



A Facile Synthesis of New Functional Polyaniline nanocomposites Based on Silver Embedded Poly (Aniline-Co-3-Trifluoromethylaniline): Chemical Characterization, Morphological and Electrical Conductivity Studies

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Abstract

In-situ chemical oxidative polymerization was used to develop a new series of HCl doped and silver embedded poly (aniline-co-3-trifluoromethylaniline) nanocomposites. In order to investigate these copolymer nanocomposites, FTIR, UV-visible spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and a conventional four probe conductivity approach were all used. The developed copolymer has excellent solubility in widely used organic solvents like DMF, THF, and NMP. The spectral value at 341 nm is related to π - π^* electronic transition of benzenoid ring and peak at 624 nm is attributed to n - π^* electronic transition of quinoid ring. The band at 1300 cm^{-1} has been accredited to the combination of C-N in quinoid and benzenoid sequences. X-ray diffraction (XRD) reveals the crystalline nature of copolymer. Surface morphological studies exhibit nanoneedle like appearance with average particle size of 150-300 nm. Because of its less good biocompatibility and less toxicity recent the most recent advances on PANI applications in biomedical fields, such as antioxidant, antimicrobial and antiviral activity, drug delivery, cancer therapy, etc

Keywords: Copolymer, Conductivity, 3-trifluoromethylaniline, Nanocomposites, Morphology.

1. Introduction

Conducting polymers are unique organic semiconducting materials that hold tremendous potential due to their numerous potential technological uses, such as in storage batteries, electrochromic devices, organic light-emitting diodes, nonlinear optics, corrosion inhibitors, and a variety of sensors, including chemical and biosensors[1-3], The most recent advances on PANI applications also includes in biomedical fields, such as antioxidant, antimicrobial and antiviral activity, drug delivery, cancer therapy, etc because of low toxicity and good biocompatibility. Due to the presence of covalent bonds, most polymers are insulators; nevertheless, some polymers can produce conductive paths when exposed to electrical stress.

Under diverse circumstances, these polymers have distinct propensities for creating conductive paths by means of doping. The electrical characteristics of polymers are expressed by a number of characteristics; including resistivity, arc resistance, dielectric constant, and dissipation factor [4]. PANI has garnered significant interest in the design and development of commercial technologies, especially flexible electronic devices, due to its low cost, excellent optical and electrical properties, good environmental stability, and good anticorrosion and mechanical properties. These properties are found in fields such as organic electronics [5], biosensors [6], chemical sensors [7], corrosion devices [8], photovoltaic cells [9], solar cells [10], organic light emitting diodes [11], and electrorheological materials [12].

In general, conductive polyaniline is synthesized by chemical oxidative polymerization of aniline in HCl by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to create emeraldine hydrochloride [13]. Protonation takes place preferentially at the imine repeat units when emeraldine base is equilibrated in a substantial excess of aqueous HCl, leading to emeraldine hydrochloride [14]. Because of doping process, this alters the polymer's structural characteristics, they become highly electrically conductive by introducing the charge carriers [15]. Many atoms may share electrons in conjugated polymers since they can de-localize throughout the polymer chain. Delocalized electrons may travel throughout the entire system and act as charge carriers that render the system conductive. This doping with oxidative process causes to produce cations, or doping it with reduction to produce anions with the addition of electrons to the backbone. An electrical field causes anions and cations to behave as charge carriers by hopping from one location to another, improving conductivity. Hence in the result of Conduction bands and enabling the movement of electrons.

Simultaneously, the copolymerization technique garnered greater interest due to its role in enhancing material solubility, processability, and ability to synthesize materials with specified mechanical, optical, and electrical properties. The use of polyaniline copolymers to combine conductivity and solubility of the substituted polyaniline for practical applications has grown significantly [16]. Studies have shown that conducting copolymers have an advantage over corresponding homopolymers in terms of conductivity, stability, and solubility [17-21]. The presence of halogen-substituted aniline in the copolymer chains, such as fluorine [22-24], chlorine [25,26], iodine [27,28], and bromine groups [29,30] in the polyaniline backbone, has received extensive research. Additionally, Kang and Yun reported that the conductivity is decreased by the substitution of electronegative groups like fluorine and chlorine [31]. According to Neoh et al., the conductivities of polyanilines with iodine and chlorine substitutes are less than 10^{-6} S/cm [32].

