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Preparation and Characterization of In-Situ Polymerized Nanocomposites Based on Polyaniline in Presence of MWCNTs

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Summary: Polyaniline (PANI) composites were prepared with both unmodified and amine modified MWCNTs with and without $BaTiO_3$ through in-situ oxidative polymerization. Uniform coating of PANI on the MWCNTs and $BaTiO_3$ surfaces was found which was evident from the Field Emission Scanning Electron Microscopic (FESEM) and High Resolution Transmission Electron Microscopic (HRTEM) images. The structure of pure and amine modified MWCNTs was identified by Fourier Transform Infrared Spectroscopy (FTIR). The thermal stability of the amine modified composite with $BaTiO_3$ is higher than that of the unmodified composite because of the better affinity between modified MWCNTs and polymer matrix and due to the higher stability of barium titanate itself. The capacitance of amine modified MWCNTs and $BaTiO_3$ composites was less than that of the pure MWCNTs composites but the thermal stability increased in amine modified MWCNTs and $BaTiO_3$ composites with respect to the pure MWCNTs composites. The maximum capacitance and energy density values were found in MWCNT/PANI composites which were equal to 523.20 F/g and 142.83 Wh/kg respectively at a scan rate of 10mv/s. Maximum power density was found to be 5147.70 W/kg in the same composite at a scan rate of 200 mv/s.

Keywords: in-situ polymerization; MWCNTs; nanocomposites; polyaniline; supercapacitor

Introduction

CNTs/conducting polymer composites prepared by in situ polymerization method for supercapacitor applications have received much attention recently. Batteries are typically low power devices with high energy density compared to capacitors, which have high power density but low energy density. So, to fill this energy-power gap, supercapacitor combines the properties of high power density and high energy density and also has long life cycles due to the absence of chemical reactions. The advantage of CNTs for supercapacitor applications[1–3] is based on their unique properties and structure, which includes high conductivity[4,5] high surface area[6–8] and high chemical stability. However, the specific capacitance of CNTs is low. Recently, many electrically conducting polymers[9,10] have been considered as challenging electrode material for supercapacitor applications because of their properties that include reasonable electrical conductivity.

In a supercapacitor, the electrolyte is electrically active and polarized, making positive ions inside it to move one way and negative ions the other way, and causing a second set of charges to form a double layer on the composite electrodes. This makes an electric double-layer that allows the electrodes to store more charge. Hence, supercapacitors are often referred to as double-layer capacitors or EDLCs. The accumulation of charges takes place in the positive voltage scan whereas in the negative voltage scan depletion of charges takes place. Extremely high capacitance

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values can be obtained with a coating of conducting polymers onto the CNTs and transition metal oxides. It is said that CNTs are the electron acceptor,[11] while the conducting polymer serves as an electron donor[12] in the CNT/electrically conductive polymer composite. The CNT matrices can provide a mesoporous structure and offer more active sites achieving high charge dynamics during supercapacitor performance in charging/discharging.[13] Carbon nanotubes greatly assist the easy passage of the charges from polymer to carbon nanotubes through polymer chains for the accumulation of charges at the interface.

Experimental Part

Materials

Multiwalled carbon nanotubes were obtained from Iljin Nano Technology, Korea, (95% purity and 20-40nm diameter). Dicyclohexylcarbodiimide (DCC) was obtained from Spectrochem Pvt. Ltd. Mumbai, (India). Ethylenediamine (EDA), ammonium persulphate (APS) and cetyltrimethylammonium bromide (CTAB) were supplied from Loba Chemie Pvt. Ltd. Mumbai (India). Aniline was obtained from E. Merck Ltd. (India). Barium titanate was bought from Loba Chemie Pvt. Ltd. Mumbai (India).

Synthesis of Composites

Modification of MWCNTs

MWCNTs were treated with a solution of H_2SO_4 and HNO_3 (weight ratio of H_2SO_4 to $HNO_3 = 3:1$) where the ratio of MWCNTs to mixed acids was 1:400 and stirred at 60 °C for 24 hours to get acid modified MWCNTs. The product was collected by centrifuging the reaction mixture and washed with distilled water several times and then dried at 1100 °C. After acid treatment, the acid functionalized MWCNTs were further modified by ethylenediamine(EDA)/dicyclohexylcarbodiimide(DCC)/THF solution with the weight ratio of EDA to DCC to MWCNTs of 25:25:1 at room temperature and stirred for 48 hours to yield amine functionalized[14] MWCNTs.

