

SYNTHESIS AND CHARACTERIZATION OF CARBON BASED POLYMER NANOCOMPOSITES FOR ENHANCED CONDUCTIVITY

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Polystyrene, polyamide, polythiophene and carbon nanotubes composites were prepared and characterized by various techniques. Carbon nanotubes were synthesized using three methods named as simple chemical, heated graphite and graphene oxide. Polythiophene was prepared by polymerization of thiophene whereas polyamide was prepared by polymerization of 4,4-oxydianiline and terephthaloyl chloride. Ter-polymer blends consist on polystyrene, polyamide and polythiophene were prepared by solution method. Carbon nanotubes diameter were calculated as 9.2 nm and π - π interaction between polymers rings and carbon nanotubes confirmed by XRD. Rutherford backscattering used to find composition of composites, RBS confirmed carbon in all samples (> 99%). Scanning electron microscopy was used to study surface morphology of composites and it confirmed shapes of carbon nanotubes with polymer blend coating. The conductivity of polymer nanocomposites was increased from 6.7×10^{-16} to 6.8×10^{-1} S/cm.

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1. Introduction

In 1991, Carbon nanoparticles were discovered by Ijima^[1]. Carbon nanotubes have gained special attention of many researchers worldwide. The strength, small dimensions, and the special physical properties of carbon nanotubes make them unique material for many fields^[2]. Many important applications of carbon nanotubes are energy storage devices, radiation sources sensors, hydrogen storage media, field emission displays, conductive materials, probes and nanometer-sized semiconductor devices^[3]. Carbon nanotubes had been synthesized by various methods like chemical vapor deposition, laser ablation of a carbon target electric arc discharge, pyrolysis of benzene in the existence of hydrogen and electrochemical synthesis^[4]. Carbon nanoparticles exhibit very good electrical, magnetic and mechanical properties which make them excellent filler for polymer composites for various applications^[5].

Polymers nanocomposites were first time used in 1993. Polymer nanocomposites mean combination of polymers and nanoparticles in which properties of both were utilized and make materials having good mechanical strength, thermal and chemical properties. Polymers are less expensive, light weight and flexible. Nanoparticles have their own properties like more reactive surface area but polymer nanocomposites develop mutual properties in one material. Polymers nanocomposites have many properties like high gas barriers, heat resistance, better conductivity, high mechanical resistance and recyclability. Literature shows that when carbon nanoparticles are added into polymers, resultant product has improved mechanical properties like increase young's modulus^[6]. Polymer nanocomposites are used for gas nanofilter. Permeability of gas can be increased in polymer nanocomposites film^[7]. Different techniques are used for synthesis of polymer nanocomposites like electrostatics method, melt processing and solution method^[8, 9]. There are many characterization techniques which used for polymer nanocomposites like XRD for structure identification, SEM for surface morphology, RBS for composition etc^[10]. Conductive and

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thermoplastic polymers nanocomposites were prepared in this research which have low resistance and used in many materials like solar panels transistor and diode etc. New polymer blends consist of polystyrene, polyamide and polythiophene with carbon nanotubes were introduced in this research work.

Conducting polymers have been attracting special attention because of its important contributions to the fields of plastic transistors, microwave components, electro-optic devices and drug delivery systems^[11]. Composites of carbon nanoparticles in the company of polythiophene have been reported with enhanced chemical and electronic properties. Usually polythiophene was synthesized from polymerization of thiophene by solution method. Polythiophene electrical conductivity was increased in composites form as compared to other polymer composites which make it better materials for future electronics fields^[12].