The silver nanoparticle was chosen for our investigation among the metal nanoparticles due to its high conductivity and greater thermal stability [33]. Silver nanoparticles are extensively utilised in catalysis [34-37]. Silver nanoparticles significantly enhance the electrical, thermal, and optical characteristics of the polymer matrix. When compared to the bulk substance, the silver nanoparticles with substantial surface areas show high chemical reactivity. The primary goal of this research is the in-situ chemical oxidative polymerization of new copolymer nanocomposites made of evenly inserted silver nanoparticles in poly (aniline-co-3-trifluoromethylaniline). The focus of this study will be on the oxidation state and protonation

level of the copolymers and how these may differ from the homopolymers because the electrical conductivity of polyanilines is connected to the protonation level.

2. Experimental Methods

2.1 Materials

Aniline (Rankem-India) and m-trifluoromethylaniline (Sigma Aldrich, USA) are purified under low pressure and stored at low-temperature for further reaction. Silver nitrate (AgNO_3) and ammonium persulfate (APS) were purchased from MERCK. Concentrated HCl and was used without further purification. Double distilled water was also used for the preparation of polymer materials were purchased from (Emplura-India) and (Hi-media). All other used chemicals are analytical grade. Double distilled water were also used for the preparation of polymer materials.

2.2 Synthesis of silver nanoparticles:

The silver nanoparticle was prepared by the following procedure [38]. First 0.1 M (3.26 gm) of DBSA is dissolved in 90 ml of distilled water. Then aniline 0.019 M (0.184 gm) is gradually added to the reaction mixture and stirred well till a transparent solution was form. After that Silver nitrate solution 0.019 M (0.339 gm) was added to the above solution by drop wise manner. Then the solution is stirred well for 15 minutes and then heated up to 90°C. Then 0.137 M (0.54 gm) of NaOH solution is added to the reaction mixture; the formation of silver nanoparticles was generated and heated further for an hour with constant stirring. The synthesized silver nanoparticle coated with DBSA colloids were cooled down without any further treatment.

2.3 Synthesis of poly (aniline-co-3-trifluoromethylaniline)- silver Nanocomposites:

Protonated poly (An-co-3-TFMA) silver embedded nanocomposite was prepared as follows. 10 mL of Ag nanoparticles was diluted with 70 mL of purified water. Then 0.05 M (0.465 g) of Aniline and 0.05 M (0.806 g) of 3-TFMA were mixed with the solution. Then 10 mL of 0.1M (2.28 g) of APS solution was added slowly drop wise to start the polymerization. The contents are stirred well for 12 hrs in an ice-cold water bath. Finally, the greenish precipitate of poly(An-co-3-TFMA) Ag copolymer obtained were filtered and washed with water, acetone and methanol in order to remove the impurities such oligomer and unreacted monomer. The product was dried in vacuum at 40°C for 24 hrs. Similar procedure was employed to synthesize different copolymers for 3:2 and 3:1 different molar ratio.

2.3 Instrumentation technique

ELICO SL-218 double beam spectroscopy was employed to record the UV-Vis spectra of diluted sample in the range of 200 to 900 nm. All the samples were dissolved in DMSO. FT-IR spectra of poly (aniline-co-m- trifluoroaniline) Ag nanocomposites were measured by SHIMADZU 8400S in the region of 400–4000 cm^{-1} using KBr pellets. Scanning electron microscopy (HR-SEM) HITACHI-SU6600L instrument operating at 25 kV was used to examine the surface morphology of the nanocomposites. The phase identification of the fine powdered sample was performed by Philips X'Pert Pro X-Ray diffractometer with Nickel filtered $\text{CuK}\alpha$ radiation ($\lambda=1.5402 \text{ \AA}$) with the operation of 40 kV. The analysis was performed in the from 5 to 80° at a speed of 2°/min. θ diffraction angle 2 The room temperature conductivity measurement of nanocomposites was measured by a standard four

probe method. The samples were palletized to a diameter of 1.5 cm and a thickness of 0.4 mm using a vacuum press at 12 MPa for 5 min.