Composites Preparation

For the preparation of composites, in 600 ml deionised water, 1.24 g cetyltrimethylammonium bromide (CTAB) and 60 mg MWCNTs were treated at room temperature and sonicated for 1 hour to obtain well dispersed suspensions. Then a solution of 0.6 ml aniline was added to the above system and sonicated for 10 minutes and 62.5 ml distilled water containing 2.04 g ammonium persulphate (APS) were added and sonication was continued for another 10 minutes. The reaction mixture was kept in a refrigerator at 1-50 °C for 24 hours, the resulting black precipitate was filtered, washed with distilled water, then with ethanol several times and dried at 1000 °C for 12 hours. The same procedure was followed to synthesize the (amine modified MWCNTs and barium titanate)/PANI composite where MWCNTs: $BaTiO_3$ were taken in 1:4 ratio.

Characterization Techniques

Fourier Transform Infrared Spectroscopy (FTIR). FTIR of nanocomposites was done using a NEXUS 870 FTIR (Thermo Nicolet) to investigate the structure of modified MWCNTs. For the IR spectrum a small amount of material was mixed with KBr in adequate level to make a disk.

Field Emission Scanning Electron Microscopy (FESEM). A Carl Zeiss-SUPRA^{TM} 40 FESEM with an accelerating voltage of 5 kV was employed to observe the morphology of coating of polymer onto the carbon nanotubes/barium titanate in the composite.

High Resolution Transmission Electron Microscopy (HR-TEM). The nanocomposites with both unmodified/modified MWCNTs and barium titanate were analyzed by high resolution transmission electron microscopy (HR-TEM, JEOL 2100), to check the coating of conducting polymer onto the carbon nanotubes. A small amount of sample was mixed with acetone and sonicated for 30 minutes. A drop of the solution was poured on the copper grid in order to perform the HR-TEM analysis.

Electrochemical Characterization

The composites based on conducting polyaniline were investigated by three electrodes Cyclic Voltametry (Gamry Instrument, 750 mA & 2 V).

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis curves were recorded with a Dupont 2100 Thermogravimetric analyzer. The TGA measurements were conducted at a heating rate of 100 °C/min under air from 30 to 8000 °C.

Results and Discussion

FTIR Study

The structure of amine modified MWCNTs was identified by FTIR spectrum. As shown in Figure 1(c) amine modified MWCNTs show the peak at 1238, 1576,3258 and 2920 cm^{-1} corresponding to the peaks of C–N stretching, N–H bending, N–H stretching and C–H stretching respectively. Acid modified MWCNTs show peaks at 1276, 1710, 3432 and 2920 cm^{-1}, which correspond to C–O stretching, C=O stretching, O–H stretching and C–H stretching respectively.

FESEM Analysis

The nanotubular morphology was verified by FESEM analysis. In this process a small amount of material were mounted on the sample holder with the help of carbon tape to find the morphology of the material. A uniform coating of polyaniline has been developed on to the carbon nanotubes in a) MWCNTs/PANI (PANIC) nanocomposite and b) amine modified MWCNTs/PANI (PANIAC) nanocomposite. From FESEM images of Figure 2.(c) MWCNTs + Ba-BaTiO$_3$/PANI (PANICB) nanocomposite and Figure 2.(d) amine modified MWCNTs + BaTiO$_3$/PANI (PANIACB) nanocomposite, it was clear that barium titanate has also been coated by polyaniline.

HRTEM Analysis

HRTEM images confirm that polyaniline has been uniformly coated on to the MWCNTs and barium titanate surfaces. The average outer diameter of pure MWCNTs was around 20 nm and the coating thickness of the concerned polymer was around 60 nm. For the amine modified MWCNTs the coating thickness of the polymer was around 40 nm. The decrease

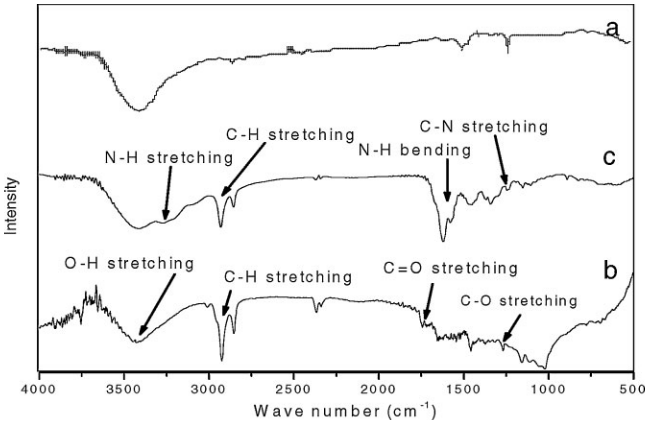

Figure 1.