Thermoplastic polymers are used as polymer matrix for carbon nanotubes. Polystyrene is very well known thermoplastic polymers and carbon nanotubes are well dispersed in this matrix. Thermal properties of polystyrene were increased with addition of multi-walled carbon nanotubes and electrical conductivity was also increased from 10^{-12} to 0.135 S/m ^[13]. When the nanotubes content is 0.32 wt%, the polystyrene with multi-walled carbon nanotubes composite had 250% increase of impact strength as compared to pure PS^[14]. Polyamide thermoplastic polymers are also having better properties with the addition of carbon nanotubes. Tensile tests of the polyamide and nano particles in composites form show a considerable increase of 27% in the young's modulus^[15]. Polyamide was synthesized by polymerization between different polymers via condensation polymerization. Homogeneous dispersion of carbon nanoparticles into polymer is very important task because there are many cases in which fillers are not easily dispersed, it depends on Vander Waals forces and surface energy^[16]. To get such composites which have homogeneous dispersion of fillers into matrix, it is compulsory to creatively control and make use of surface contacts among polymeric chains and carbon nanotubes in order to get sufficient dispersion throughout the matrix^[16]. Synthesis of more thermoplastic and conducting polymer nanocomposites is quite difficult. To obtain thermoplastic and conducting polymer nanocomposites used three different polymers that are polystyrene, polyamide and polythiophene that fulfilled our desired polymer nanocomposites.

In this research carbon nanotubes were synthesized by various methods. In second phase polyamide and polythiophene were prepared by solution method. Finally Polystyrene/Polyamide/Polythiophene and carbon nanotubes composites were also prepared by solution method^[17].

2. Materials and methods

Materials

Polystyrene (PS, average M_w 35,000), thiophene ($\geq 99\%$), graphite fine powder, 4,4-oxydianiline (97%), terephthaloyl chloride ($\geq 99\%$), nitric acid (70%), potassium chlorate (98%), sodium hydroxide ($\geq 97\%$), sulfuric acid (99.99%), hydrogen peroxide (30% (w/w) in H_2O , contains stabilizer), sodium nitrate (99%), ferric chloride (III) hydrated (ACS reagent, 97%), dimethyl sulfoxide (anhydrous, $\geq 99.9\%$) and tetrahydrofuran (anhydrous, $\geq 99.9\%$).

Synthesis of carbon nanotubes through various routes

In heated graphite method, graphite was heated at 800°C in furnace and then heated graphite was immediately dipped into cold water. In heated graphite method when highly heated graphite (800°C) was put into cold water (0°C) at that time graphite temperature was still high that provided much power for graphite sheet to fold into tubes. Finally it was filtered and dried. Final product was carbon nanotubes^[18].

In simple chemical method, one solution was containing graphite (5 g) with water (5 mL) and other solution was containing nitric acid (25 mL) and sulphuric acid (50 mL) were prepared separately at low temperature (0°C) under stirring. Then both solutions were poured in another flask and also added potassium chlorate (25 g) into same mixture at (0°C). Solution was stirred for

36 h at room temperature, and then refluxed for 12 h at 85°C. Finally solution was centrifuged, neutralized and filtered. Final product was carbon nanotubes^[19].

In graphene oxide method, one solution was prepared by adding graphite (5 g) and sulfuric acid (225 mL) in a flask at 0°C under 1 h stirring. Then sodium nitrate (5 g) was added into same mixture at room temperature. In next step distilled water (600 mL) was also added into same mixture at 90°C under stirring and then whole solution was poured into water (1500 mL). Hydrogen per oxide (50 mL) was added into same mixture and then filtered and dried. Filtered product was graphene oxide. Again solution was prepared by adding graphene oxide (3 g) and nitric acid (300 mL) into flask and sonicated. For neutralization, solution was poured into distilled water (3000 mL) and centrifuged (5000 rpm). Again mixture was poured into distilled water (600 mL), centrifuged and poured into distilled water (3000 mL). Finally solution was filtered and dried for 24 h at 70°C. Final product was carbon nanotubes^[20]. In all processes acids were used for separation and oxidation of graphite layer.

Synthesis of polyamide

Two solutions one containing terephthaloyl chloride (2.03 g) and other containing 4,4-oxydianiline were prepared separately both in DMSO (20 mL) by constant stirring at room temperature. After preparation, both solutions were mixed and refluxed for polymerization at 120°C. Then whole solution was put into distilled water and filtered^[21].