3. Results and Discussion:

3.1 Solubility

There are numerous study publications that explore PANI's solubility in the literature [39-41]. The synthesized copolymer nanocomposites were subjected to solubility tests in a variety of polar and non-polar solvents at room temperature. All the samples were dissolved in organic solvents like dimethyl sulfoxide, dimethylformamide, n-methyl pyrrolidone, and tetrahydrofuron. The polymer composites show better solubility in polar solvents. This may be due to the substitution in the aniline decreases the rigidity of the polymer chains. Solubility of the copolymer is increased with increasing the comonomer concentration in the feed. The copolymer's torsional angle renders it more soluble, which lowers the forces that bind molecules together. The copolymer sample's methyl group is responsible for hydrogen bonding, salvation, as well as modifications to the torsional angle [42]. The steric effect of substituent makes the polymer chain to twist. Branches in the polymer chain makes more deformation and more amorphous in nature. Since the polymer is amorphous, the solvent molecules penetrate easily in to polymer and exhibited enhanced solubility.

3.2 Absorption Spectra

The optical absorption spectra of Ag embedded poly (An-co-3-TFMA) in the Fig.1. According to the previously reported results the spectral value at 341 nm is ascribed to $\pi-\pi^*$ electronic transition of benzenoid ring and peak at 624 nm is attributed to $n-\pi^*$ electronic transition of quinoid ring [43]. When the comonomer feed was gradually increased, a blue shift occurred in the distinctive band between 341 and 624 nm. The Ag embedded nanocomposites show bathochromic shift. The alkyl substitution of the m-trifluoromethyl aniline is what causes the blue shift. The photons are joined at the interface of the polymer-metal nanocomposites and improve charge density oscillation that produces a strong absorption peak at specific wavelength. These explanations confirm the silver nanoparticles attached with nitrogen atom. Compared to homopolymer polyaniline, the insertion of a fluoro group in the phenyl rings significantly changes the system's planarity and the pi orbital overlapping.

The polaronic transition is accountable for the absorption band of about 410 nm, which confirms the synthesized copolymer is an emeraldine salt. The Ag embedded copolymer exhibit bathochromic shift increase of effective mass of conduction electrons. When light energy is incident on a polymer metal nanocomposite, charge density oscillations are induced due to combinations of photons at the interface and create a strong absorption band at a particular wavelength.

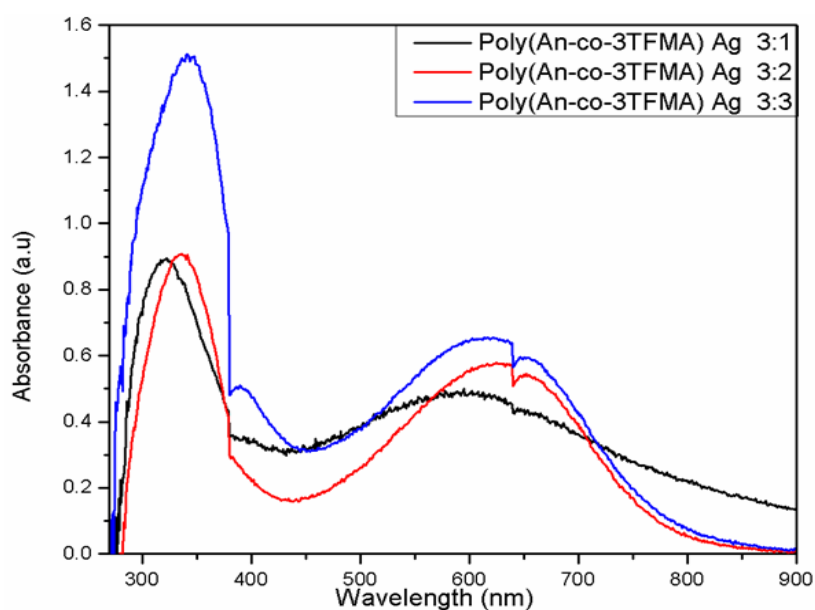


Fig.1 Optical Absorption Spectra of Ag Embedded Poly (An-co-3-TFMA)

