

TiO₂/PANI nanocomposite loaded in PVA for anticorrosive applications

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We report the morphological and electrical study of a composite of polyvinyl alcohol (PVA) and nanotitanium dioxide (TiO₂-50 nm) in conducting polymer polyaniline (PANI). The composite was synthesized using in-situ polymerization technique. The composite was characterized in terms of morphology and electrical properties using scanning electron microscopy and DC electrical conductivity (σ_{dc}). We observed that the DC electrical conductivity of the composite film increased with increasing the loading of nanocomposite material from 20 % to 40 % into PVA stabilizer. The DC conductivity results showed that the molecular chain contribution of the nanocomposite material (nano-TiO₂+ PANI) was the prominent carrier in the composite film made of the nanocomposite and PVA stabilizer.

Keywords: *DC conductivity; nanocomposite; in situ polymerization; corrosion; PVA*

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1. Introduction

Conducting polymers have emerged as a separate class of materials with the development of new technologies and their applications in various fields. Among a number of conducting polymers, polyaniline (PANI) shows remarkable properties and thereby corresponding applications in sensors [1–3], solar cells [4], corrosion coatings [5], electronic devices [6], field effect transistors [7], electromagnetic shielding [8], etc. To achieve high electrical conductivities, polyaniline can be doped with protonic acids [9–11]. But simultaneously, other factors, like its processing [12–14] and lack of solubility in common solvents, restrict its applications. The compatibility of PANI with polyvinyl alcohol (PVA) [15–17], results from molecular interactions [17] which lead to a change in its specific properties associated with solubility [18], electrical conductivity [15, 19], and mechanical

properties [20]. PVA is soluble both in hot and cold water, which makes it a suitable material for the synthesis with PANI [21, 22]. PVA has several advantages that make it an appropriate choice to be used for developing a composite which distinguish itself from other composites like PMMA [23] and polyethylene oxide [24].

In the present study, we have synthesized the nanocomposite of nano-TiO₂ and PANI which then was loaded in polyvinyl alcohol matrix. We have studied different weight percentage loading ratios, i.e. from 20 wt.% to 40 wt.% by the morphological and electrical analysis.

2. Experimental

2.1. Materials

The chemicals: aniline (Emerck), polyvinyl alcohol (Emerck), titanium dioxide 50 nm (SRL), HCl (Emerck), ammonium peroxodisulfate (Emerck) used in the processing of the composite were of analytical grade.

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2.2. Synthesis of composite

The synthesis of nanocomposite material (TiO₂/PANI) was carried out in a 250 mL round-bottom flask equipped with a stirring assembly. First, 1 g of TiO₂ nanoparticles (size of 50 nm) were dispersed in 50 mL of 1N HCl solution under ultrasonic vibrations to reduce the aggregation of TiO₂ nanoparticles and then 2 mL aniline were added dropwise into the solution under constant stirring. After one hour, a solution of 4.9984 g of ammonium peroxydisulphate ((NH₄)₂S₂O₈) and 1N HCl were added dropwise into the aniline and TiO₂ solution. Polymerization was carried out at a temperature of 0 °C to 5 °C with controlled stirring for 5 h. Dark green TiO₂/PANI composite was then filtered and washed with distilled water several times. So, the core shell nanocomposite of (TiO₂/PANI) was synthesized without any surfactant. The PVA solution was prepared by dissolving PVA powder in 300 mL of distilled water at temperature of 80 °C to 90 °C under continuous stirring for 3 hours. Core shell nanocomposite (TiO₂/PANI) was then added into the PVA solution at different weight percentage ratios 20 wt.% to 40 wt.% at room temperature and the mixture was continuously stirred for 10 hours. The blended solution was allowed to dry in a Petri dish under ambient temperature for four to five days. The obtained sheets of the nanocomposite materials were used in such form for characterization.