FTIR spectrum of (a) Pure MWCNT (b) Acid modified MWCNT and (c) Amine modified MWCNT.

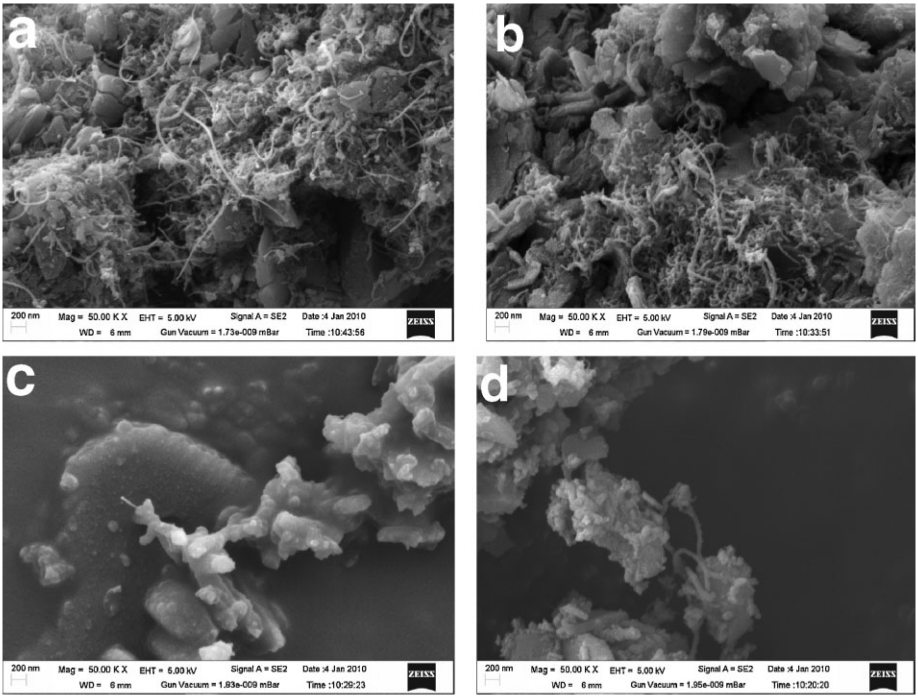

Figure 2.
FESEM images of (a) PANIC nanocomposite (b) PANIAC nanocomposite (c) PANICB nanocomposite (d) PANIACB nanocomposite.

in coating thickness of amine modified MWCNTs composites may be due to the repulsive interaction between the nitrogen atoms of aniline and $-NH_2$ group[15,16] (amine containing MWCNTs) which will develops a charge accumulation region at the interface. Figure 3.(a–d) shows the uniform coating of polyaniline on both unmodified and modified MWCNTs.

Electrochemical Study

The electrodes were made into pellets (20 mg) by pressing the material in a hydraulic press at the pressure of about 5 tons. The capacitor was built from a pellet of composite separated with a porous cellulose nitrate paper in a sample holder. The sample holder was made of Teflon which includes the working electrode connected with a platinum wire; counter electrode made of platinum foil and reference electrodes were connected with a salt bridge. The electrochemical performance was determined in 1M aqueous KCl solutions using galvanostatic, voltammetry and impedance spectroscopy techniques by three electrode cell. Cyclic voltammetry characteristics of the composites electrode were recorded at different scan rates from 10 to 200 mV/s. The capacitance was calculated from the capacitive current (for non-rectangular shape), the formula[17] used was

$$C_{sp} = (I_+ - I_-)/v \times m$$

where I_+ and I_- are maximum current in positive voltage scan and in the negative voltage scan respectively, v is the scan rate and m is the mass of the composite electrode materials. In case of three-electrode cells, the capacitance values are the capacitance per electrode. It is noteworthy that pure nanotubes pointed out very low capacitance values not exceeding 20 F/g.[15] Hence, taking into account that the proportion of CNTs in the composite is