3.3 Functional group spectra

Figure 2 shows the FT-IR spectra of Ag embedded poly (An-co-3-TFMA) copolymers. The band at 1300 cm^{-1} has been accredited to the combination of C-N in quinoid and benzenoid sequences. The quinoid and benzenoid sequences in the polymer chain is related to the band at 1580 cm^{-1} and 1485 cm^{-1} respectively. The presence of these two bands demonstrates unequivocally that PANI units make up the copolymers. The peak at 1040 cm^{-1} is due to the presence of a halogen (fluoro) group in the copolymer. The N-H bending vibration and symmetric C=C stretching vibration modes of the benzenoid unit are represented by the bands at 1325 , 1328 , and 1335 cm^{-1} . The characteristic band at 2360 is attributed to the C-H stretching of methyl group [45]. The band at 1230 cm^{-1} is attributed to doped copolymer proton absorption [46].

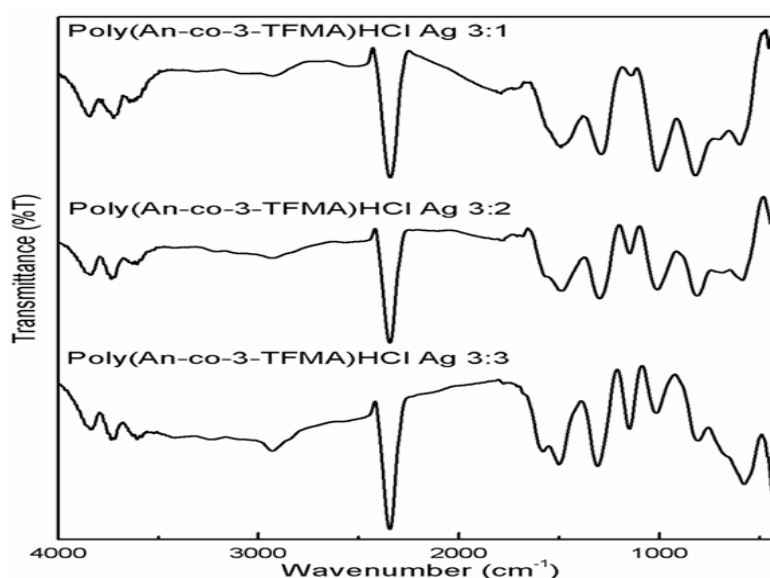


Fig.2 FT-IR Spectral Analysis of Ag Embedded Poly (An-co-3-TFMA)

3.4 Structural studies

The powdered XRD pattern of HCl doped Ag dispersed poly (An-co-3-TFMA) nanocomposites is shown in Fig. 3. A broad band at $2\theta = 25^\circ$ is due to the amorphous nature of the poly (An-co-3-TFMA) [47]. The steric effect of substituted bulky trifluoromethyl group causes random arrangement of polymer chains and the weak force of attraction between the chains resulting amorphous nature. Substitution of bulky trifluoromethyl group in the polymer chain offered steric hindrance which results the irregular arrangement of the polymer chain. The sharpness of the peak increases as the concentration of the trifluoromethylaniline increases indicates the better crystallinity of the copolymer. Some peaks at 15° and 20° are due to semi-crystalline or amorphous nature of the copolymer. The appearance of sharp peak at 27° , 32° , 46° and 77° with low intensity indicates the presence of silver nanoparticles. These peaks confirm the Ag dispersion in the polymer chain and agreed with the values in JCPDS no. 85-1355. The crystallinity increases as the comonomer concentration is increased due to the bromoaniline encourages the crystalline nature. When comparing to the pure copolymer system the silver dispersed copolymer indicates more crystalline nature.