2.3. Characterization

The morphology of the nanocomposite materials was studied using a scanning electron microscope (SEM Model: 6610 LV). The DC electrical conductivity of the composite film was investigated for different compositions of nanocomposite (TiO₂/PANI) materials with a Keithley 6487 unit. For electrical study silver was used as electrode material. All measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the SEM micrographs (magnification of × 1000 to × 3000 at 5 kV) for the

core-shell TiO₂/PANI nanocomposite material. The SEM micrographs show that the TiO₂ nanoparticles are fully covered with polyaniline. This could be due to the formation of the core shell structure of TiO₂/PANI i.e. the formation of PANI shell on the surface of TiO₂ nanoparticles which caused repulsion forces between the nanoparticles and prevented their agglomeration [25, 26].

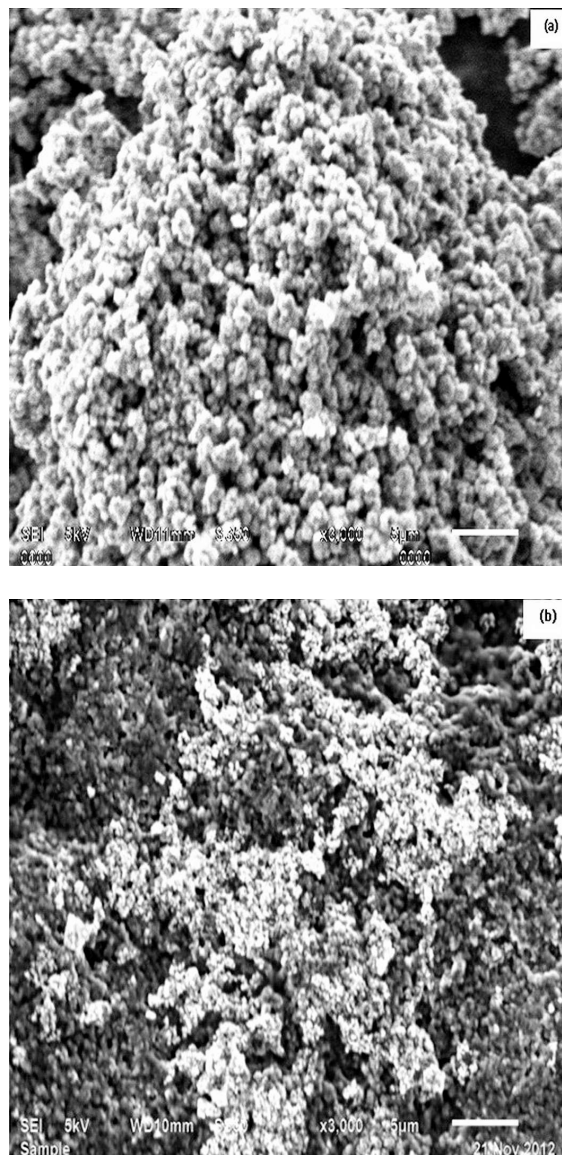


Fig. 1. SEM micrographs of core-shell TiO₂/PANI nanocomposite at two magnifications.

Fig. 2 shows the SEM micrographs of a 40 wt.% TiO₂/PANI nanocomposite loaded to PVA.

The micrographs reveal that on addition of core-shell TiO₂/PANI nanocomposite to PVA, a homogeneously distributed fibrous type structure has been obtained. PVA as stabilizer helped also in developing this fibrous structure due to cross linking of PANI and PVA [27]. Similar results were also reported by Somani et al. [28] for the surface of TiO₂ when PANI content was high.

