode (17). In the FTIR spectrum of the MWCNTs-NH<sub>2</sub>, the peak at 3200 cm<sup>-1</sup> corresponds to the characteristic N-H stretching of the CONH group. The C-H stretching peaks at 2900 cm<sup>-1</sup> and 2845 cm<sup>-1</sup> indicate the covalent bonding of ethylene diamine on MWCNT. Evidently, as a result of the adsorption of CO on the MWCNT, broad bands in the C-O stretch region appeared. Two bands at a frequency higher than the gas-phase CO frequency are found: A band around 2330 cm<sup>-1</sup> and a band near 2108 cm<sup>-1</sup> (19,20).



**Figure 3:** The FTIR spectra of MWCNT (in red), MWCNTs-COOH (in blue) and MWCNTs-NH<sub>2</sub> (in green).

### Structural Characterization of Polyimide Films

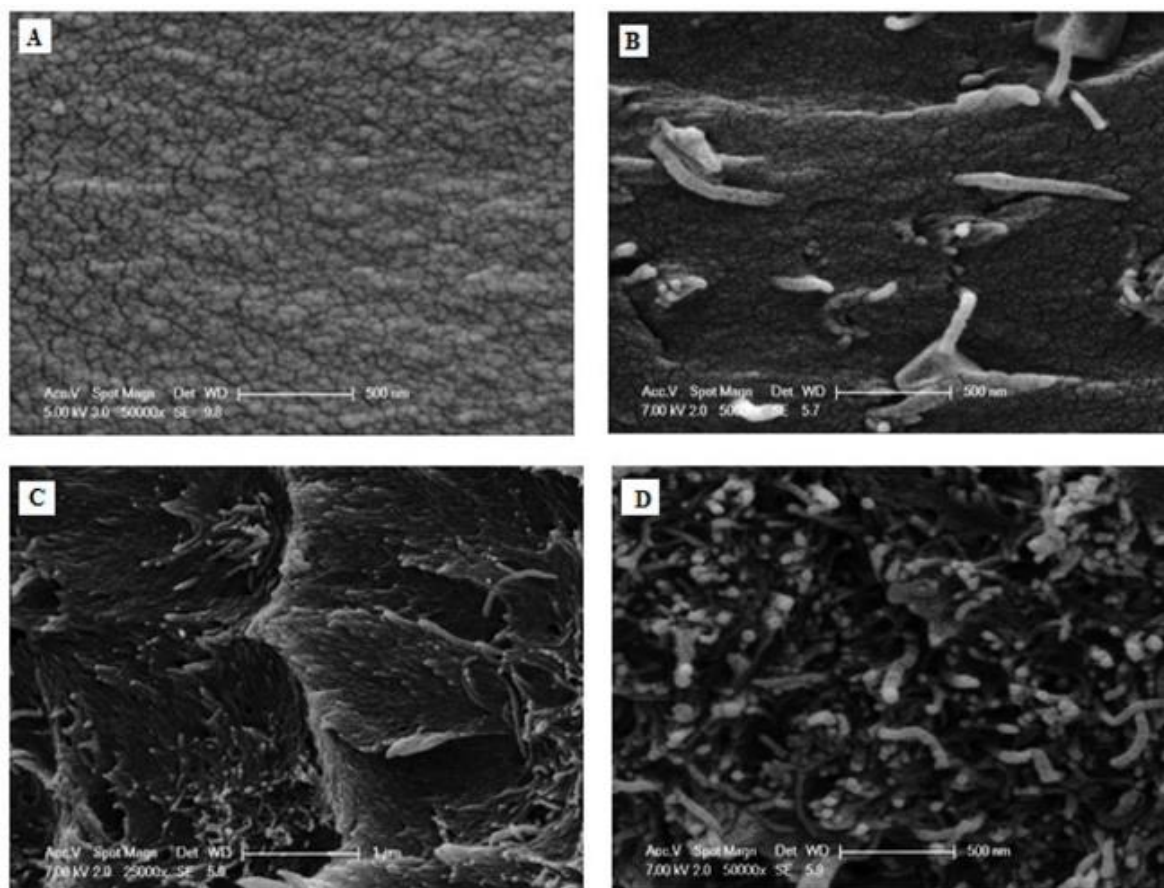
Figure 4 shows the FTIR spectra of the polyamic acid and polyimide/MWCNTs films. In the spectrum of the polyamic acid (spectrum A), the characteristic amide band of polyamic acid is observed at 1617 cm<sup>-1</sup>. As can be seen from spectrum B to F, the amide stretching peak disappeared after thermal imidization of polyamic acid solution. The absence of this peak indicates that imidization was successfully carried out. The new bands at 1777 and 1715 cm<sup>-1</sup> correspond to asymmetric and symmetric carbonyl stretching of the polyimides, respectively. The stretching absorptions of -C-N-C- were observed at 1370 cm<sup>-1</sup> and 1150 cm<sup>-1</sup> (21).