Synthesis of Polythiophene

Two solutions one containing thiophene (1 mL) and other having FeCl₃.6H₂O (2.5 g) were prepared separately in 0.1M HCL (100 mL) under stirring at room temperature. FeCl₃.6H₂O was used as oxidized agent. Then one solution was added drop wise into second solution under stirring. For neutralization 10% NaOH solution was added into same mixture and filtered^[22].

Synthesis of composites based on polystyrene/polyamide/polythiophene and carbon nanotubes

Polystyrene, polyamide and polythiophene were refluxed in tetrahydrofuran (10 mL) for 6 h at 80°C using round bottom flask. Carbon nanotubes (0.01- 0.5 g) was then added to the above ter-blend and refluxed again for 2 h at 80°C. Then the solution was poured into dish for film. Different composites were prepared by using this route with different ratios of carbon nanotubes. All samples with codes, names and concentration are shown in Table 1.

Table 1. Synthesis Routes of Carbon nanotubes, Names Codes and Ratios of PS/PA/PT/CNP Composites.

Carbon Nanotubes Synthesis routes	Sample Name	Sample Code	PS/PA/PT (g)	CNP (g)
Heated graphite	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.01)	PS/PA/PT/CNT _{HG} 0.01	0.94/0.05/0.01	0.01
	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.05)	PS/PA/PT/CNT _{HG} 0.05	0.94/0.05/0.01	0.05
	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.1)	PS/PA/PT/CNT _{HG} 0.1	0.94/0.05/0.01	0.1
	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.3)	PS/PA/PT/CNT _{HG} 0.3	0.94/0.05/0.01	0.3
	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.5)	PS/PA/PT/CNT _{HG} 0.5	0.94/0.05/0.01	0.5
Simple chemical	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.01)	PS/PA/PT/CNT _{SC} 0.01	0.94/0.05/0.01	0.01
	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.05)	PS/PA/PT/CNT _{SC} 0.05	0.94/0.05/0.01	0.05
	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.1)	PS/PA/PT/CNT _{SC} 0.1	0.94/0.05/0.01	0.1
	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.3)	PS/PA/PT/CNT _{SC} 0.3	0.94/0.05/0.01	0.3
	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.5)	PS/PA/PT/CNT _{SC} 0.5	0.94/0.05/0.01	0.5
Graphene oxide method	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.01)	PS/PA/PT/CNT _{GO} 0.01	0.94/0.05/0.01	0.01
	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.05)	PS/PA/PT/CNT _{GO} 0.05	0.94/0.05/0.01	0.05
	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.1)	PS/PA/PT/CNT _{GO} 0.1	0.94/0.05/0.01	0.1
	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.3)	PS/PA/PT/CNT _{GO} 0.3	0.94/0.05/0.01	0.3
	Polystyrene/Polyamide/Polythiophene/Carbon nanotubes (0.5)	PS/PA/PT/CNT _{GO} 0.5	0.94/0.05/0.01	0.5

3. Results and Discussion

XRD Analysis

X-ray diffraction was used to estimate the diameter size of carbon nanotubes and to study structure of composites. Carbon nanotubes diameter sizes were calculated as simple chemical (9.2 nm), graphene oxide method (9.7 nm) and heated graphite (46 nm) by using XRD spectra. One thing cleared that chemical methods are best for getting small size particles. Figure 1, 2 and 3 shows XRD spectra of all samples of different fillers synthesis routes in comparison form. All spectra show peaks of carbon nanotubes at 27° which confirmed the presence of carbon nanotubes in composites form and sharpness and high intensity of peaks show high crystalline samples but broad peaks show amorphous samples. XRD has played vital role to identify structure of substance and especially it is very important tool for distinguished between amorphous and crystalline materials by peaks intensity and broadness. Polymers are amorphous materials and its spectra very broad and low intense but in present all spectra sharp and highly intense which confirmed crystalline order of polymer nanocomposite increase with addition of CNTs because CNTs are very crystalline materials.