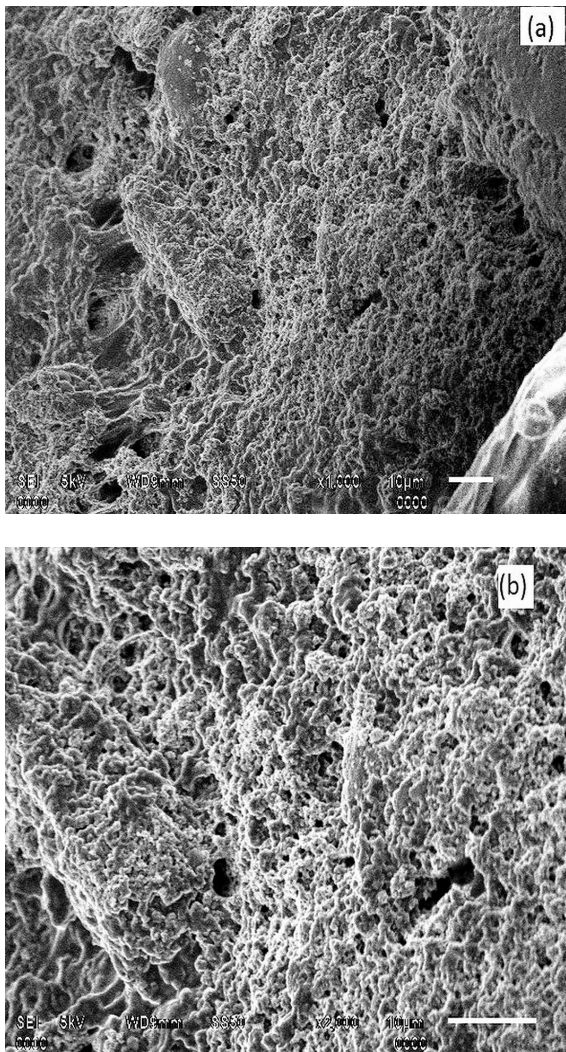


Fig. 2. SEM micrographs of core-shell TiO₂/PANI nanocomposite loaded in PVA stabilizer.

The DC electrical conductivity of the composite film for different compositions of nanocomposite (TiO₂/PANI) materials loaded in PVA materials was investigated with a Keithley 6487 unit in which probe distance was maintained

at 1 mm and film thickness was 0.745 mm. Fig. 3 shows the variation of DC electrical conductivity ($\log\sigma$) with increasing doping concentration of core-shell TiO₂/PANI nanocomposite to PVA stabilizer at room temperature in the voltage range of 10 V to 100 V. The variation of conductivity over this voltage range clearly shows that with the increase of core-shell TiO₂/PANI nanocomposite loading to PVA, the conductivity increases with increasing voltage. It can be observed that at room temperature the DC conductivity of core-shell TiO₂/PANI nanocomposite loaded PVA varies from 1.54×10^{-12} S/cm to 3.21×10^{-7} S/cm with increasing content of the nanocomposite from 20 wt.% to 40 wt.%. This increase in conductivity may be attributed to the increased amount of TiO₂/PANI which maximizes the number of carriers. The highest number of carriers can further be attained by the delocalization effect of doping process and the formation of polarons or bipolarons in the composite structure, thereby increasing the conductivity of nanocomposite [29–33]. The increase in conductivity may also be explained on the basis of good correlation (discussed later) between PANI and TiO₂ [34] and thereby lower resistance and faster response which can be offered by the nanocomposite (TiO₂/PANI) for the transport of electrons between conduction band of TiO₂ to lower the orbitals of polyaniline [35].

Fig. 4 shows a comparison of our results for DC conductivity (σ) of core-shell TiO₂/PANI nanocomposite loaded in PVA from 20 wt.% to 40 wt.% with (i) PANI-HCl loaded in PVA stabilizer where PANI volume percentage varies from 20 % to 40 % [33] and (ii) PANI-SnO₂ hybrid nanocomposite where SnO₂ nanoparticles increases from 20 % to 40 % [32]. We have further compared the correlation coefficient from our results with PANI-PVA [33], PANI-SnO₂ nanohybrid material [32] and nano-TiO₂+ PANI [36]. The values of the correlation coefficients have been given in Table 1. The correlation coefficient shows that the synthesized PANI was deposited on the surface of nano-TiO₂ material and formed encapsulated structure [36]. This encapsulated nanocomposite material (nano-TiO₂+ PANI) when loaded to PVA