**Figure 4:** The FTIR spectra of the polyamic acid and polyimide/MWCNTs films. A)PAA, B) BTDA-ODA-%1 MWCNTs, C) BTDA-ODA-%3 MWCNTs, D) BTDA-ODA-%4 MWCNTs, E) BTDA-ODA-%5 MWCNTs and F) BTDA-ODA-%6 MWCNTs

### Morphology of Polyimide films

Morphology of the polyimide films were investigated by scanning electron microscopy (SEM). The SEM micrographs are shown in Figure 5a-d. Homogenous dispersion was obtained at a certain amount of MWCNTs as confirmed by SEM images. The amine-tethered MWCNTs were dispersed in the polyimide matrix in individual tubes. Carbon nanotubes tend to agglomerate due to strong interfacial forces such as van der Waals interactions and geometry (22). To overcome the agglomeration of MWCNTs by modification is a critical challenge. Kim *et al.* reported that the strong interfacial interactions between modified MWCNTs with polyimide matrix take place by covalent and hydrogen bonds. In addition, the modification of MWCNTs provides the chemical compatibility between the PI matrix and the modified CNTs (23). The addition of MWCNT changed the morphology of polyimide. It is said that the surface roughness of films increased.

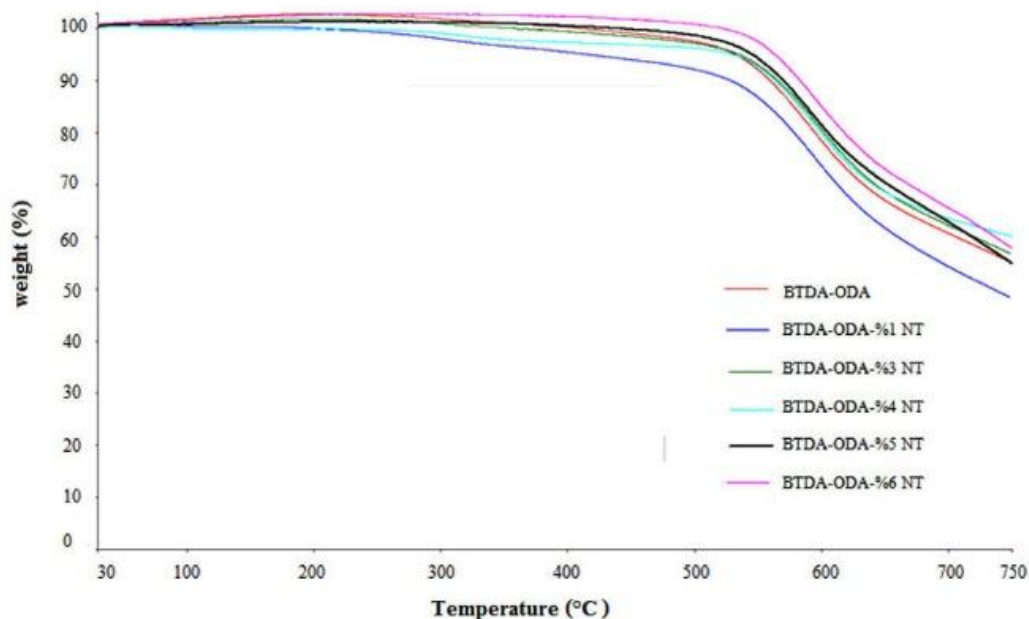


**Figure 5:** The SEM micrographs of (A) BTDA-ODA (50.000x), (B) BTDA-ODA-%1 MWCNTs (50.000x), (C) BTDA-ODA-%4 MWCNTs (25.000x) and (D) BTDA-ODA-%6 MWCNTs (50.000x).