Figure 2 shows high intensity and sharp peaks of carbon nanotubes at 27° which confirmed high crystalline materials obtained by heated graphite routes. All XRD spectra shows small peaks at 28° which are due to presence of polythiophene in composites because polymer blend was consist on polystyrene, polyamide and polythiophene. Figure 1 shows double peaks round about 26° which confirmed presence of some graphite which is not convert into carbon nanotubes and figure 3 also shows presence of graphene peaks at 12° ^[23, 24]. In all XRD spectra broad peaks at $18-24^{\circ}$ shows presence of polymer blend in amorphous form and π - π interaction between polymers rings and carbon nanotubes^[7, 11, 25].

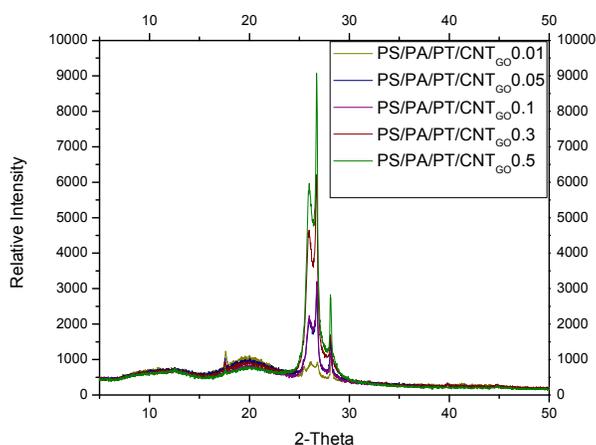


Fig.: 1. XRD spectra comparison of PS/PA/PT/CNT_{Go}0.01, PS/PA/PT/CNT_{Go}0.05, PS/PA/PT/CNT_{Go}0.1, PS/PA/PT/CNT_{Go}0.3 and PS/PA/PT/CNT_{Go}0.5

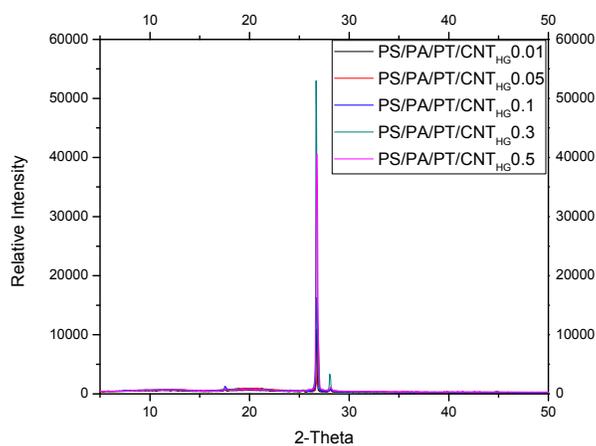


Fig.2. XRD spectra comparison of PS/PA/PT/CNT_{Hg}0.01, PS/PA/PT/CNT_{Hg}0.05, PS/PA/PT/CNT_{Hg}0.1, PS/PA/PT/CNT_{Hg}0.3 and PS/PA/PT/CNT_{Hg}0.5

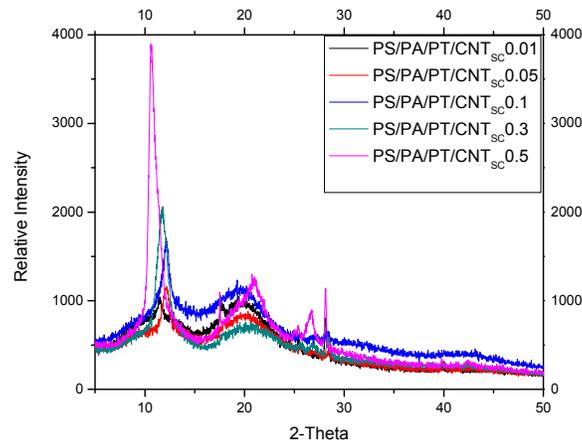


Fig.3.XRD spectra comparison of PS/PA/PT/CNT_{sc}0.01, PS/PA/PT/CNT_{sc}0.05, PS/PA/PT/CNT_{sc}0.1, PS/PA/PT/CNT_{sc}0.3 and PS/PA/PT/CNT_{sc}0.5