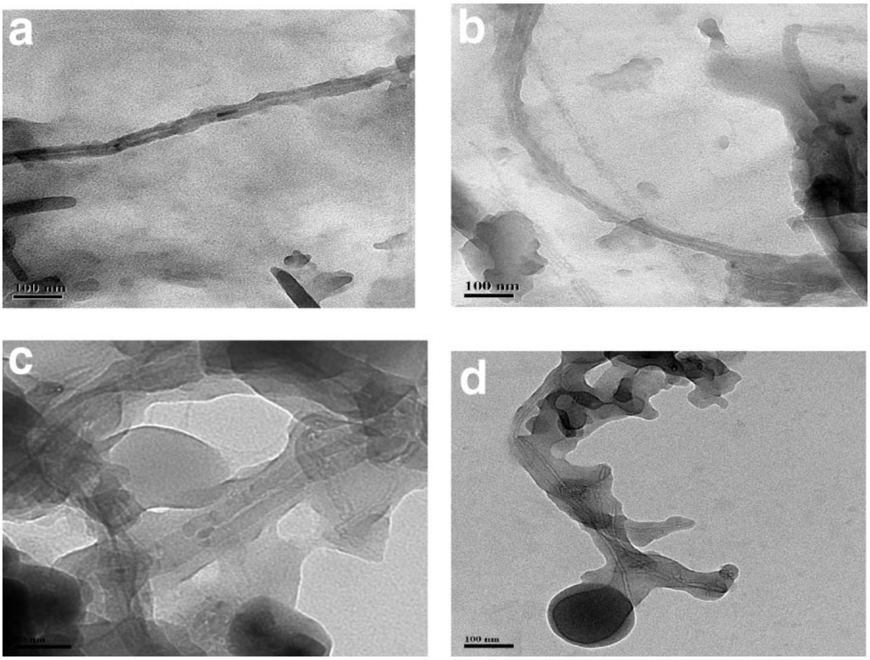

Figure 3.
HRTEM images of (a) PANIC nanocomposite (b) PANIAC nanocomposite (c) PANICB nanocomposite (d) PANIACB nanocomposite.

only 10 wt. %, the total capacitance is mainly due to the conducting polymer. On the other hand, barium titanate[18–21] was used to acquire high thermal stability and to reduce the energy and power dissipation. CNTs and barium titanate assist to increase the thermal stability and reduce the shrinkage of composite electrodes during multiple charging-discharging.

Cyclic Voltammograms of pure polyaniline and its composites are shown below. For galvanostatic charge/discharge cycling, the applied voltage ranged between −0.4 V to 1.0 V for polyaniline composites. The specific capacitance estimated using a three electrode cell was 523.2 F/g in PANIC which was higher than the pure PANI at the scan rate 10 mV/s. It is well seen that depending on the selected potential range for calculation, the capacitance can vary. The decrease in capacitance is perhaps because of the fact that the electrolyte ions cannot accumulate sufficiently at the interface of the conducting polymer–carbon nanotube/ barium titanate interface which gives rise to the maximum specific capacitance values. In case of barium titanate composites specific capacitance were diminished in greater extent because of its non conductivity which prevents easy passage of charges. As the scan rate was increased the specific capacitance values were decreased due to the greater charge mobilization per unit time as shown in Figure 4 (VI). The specific capacitance values calculated from Figure 4 (I–V). were presented in Table 1.

The specific capacitance of PANIC is larger than that of pristine PANI because the porous structure of MWCNTs assists the doping ions to enter into or eject from the composite pellet more easily.

Energy density (E)[19] is a term used for the amount of energy stored in a given system or region of space per unit volume, or per unit mass, depending on the context. $E = 1/2\ CV^2$, Where, C = specific capacitance in F/g and V = Operating voltage and power density (P) = E/t, Where, t = time in second for a complete cycle. The energy