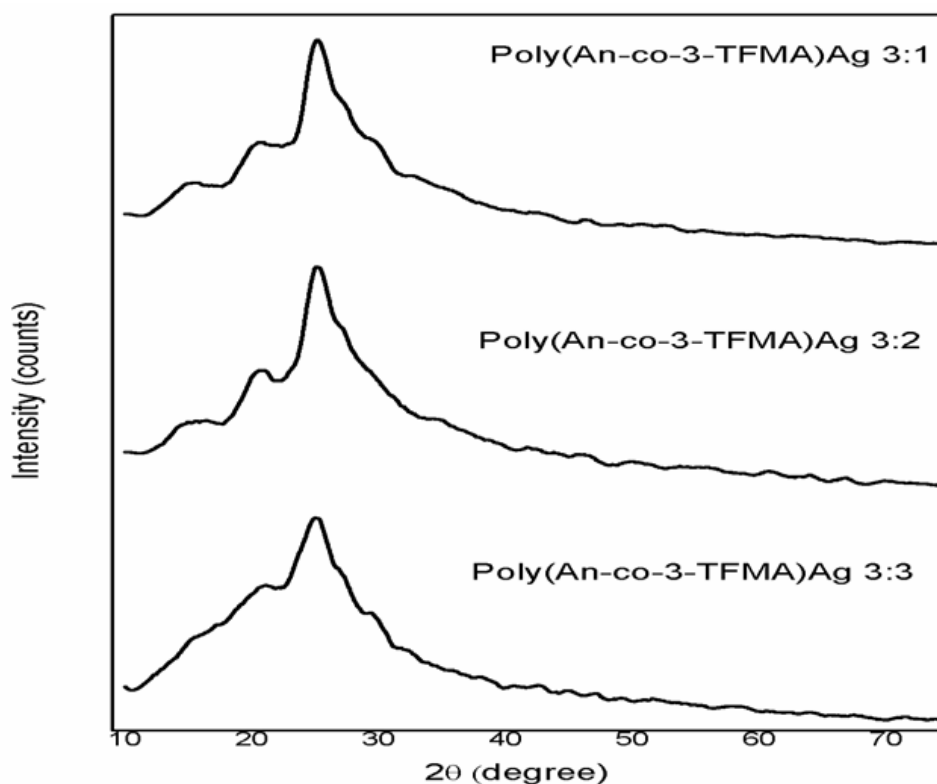


Fig.3 XRD Spectrum of Ag Embedded Poly (An-co-3-TFMA)

3.5 Surface Morphology

Fig.4 (i, ii, iii&iv) shows the SEM images of HCl aided Ag embedded poly (An-co-3-TFMA) nanocomposites. It shows the large number of spherical granular structures with agglomerated particles. The average size of the particle is 200 nm. It also exhibits a nanoneedle like appearance with average particle size of 150-300 nm. It attributes the interaction between the aniline and 3-trifluoromethylaniline molecules. The spherical shape is due to the shape of coiling of polymer chains.

