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OPTICAL, STRUCTURAL, THERMAL AND MORPHOLOGICAL CHARACTERIZATION OF 4, 4'-DIAMINODIPHENYL SULPHONE/TITANIUM DIOXIDE/MULTIWALLED CARBON NANOTUBE NANOCOMPOSITES

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ABSTRACT

Polymeric nanocomposites based on electroactive conductive polymers with nanoparticle fillers have won considerable attention in recent years due to its highly desirable multifunctional characteristics. In the present study, 4, 4'-diaminodiphenyl sulphone has been polymerized and composites were prepared by adding TiO₂ and multiwalled carbon nanotube to the polymer by magnetic stirring. These nanocomposites have been characterized using analytical techniques such as UV-Vis, FT-IR, XRD, FE-SEM, EDS and TGA/ DTA analysis. The incorporation of multiwalled carbon nanotube and titanium dioxide in poly 4, 4'-diaminodiphenyl sulphone has been endorsed by FT-IR analysis. It showed that the peak at 453, 431 cm⁻¹ confirms the stretching vibration of the Ti-O bond of TiO₂ and the absorption peaks at 2925 and 2283 cm⁻¹ are imputed to symmetrical telescopic vibrations of the methylene group (-CH2-) of carbon nanotubes. This confirms the incorporation of TiO₂ and multi-walled carbon nanotubes into the polymer matrix in the prepared nanocomposites. The XRD pattern showed formation in the nanoscale range (5.94 nm). SEM analysis showed that the variation in polymer morphology depended mainly on titanium dioxide and multi-walled carbon nanotubes.

Keywords: Nano composites, 4, 4'-diaminodiphenyl sulphone, Titanium dioxide, Multiwalled carbon nanotube.

1. INTRODUCTION

The conductive polymer and its compounds attracted the attention of researchers to these materials because of its widespread applications in organic light-emitting diodes (OLEDs), polymer solar cells, antistatic coatings and electromagnetic interference (EMI) shielding [1]. In recent years, polymer nanocomposites based on active conductive polymers and nanoparticulate fillers have attracted great attention. Nanocomposites differ from conventional composites owing to the unexpected high surface-to-volume ratio of the reinforcement phase and their superior aspect ratio. The reinforcing material can consist of particles (for example, minerals), sheets (for example, piles of exfoliated clay) or fibers (for example, carbon nanotubes or electrospun fibers). The interface area between the matrix and the supercharging phase is typically an order of magnitude greater than for conventional composite materials. This large area augmentation means that a relatively small amount of nano-scale reinforcement can have an observable effect on the macroscopic properties of the composite, such as improved electrical and thermal conductivity, elevated optical properties, dielectric properties, heat resistance or mechanical properties for instance stiffness, strength and resistance to wear and damage [2]. Carbon nanomaterials have attracted great attention in different fields of research for their fascinating chemical, electronic and mechanical properties [3]. Among them, carbon nanotubes (CNTs) have been widely used in the detection of biomolecules, due to their unique structures, high stabilities, low resistivities, and high surface to volume ratios [4, 5]. The well-known effective metal oxide of titanium, TiO₂ as semiconductors, grabs the attention of researchers due to its unique physical and chemical properties. In addition, TiO₂ has other amenities, such as abundance, low cost, non-toxicity, strong oxidizer, structural and chemical stability. Based on these properties, TiO₂ has been applied in many

fields, including photocatalysis, sensors, solar cells and lithium-ion batteries [6-10]. Aniline-based copolymers have gained importance in recent times. These compounds consist of aniline units and other monomers responsible for significantly different behavior standards compared to pure homo-polymers [11-13]. The use of diphenylamine derivative as one of the monomers during polymerization process provides a simple way of modification. In the present study, conductive poly (4, 4'-diaminodiphenylsulfone) (PDDS) was prepared by a chemical oxidative polymerization process. PDDS nanocomposites with titanium dioxide and multi-walled carbon nanotubes were prepared and their properties investigated.

2. MATERIAL AND METHODS

2.1. Synthesis of Poly (4, 4'-diaminodiphenylsulfone) (PDDS)

To the solution of the monomer 4, 4'-diaminodiphenylsulfone (0.1 M), in the HCl (1 M), the oxidant FeCl_3 (0.01 M) was added drop wise and stirred using magnetic stirrer at 25°C for 24 hours to complete polymerization. The polymer formed was collected by filtration and washed several times with water and ethanol and dried in vacuo.

2.2. Synthesis of Poly (4, 4'-diaminodiphenylsulfone) with titanium dioxide nano composites (DT)

To the solution of monomer 4, 4'-diaminodiphenylsulfone (0.1M), in HCl (1M), oxidant FeCl₃ (0.01M) was added drop wise with constant stirring. To the reaction mixture TiO₂ (0.2g) was added and stirred using magnetic stirrer at 25°C for 24 hours to complete the polymerization. The fabricated composite was collected by filtration and washed several times with water and ethanol and dried in vacuo.