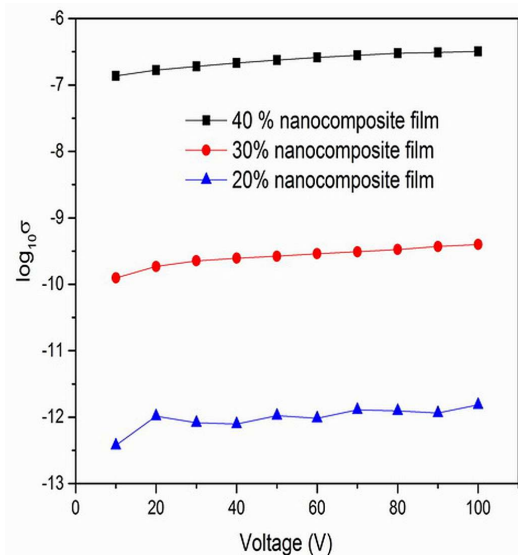


Fig. 3. Variation of $\log\sigma$ with voltage for different composite film.

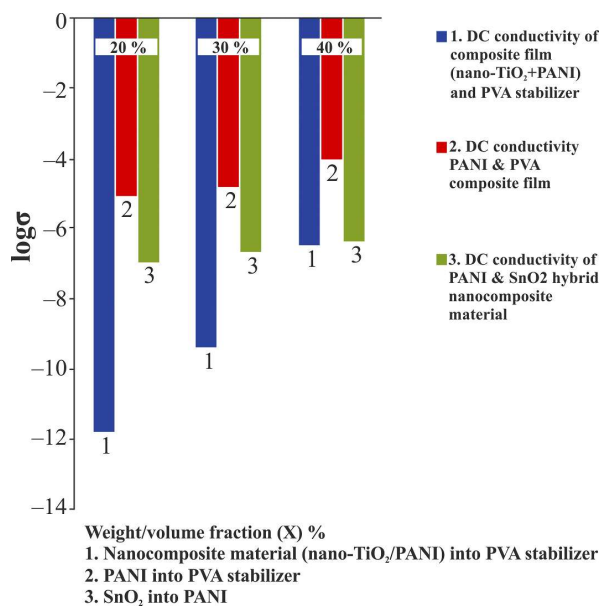


Fig. 4. Comparison of DC conductivities of different composite materials.

stabilizer made a conductive nanocomposite which showed a good correlation coefficient, i.e. 0.997, and forecasted correlation coefficient of 0.999 (Table 1). The DC conductivity of PANI/PCC [35] was 1.03×10^{-5} S/cm for anticorrosive performance on mild steel surfaces. Our results of DC conductivity are also in agreement with the reported ones and

Table 1. Comparison of correlation coefficient for core-shell TiO₂/PANI nanocomposite loaded to PVA (this work) with PANI and PVA [33], PANI-SnO₂ nanohybrid material [32], nano-TiO₂+ PANI [36].

Sample	Correlation coefficient	Forecasted correlation coefficient
This work	0.997	0.999
[33]	0.914	0.914
[4]	0.999	0.999
[3]	0.99998	0.99998

the reported nanocomposite loaded in PVA matrix might be explored for anticorrosive applications on steel surfaces.

4. Conclusions

We have synthesized the core-shell nanocomposite of nanotitanium dioxide in polyaniline. The flexible and conductive films have been prepared with blending of different percentages of core-shell TiO₂/PANI composite in water soluble polymer PVA. We have observed regular shape and fibrous structure of PANI-TiO₂-PVA composite film. The DC electrical conductivity of this composite material was found to increase from 1.54×10^{-12} S/cm to 3.21×10^{-7} S/cm with increasing amount of the nanocomposite (from 20 wt.% to 40 wt.%). Looking at the electrical results and comparing them with other materials of similar kind, these compositions may be explored for electrical, electronics-related and anticorrosive applications.

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