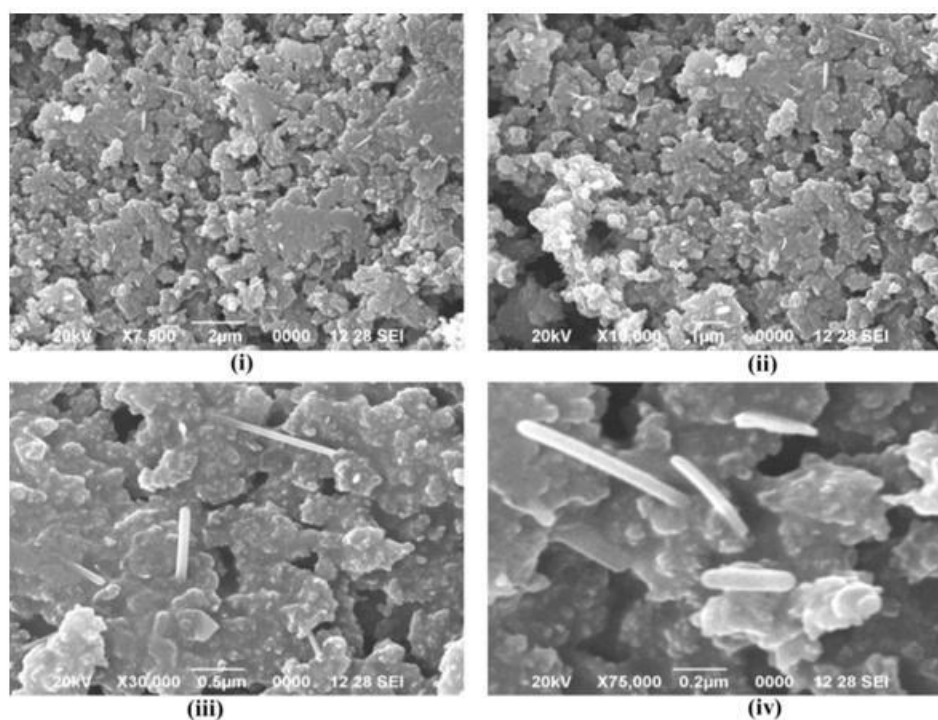


Fig. 4 SEM images of Ag embedded poly (An-co-3-TFMA)

Fig.4 (iv) showed that the nanocomposites are similar to single nano needle with an average length of 500-700 nm encapsulated in the polymer matrix. Nanorod like structure has formed due to the huge number of agglomerated particles stacked one over the other. The aniline nucleates become stable due to π - π interactions among phenazine containing oligomers. The one dimensional needle structure is obtained due to formation of these new nucleates on hydrophobic front of the growing fiber [48]

3.6 Electrical Conductivity

The electrical conductivity of Ag-embedded poly (An-co-3-TFMA) copolymer is shown in the table 1. The usual four-probe method was used to assess the electrical conductivities of Ag-embedded poly (An-co-3-TFMA) nanocomposites and polyaniline (PANI) at room temperature. Pure polyaniline has a measured conductivity of 10^{-2} S/cm [50]. The Ag dispersed poly (An-co-3-TFMA) nanocomposites is found to be 4.54×10^{-6} S/cm. This may be due to the side chains' steric barrier and the reduced conjugations are to blame for the reduced conductivity. Steric hindrance decreases the conductivity of polymers and restricts the flow of charge carriers [51].

Table .1 Electrical Conductivity Values of nanocomposites

Copolymer compositions	Conductivity (S/cm)
Polyaniline-HCl	1.98×10^{-2}
HCl doped Poly (An-co-3-TFMA) Ag 3(An):1(3-TFMA)	1.34×10^{-5}
HCl doped Poly (An-co-3-TFMA) Ag 3 (An) :2 (3-TFMA)	2.50×10^{-5}
HCl doped Poly (An-co-3-TFMA) Ag 3 (An) :3 (3-TFMA)	4.54×10^{-6}

As the concentration of comonomer increases in the feed, the electrical conductivity of Ag dispersed poly (An-co-3-TFMA) nanocomposites decrease. This is due to the increasing concentration of electronegative fluorine atoms reduces the mobility of the charge carriers along the polymer chain. Low conductivity is caused by the electronegative fluorine atom, which slows down the electron charge transport [52]. When the comonomer concentration is increases in the feed ratio, the electrical conductivity is decreased. This is due to the electronegative fluorine atom hinder the mobility of the charge carriers and increases disorder in the polymer matrix.

4. Conclusions

The HCl doped Ag embedded poly (An-3-TFMA) nanocomposites were synthesized by chemical oxidative in-situ polymerization method. In comparison to polyaniline, the copolymer has improved solubility. The nanocomposites are soluble in polar solvents like DMSO, DMF, and NMP with high efficacy. FT-IR and UV validated the chemical composition and absorption of nanocomposites. Due to the addition of Ag nanoparticles, the XRD pattern endorses the crystalline character that the nanocomposites possess. The SEM images indicate that the development of these new nucleates on the hydrophobic front of the developing fiber results in the formation of a one-dimensional needle structure. The increase in electronegative fluorine atom concentration limits the mobility of the charge carriers along the polymer chain, which results in a decrease in electrical conductivity. The application of these prepared polymeric materials is studied in the future in the form of humidity sensor and electromagnetic shielding purposes.

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