2.3. Synthesis of Poly (4, 4'-diaminodiphenylsulfone) with multi walled carbon nanotube (DM)

To the solution of monomer 4, 4'-diaminodiphenylsulfone (0.1M), in HCl (1M), oxidant FeCl₃ (0.01M) was added drop wise with constant stirring. To the reaction mixture Multiwalled carbon nanotube (0.2g) was added and stirred using magnetic stirrer at 25°C for 24 hours to complete the polymerization. The formed composite was collected by filtration and washed several times with water and ethanol and dried in vacuo.

2.4. Synthesis of Poly (4, 4'-diaminodiphenylsulfone) with titanium dioxide and multi walled carbon nanotube nano composites (DTM)

To the solution of monomer 4, 4'-diaminodiphenylsulfone (0.1M), in HCl (1M), oxidant FeCl_3 (0.01M) was added drop wise with constant stirring. To the reaction mixture Titanium dioxide (0.2g) and Multiwalled carbon nanotube (0.2g) was added and stirred using magnetic stirrer at 25°C for 24 hours to complete the polymerization. The composite generated was collected by filtration and washed several times with water and ethanol and dried in vacuo.

2.5. Characterization

The prepared nanocomposites were characterized by various instrumental techniques. The FT-IR measurements of prepared nanocomposites as KBr disks were performed on a Thermo Scientific Nicolet iS5 FT-IR spectrometer in the frequency range of 400 to 4000 cm^{-1} . UV-Vis spectra of the samples in DMF were taken using JASCO-V 630 dual beam spectrophotometer in the wavelength region 200 to 900 nm with a scanning speed of 400 nm/min. X-ray diffraction patterns of the polymers were obtained by employing XPERT-PRO diffractometer using CuK α (k α = 1.54060) radiation. The diffractometer was operated at 40 Kv and 30 mA. Powder X-ray diffraction pattern was recorded. The morphological study of the polymers were carried out using Field Emission Scanning electron microscope (FE-SEM) with Energy Dispersive X-ray Spectroscopy (EDS) analysis was obtained using TESCAN MIRA3 XMU. Thermal study of the nanocomposites was studied by analyzing the weight loss pattern upon subjecting the material to heat using Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) techniques. The thermograms were recorded using EXSTAR/6300 TG/DTA instrument with programmable rate of 0.01- 100° C/min.

3. RESULTS AND DISCUSSION

3.1. UV-Vis spectra

The UV-Visible spectra of the constituents and the composites are given in fig. 1. The absorption spectra for Multi walled carbon nanotube shows a peak around 298nm, due to different plasmon resonances of free π electrons of the nanotubes present in the MWCNT [14]. The absorption spectra for Poly diaminodiphenyl sulfone (PDDS) shows a hump around 292 nm due to the π - π * transitions of the conjugated benzenoid band in the

polymer [15]. This peak shifts slightly to higher wavelength confirming the presence of benzene ring in the prepared nanocomposites. PDDS/ TiO₂ nanocomposite (DT) shows a broad band around 400 nm, which is assigned to polaron- π * transition. The broadness suggests the existence of quinine-imine moieties. Bathochromic shift of this absorption peak was observed for prepared nanocomposites from that of PDDS indicating the formation of DM and DTM. The spectrum of DT shows a band at 294 nm due to the n- σ * transitions

of TiO₂, which shows hypsochromic shift when compared to the absorbance at 300 nm for TiO₂ nanoparticles [16]. By comparing the relative peak heights at 296 nm and 400 nm, we can see that DTM nanocomposites exhibit higher absorbance than other nanocomposites. This suggests that there is an interaction between the benzenoid rings of PDDS, multi-walled carbon nanotubes, and titanium dioxide that enhances the formation of the polaron- π * transition of the polymer chain.



Fig. 1: UV-Vis spectra of a) MWCNT b) DM c) DT d) DTM e) TiO₂ f) PDDS.