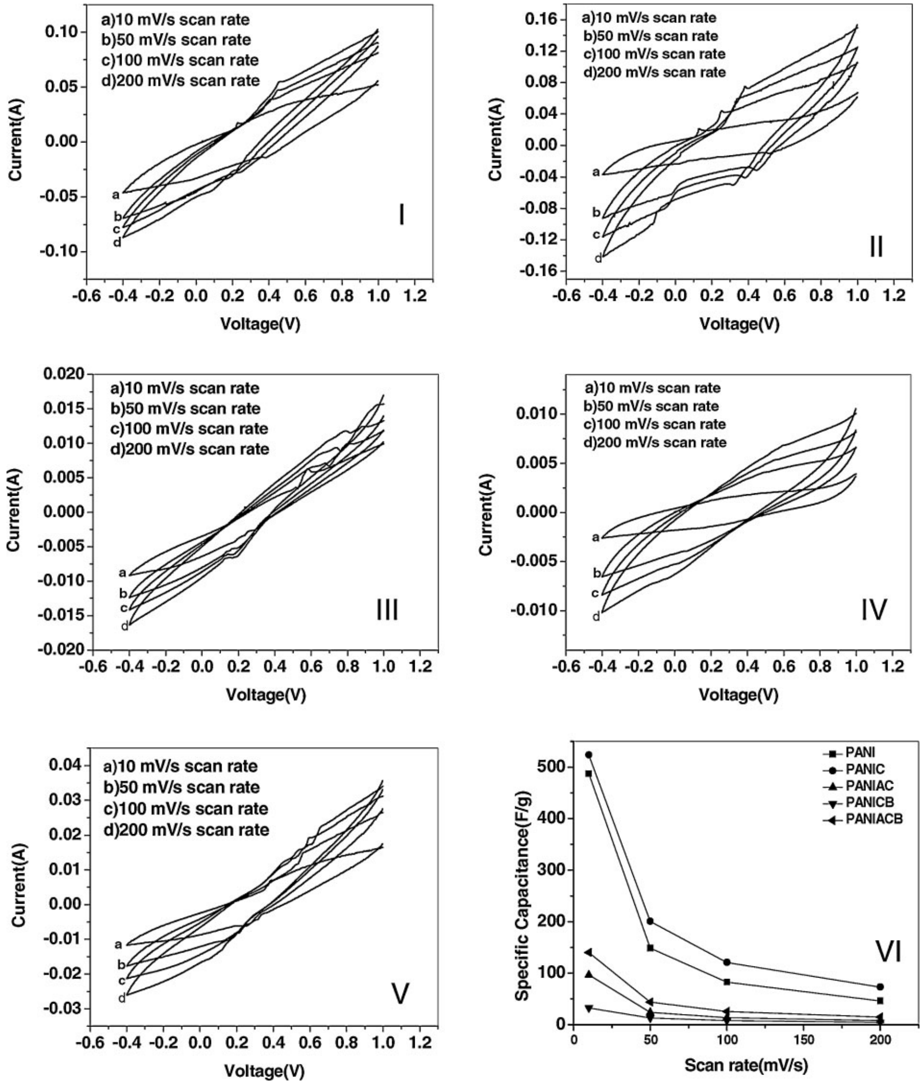

Figure 4.

Cyclic Voltammogram (CV) of (I) Pure PANI (II) PANIC nanocomposite (III) PANIAC nanocomposite (IV) PANICB nanocomposite (V) PANIACB nanocomposite,(VI) Scan rate vs. Specific Capacitance plot for polyaniline composites.

Table 1.

Specific capacitance of polyaniline composites at different scan rate.

Sample	Sp. Capacitance (F/g) at scan rate			
	10 mV/s	50 mV/s	100 mV/s	200 mV/s
PANI	487.15	148.57	82.86	46.43
PANIC	523.2	200.7	120.95	73.35
PANIAC	97.1	24.38	13.81	8.07
PANICB	32.65	13.18	8.31	5.1
PANIACB	140.5	44.17	26.285	15.15

density values calculated from Figure 4 (I–V) are presented in Table 2.

The power density values calculated from Figure 4 (I–V), are presented in Table 3. The power density of PANIC was larger than that of pristine PANI.

Impedance Study

Electrical impedance,[22–24] or simply impedance, describes a measure of opposition to

Table 2.
Energy density of polyaniline composites at different scan rate.

Sample	Energy Density (Wh/kg) at scan rate			
	10 mV/s	50 mV/s	100 mV/s	200 mV/s
PANI	132.99	40.56	22.62	12.68
PANIC	142.83	54.79	33.02	20.02
PANIAC	26.5	6.66	3.77	2.2
PANICB	8.91	3.6	2.27	1.39
PANIACB	38.36	12.06	7.18	4.13

Table 3.
Power density of polyaniline composites at different scan rate.

Sample	Power Density (W/kg) at scan rate			
	10 mV/s	50 mV/s	100 mV/s	200 mV/s
PANI	1705.03	2599.98	2907.56	3258.46
PANIC	1831.2	3513.25	4244.13	5147.7
PANIAC	339.85	426.65	484.59	564.9
PANICB	114.28	230.65	290.85	357.74
PANIACB	491.75	772.98	919.98	1062.88

alternating current (AC). The semicircle is a characteristic of a single time constant. The impedances were varied for different composites of polyaniline. The EIS (Electrochemical Impedance Spectroscopy) data were analyzed using Nyquist plots. Nyquist plots show the frequency response of the electrode/ electrolyte system and are a plot of the imaginary component of the impedance against the real component. Each data point is at a different frequency with the lower left portion of the curve corresponding to the higher frequencies.