RBS Analysis for Composites

PS/PA/PT/CNT_{sc} was characterized as RBS which shows composition of composites (Figure4). Carbon, nitrogen, oxygen and sulphur peaks were appeared 400, 500, 600 and 1100 respectively. Table 2 shows compositions of PS/PA/PT/CNP_{sc} that were found as carbon 99%, nitrogen 0.1%, oxygen 0.1% and sulphur 0.1%. RBS confirmed carbon in all samples (> 99%) because our system consist of polystyrene, polyamide, polythiophene and carbon nanoparticles and all these have carbon as main component.

Composites also have sulphur due to polythiophene and oxygen and nitrogen due to polyamide. Polymer nanocomposites have presence of sulphur due to polythiophene and oxygen and nitrogen due to polyamide. Very small peaks are present at 900 which is due to impurity because acid, base and other chemicals were also used during preparation of CNTs. Maximum chemicals were removed during washing but some small amount present which is also remove by more care during preparation.

Table 2. Composition of PS/PA/PT/CNP_{sc}.

Element Name	Carbon	Nitrogen	Oxygen	Sulphur
Composition(%)	99	0.1	0.1	0.1

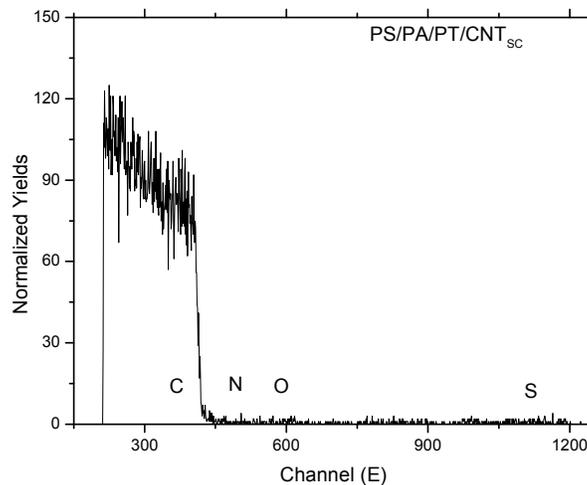


Fig 4. RBS spectra of PS/PA/PT/CNT_{sc}.

SEM Analysis

Scanning electron microscope was used to study surface morphology composites, only two composites namely PS/PA/PT/CNT_{GO} and PS/PA/PT/CNT_{SC} shows the promising results. It confirmed formation of carbon nanotubes which have small diameter and long length and some CNT are in curled form as shown 5 (a,b). This reveals the authenticity of the above mentioned methods for synthesis of CNTs. SEM is very important to see interaction between polymer and CNTs. It is worth mentioning that the size and shape of CNT can further be improved by controlling the composition of the chemicals and compact instrumentations.

However, in the present case, this method is more economical and robust. It is important to note that coating of polymers on carbon nanotubes which in-turn increased the diameter of the CNTs. This shows good interaction between polymers blend and CNT. Some other particles are also observed (figure 5a,b) in addition to the CNTs which may be due to an artifact. Dispersion of CNTs into polymer blend is very difficult task because CNTs does not make any bond with polymer bend, it interact only due to Van der Waals and electrostatics force. Fig 5 (a,b) shows good dispersion of CNTs into polymers blend and dispersion can also be more increase by increasing stirring time during preparation of polymer nanocomposites. Dispersion of CNTs into polymer blend is also depends on synthesis method and in this case SEM micrographs shows solution method best for excellent dispersion into polymer blend.