3.2. IR spectra

The FT-IR spectra of the nanocomposites are shown in fig.2. A wide band is seen around 3371 cm-1 due to N-H stretching vibration of the imino group of the polymer chain in all the composites [17]. The peak at 1406 cm⁻¹ is assigned to S=O stretching vibrations in PDDS. The peaks at 1294 cm⁻¹ in all spectra are affiliated with C-N stretching into benzenoid units. The peaks at 831cm⁻¹ can be imputed to the C-S vibrations in polymer. Aromatic C-H stretching vibrations are present at 691 cm⁻¹. It can be observed from the spectra of nano-composites DT, DM and DTM that the characteristic PDDS bands move to a lower wavenumber, indicating that there is a strong interaction between TiO₂, multi-walled carbon nanotubes and polymer chains [18]. The change in polymer peaks of nanocomposites is due to the formation of hydrogen bonds between the oxygen of TiO₂ and the hydrogen of the -NH- group present in the polymer [19]. In addition to the previous peaks, the presence of the peak at 453, 431 cm⁻¹ confirms the Ti-O bond stretching vibration of TiO_2 and this confirms the incorporation of TiO_2 into

the polymer matrix in DT and DTM nanocomposites [20]. The absorption peaks at 2925 and 2283 cm⁻¹ is attributed to symmetrical telescopic vibration of methylene group (-CH₂-) of carbon nanotubes in DM and DTM [21]. The peaks around 1590 cm⁻¹ are syndicated with the C = C stretch of multi-wall carbon nanotubes present in DM and DTM nanocomposites [22-24].

3.3. XRD analysis

The results of x-ray diffraction are exhibited in fig. 3. XRD pattern of PDDS does not show any sharp peaks which is due to the amorphous characteristic of the polymer [25].

The XRD spectrum of DT is shown in fig. 3. The peaks at $2\theta = 27.68$, 36.30, 39.40, 41.43, 44.25 and 54.53 can be mapped to the crystal planes (1 1 0), (1 0 1), (2 0 0), (1 1 1), (1 2 0) and (2 1 1) corresponding to the well of the JCPDS card No. 96-900-1680 [26]. The grain size was calculated by Scherrer's formula [27] and the particle size is observed to be 7.73 nm. XRD models of DT composites show characteristic peaks not

only for PDDS but also for TiO_2 nanoparticles, which demonstrates the existence of TiO_2 nanoparticles in the composites. This confirms that the DT nanocomposites become semi-crystalline because TiO_2 is present in the nanocomposite. PDDS deposited on the surface of TiO_2

particles were influenced by crystallization behavior of TiO₂ particles in nanocomposites [28]. The XRD spectrum of DM shows a peak at $2\theta = 26.14$ which can be attributed to the plane (0 0 2) which agrees well with the JCPDS card No. 96-101-1061 [29]. The particle size is 1.66 nm.



Wavenumbers(cm⁻¹)

| Fig. 2: IR-spectra of a) | PDDS b |) DT c |) DM d) |) DTM |
|--------------------------|--------|--------|---------|-------|
|--------------------------|--------|--------|---------|-------|

| Table 1: Comparison of FT-II | k spectral data of a |) PDDS b) DT c |) DM d) DT | M |
|------------------------------|----------------------|----------------|------------|---|
|------------------------------|----------------------|----------------|------------|---|

| Polymer | v(N-H) stretch of NH group (cm ⁻¹) | v(S=O) _s (cm ⁻¹) | (C=C) Of aromatic rings (cm ⁻¹) | (-CH ₂ -) of carbon nanotubes (cm ⁻¹) | v(C-N) _s (cm ⁻¹) | v(C-S) _s (cm ⁻¹) | Aromatic (C-H) _s (cm ⁻¹) | M-O bond stretch of TiO ₂ (cm ⁻¹) |
|---------|---|--|---|---|--|--|---|--|
| PDDS | 3371 | 1406 | - | - | 1294 | 722 | 691 | - |
| DT | 3366 | 1407 | - | - | 1293 | 831 | 553 | 453 |
| DM | 3458 | 1462 | 1591 | 2925 | 1293 | 832 | 689 | - |
| DTM | 3359 | 1468 | 1592 | 2283 | 1293 | 851 | 660 | 431 |

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The XRD pattern of DM nanocomposite shows partial amorphous and partial crystalline nature. Here the sharp peaks show that the nanocomposite has acquired crystalline nature due to the presence of multiwalled carbon nanotube.

The XRD spectrum of DTM shows peaks at 2θ = 27.58, 36.22, 41.38, 44.14, 54.46 and 56.51 which can be ascribed to the planes (1 1 0), (1 0 1), (1 1 1), (1 0 1), (1 2 0) and (2 1 1) which correspond to the JCPDS Card No. 96-410-2356 [30] and the particle size is 5.94 nm. The XRD patterns of DTM nanocomposites become more crystalline as the Multiwalled carbon naanotube and TiO₂ is present in the nanocomposite.

3.4. FE-SEM and EDS analysis

Scanning electron microscopy was used to analyze the morphology and the growth characteristics of the prepared nanocomposites are shown below. Fig. 4a.

shows the morphology of PDDS to be granular and uniform. EDS results reveal that the polymer contains Carbon, Nitrogen, Oxygen and Sulphur in 64%, 2.60%, 26.81% and 6.59% respectively as shown in the fig.4 b.