Ideal capacitor behavior is achieved when slope of the curve is very high. Large semicircles observed for these electrodes are indicative of high interfacial charge-transfer resistance, which can be attributed to the poor electrical conductivity of these materials. The sloped portion of the Nyquist plots is the Warburg resistance resulting from the frequency dependence of ion diffusion/transport in the electrolyte. The larger Warburg region of these electrodes indicates greater variations in ion diffusion path lengths and increased obstruction of ion movement.

The EIS curves of polyaniline composites are shown in Figure 5. Two well separated patterns were observed: one semicircle indicating single time constant and a straight line explaining Warburg resistance. The difference in the real part of the impedance between low and high frequencies was used to evaluate the value of electrochemical charge transfer resistance (Rct). The charge transfer resistance in PANI is about 4.7 Ω which verified a

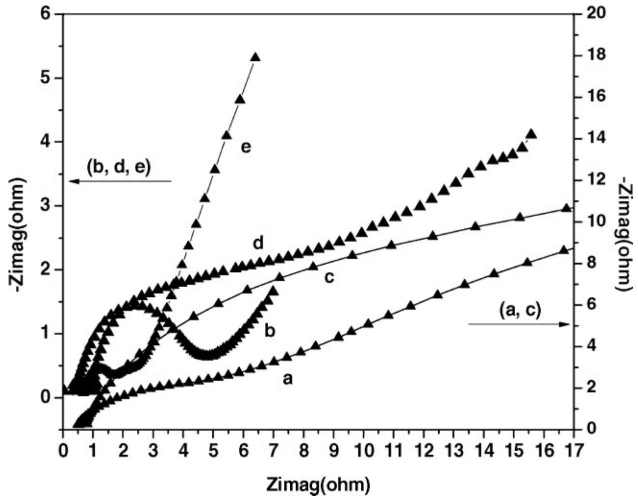

Figure 5.
Impedance study of (a) Pure PANI (b) PANIC nanocomposite (c) PANIAC nanocomposite (d) PANICB nanocomposite (e) PANIACB nanocomposite.

good capacitance behavior of the system at various discharging state. In case of PANIC, the Rct value was 1.7 Ω calculated from Figure 5.b. The Rct value was decreased in PANICB further and then it was increased to 6 Ω in PANIACB.

Thermal Analysis

The TGA measurements were conducted with 15 mg of sample in the sample holder keeping a heating rate of 10 °C/min under air atmosphere from 30 to 800 °C. An important characterization of polymer composite electrode is their thermal stability at elevated temperature. It has been found that the thermal stability of composites is much higher than pure polymer. This is due to the better affinity[25,26] between the polymer matrix and CNT. Barium titanate composites have much higher stability because of the higher stability of the barium titanate itself.

In case of polyaniline composites TGA plots reveal that all composites are quite stable up to 300 °C. Rapid degradation takes place between 300 °C–600 °C. Details from thermogravimetric analysis of the polyaniline composites determined from Figure 6 are summarized in Table 4.

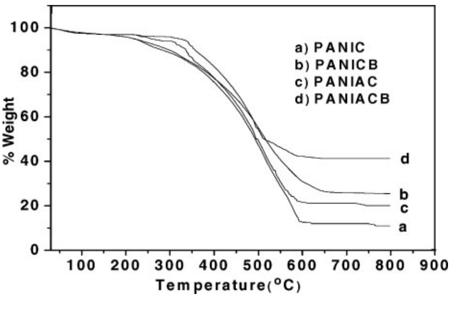

Figure 6.
TGA thermogram of polyaniline composites.

Table 4.
TGA parameters of polyaniline composites.

Sample	10% wt. loss temp. (°C)	40% wt. loss temp. (°C)
PANIC	282	462
PANIAC	300	469
PANICB	336	482
PANIACB	357	484

Conclusion

In-situ oxidative polymerization process leads to uniform coating of PANI on MWCNT and mixture of MWCNT and $BaTiO_3$, which has been confirmed by FESEM and HR-TEM. However, the PANI coating thickness is low, when MWCNT has been pre-modified with amine. The specific capacitance, energy density and power density values were considerably higher for the unmodified MWCNT composites than the modified composites. However, the modified MWCNT-PANI composites having better thermal stabilities compared to unmodified MWCNT composites. The presence of $BaTiO_3$ in the composites improves the thermal stability considerably accompanied by lower shrinkage under charging-discharging process.

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