### Thermal properties of MWCTs/polyimide composite films

Figure 6 shows TGA curves of neat polyimide and MWCTs/polyimide composite films. 5 wt% weight loss temperatures ( $T_{5\%}$ ), maximum weight loss temperatures ( $T_{max\%}$ ), and the residual char of the films are listed in Table 2. Aromatic polyimides exhibit high thermal stability because of their regular aromatic groups (24). The aromatic polyimides start to decompose after about 400 °C (25). As can be seen in Figure 6, TGA curves of the films exhibited one step degradation under nitrogen atmosphere. The maximum weight loss temperature ( $T_{max}$ ) was found to slightly increase with increasing amount of modified-MWCNTs. It is known that MWCNTs make contribution to the thermal stability and decomposition rate (26). As expected, char yield of the polyimides gradually increased with addition of MWCNTs.





**Figure 6:** TGA thermograms of the BTDA-ODA polyimide and MWCNTs/Polyimide composite films in nitrogen atmosphere.

The glass transitions temperatures ( $T_g$ ) of polyimide films were investigated by differential scanning calorimeter. The  $T_g$  for BTDA-ODA polyimide film was 275 °C. DSC curves show that the addition of MWCNTs causes  $T_g$  values of the MWCNTs/polyimide composite films to increase. The results are listed in Table 2. The increasing  $T_g$  values demonstrated that amine modified MWCNTs were covalently bonded to the polyimide chains. The secondary network structure occurs by addition of MWCNTs to the BTDA-ODA crosslinked structure (27).

**Table 2:** Thermal and Mechanical properties of polyimide films.

Codes	T%5 (T °C)	T <sub>max</sub> (T °C)	Char (%)	T <sub>g</sub> (°C)	E-modulus (MPa)
BTDA-ODA	415	553	48.45	275	743
BTDA-ODA-1% MWCNTs	535	603	55.33	277	1011
BTDA-ODA-3% MWCNTs	528	555	56.00	280	1036
BTDA-ODA-4% MWCNTs	531	565	60.10	287	1040
BTDA-ODA-5% MWCNTs	544	571	54.76	289	1091
BTDA-ODA-6% MWCNTs	563	590	57.56	304	1119

### Mechanical properties of MWCNTs/polyimide composite films

The Young's modulus of the composite polyimide films are given in Table 2. The presence of MWCNTs increased the modulus of composite films compared to BTDA-ODA neat film. The modulus of BTDA-ODA polyimide film was found as 743 MPa. However, the modulus of the composite polyimide films increased with addition of amine-tethered MWCNTs. The modulus of BTDA-ODA-1% MWCNT and BTDA-ODA-3% MWCNT composite polyimide films were found as 1011 and 1036 MPa, respectively. Moreover, 1%, 2%, 3%, 4%, 5%

and 6% MWCNTs containing polyimide films showed higher modulus than BTDA-ODA polyimide film.

## CONCLUSIONS

BTDA-ODA polyimide and BTDA-ODA-MWCNTs composite polyimide films were successfully prepared via in situ polymerization process. MWCNTs were functionalized with amine groups, to bond with the polyimide matrix. The addition of amine functionalized MWCNTs into a BTDA-ODA polyimide led to obvious improvements in the thermal and mechanical properties. SEM investigations indicate that MWCNTs were homogeneously dispersed in the polyimide matrix. The successful modification and attachment of MWCNTs into the polymeric matrix will create various applications for nanocomposite area.

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