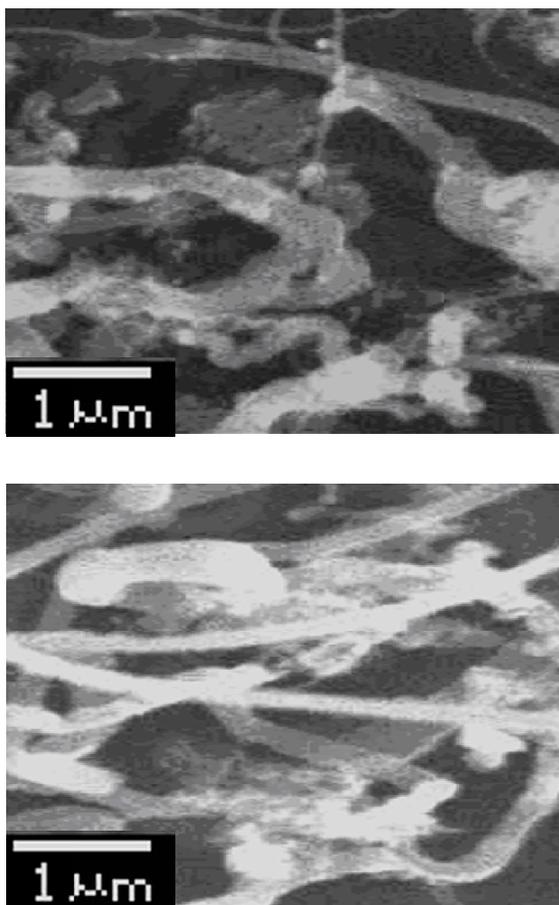


Fig. 5. SEM micrograph of a) PS/PA/PT/CNT_{GO} and b) PS/PA/PT/CNT_{SC}^[26]

Electrical Conductivity

Two probe method was used for measure voltage and current. The measurement was performed directly from thin film and then finds length, width and area of thin film. Resistance of thin film was calculated by find slope of graph between voltage and current. Resistivity was

measured by using $\rho = RA/L$ and then took its inverse for conductivity. In this research polymer matrix main content is polystyrene. Conductivity of polystyrene is about 6.7×10^{-16} S/cm in pure form^[27]. In this case conductivity of composites is found to be 6.8×10^{-1} S/cm. This drastic enhancement of conductivity attributes to the fact that carbon contents played a vital role in the composite. Furthermore, it is worth mentioning that the possible reason of this magically enhanced conduct is consequence of the uniform dispersion of the carbon nano tube in polymer blend. Conductivity can also be enhancing more by increasing filler (CNTs) content into polymer blend.

A comparison of the increase in conductivity through various routes is shown in table 3 where conductivity of composites increase from 6.7×10^{-16} to 1.7×10^{-1} , 1.9×10^{-1} and 6.8×10^{-1} S/cm with addition of carbon nanotubes by simple chemical, heated graphite and graphene oxide respectively. Table 3 shows that conductivity of composites increases in all routes but graphene oxide method is best. Electrical conductivity of sample depends on carrier concentration but in polymer blends carrier concentration is very low, with addition of CNTs into blends increases the carrier concentration which leads to enhance several order times conductivity of composites as compare to bulk polymer. This enhanced electrical property of polymer nanocomposite was very useful in electronics field.

Table 3. Conductivity of PS/PA/PT/CNT_{SC}, PS/PA/PT/CNT_{HG} and PS/PA/PT/CNT_{GO}

Composites	PS/PA/PT/CNT _{SC}	PS/PA/PT/CNT _{HG}	PS/PA/PT/CNT _{GO}
Conductivity	1.7×10^{-1} S/cm	1.9×10^{-1} S/cm	6.3×10^{-1} S/cm

4. Conclusion

Three routes (simple chemical, heated graphite and graphene oxide) were used for synthesis of carbon nanotubes. Polymer matrix consisting on polystyrene, polythiophene and polyamide was mixed with carbon nanotubes for preparation of composites by solution method. XRD confirmed polymer nanocomposites structure and also assured that simple chemical method is best for preparation of small carbon nanotubes. SEM results confirmed uniform dispersion of CNTs into polymer blend. RBS is excellent technique for finding composition of polymer nanocomposites. Results of conductivity show that graphene oxide method is most suitable for enhancement of conductivity.

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