Morphology of DT (fig.5a) shows some larger spheres covered by smaller spheres. Here the larger spheres indicates the polymer PDDS [31] and the smaller spheres indicate the titanium dioxide. EDS results affirm that the composition of carbon, nitrogen, oxygen, sulfur and titanium is 32.17%, 13.8%, 27.41%, 0.51% and 26.11% respectively, as shown in fig. 5b.

Morphology of DM (fig.6a) shows some larger spheres covered by tube like structure. Here the larger spheres indicates the polymer PDDS and the tube like structure indicate the multiwalled carbon nanotube [21]. The results of the EDS reveal that the composite constitutes carbon, nitrogen, oxygen and sulfur at 74.16%, 1.89%, 10.38% and 13.57% respectively as shown in fig. 6b.





Fig. 3: XRD patterns of PDDS, DT, DM, DTM nanocomposites

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Fig. 4a: SEM image of PDDS



Fig. 4b: EDS image of PDDS



Fig. 5a: SEM image of DT



Fig. 5b: EDS image of DT



Fig. 6a: SEM image of DM



Fig. 6b: EDS image of DM

In the fig.7a. the morphology of DTM shows that the polymer surface has highly agglomerated grains due to multi-walled carbon nanotubes and TiO_2 nanoparticles are dispersed uniformly in the polymer matrix and this can modify the properties of the PDDS. The figure shows that the granular shapes indicates titanium dioxide and the polymer PDDS. Tube like structures indicates multiwalled carbon nanotube. From the

image, it is evident that DTM nanocomposites have the properties of PDDS, multiwalled carbon nanotubes and TiO_2 . EDS results show that the composite contains carbon, nitrogen, oxygen, sulfur and Titanium elements in percentages of 23.19, 3.25, 22.70, 7.10 and 43.76 respectively, as shown in fig. 7b. Confirm the formation of DTM nanocomposites.



Fig. 7a: SEM image of DTM





3.5. TG/ DTA analysis

TG/DTA techniques establish the thermal stability of the prepared nanocomposites. Fig.8 and 9 shows the TGA/DTA curves of DT and DM. It can be seen that four stages of weight loss events were observed in the temperature range of 80 to 1000°C. The first stage of weight loss below 100°C is due to moisture loss, the second weight loss in the range of 300°C is due to the evaporation of inorganic materials [32] and the third major weight loss around 400-500°C is due to the evaporation of organic material [33]. The fourth weight loss around 780-800°C is due to the evaporation of other non reactive materials present in the nanocomposites. The weight loss is gradual and not sharp as the composite is partially amorphous.

Fig.10 shows the TGA/DTA curves of DTM. It could be seen that five stages of weight loss events were observed in the temperature range of 80 to 1000° C. The first stage of Weight loss below 100° C is due to loss of moisture, the second weight loss occurring in the range of 200°C is owing to some traces of densification of the amorphous TiO₂ network by the contraction of



Temperature ⁰c

Fig. 8: TG/DTA image of DT



Fig. 10: TG/DTA image of DTM

distance between layers. The shrinkage can easily be seen in the structure. Condensation, due to free bonds due to the elimination of the -OH group and shorten the distance between layers and possibly generate space between walls confirming the formation of mesoporous nanotubes [34-36]. The third weight loss at 380°C is due to the evaporation of inorganic materials and the fourth major weight loss around 420°C is owing to the multi-walled carbon nanotube combustion reaction. The fifth weight loss around 600-800°C is due to the evaporation of other non-reactive materials present in the nanocomposites.



Temperature %

Fig. 9: TG/DTA image of DM

4. CONCLUSION

Polymeric nanocomposites synthesized by chemical method were categorized by analytical techniques such as UV-Vis, FT-IR, XRD, FE-SEM, EDS, and TGA/ DTA analysis. FT-IR spectra confirmed the interaction of the multiwalled carbon nanotube and titanium dioxide in the PDDS matrices. FT-IR peaks at 453, 431 $\rm cm^{-1}$ affirm presence of TiO₂ and the absorption peaks at 2925 and 2283 cm⁻¹ are attributed to the symmetrical telescopic vibrations of the methylene group (-CH2-) of carbon nanotubes. The FE-SEM images show that the morphology of DTM has the polymer surfaces with highly agglomerated grains due to multiwalled carbon nanotube and TiO₂ nanoparticles uniformly dispersed in the polymer matrix. This may change the properties of PDDS. It is clear that DTM nanocomposites have the properties of PDDS, multi-wall carbon nanotubes and TiO₂ nanoparticles. XRD results show that the particle

size of the polymer nanocomposites (DTM) is 5.94 nm. The thermal behavior of the composite material confirms the improved thermal stability of the intercalated titanium dioxide and multiwalled carbon nanotube. These properties can make this nanocomposite attractive for practical applications such as processable biosensor and energy storage devices.

Conflict of interest

None declared

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