Research Article ISSN 2832-9384

Journal of Materials and Polymer Science

In Situ Synthesis of Polyaniline Nanohybrid and Formulation of Polyaniline/ Carboxymethyl cellulose/Ethylene Glycol Nanocomposite: Study of its Conducting and Antibacterial Properties

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Submitted : 22 Aug 2023 ; Published : 20 Nov 2023

Citation : Yakubu, A. et al (2023). In Situ Synthesis of Polyaniline Nanohybrid and Formulation of Polyaniline/Carboxymethyl cellulose/Ethylene Glycol Nanocomposite: Study of its Conducting and Antibacterial Properties. *J mate poly sci, 3*(4): 1-9.
DOI : https://doi.org/10.47485/2832-9384.1041

Abstract

Polyaniline (PANI) has received great attention as a conducting polymer from researchers in the field of organic synthesis and development of conducting nanocomposite polymer technology for superconductors. Different methods of PANI synthesis are being sought for the obtainment of electrically robust PANI composites for electronic and other useful applications. Different inorganic matrices have been considered for this purpose. This study attempts to prepare PANI In situ on arginine-modified nanoclay template by chemical oxidation polymerization. Further, the PANI/Arginine-modified nanoclay was used to prepare PANI/Arginine-Nanoclay/Carboxymethyl cellulose/ Ethylene glycol conducting film with robust electric conductivity (EC). Electrical conductivities, anti-bacterial evaluation, Fourier-transform infrared spectroscopy (FT-IR), thermogravimetry analysis (TGA), differential thermogravimetry analysis (DTG) and Scanning Electron Microscopy (SEM) were used for the characterization studies and property evaluation. The electrical conductivities of PANI/Arginine-Nanoclay/Carboxymethyl cellulose/Ethylene glycol nanocomposite film reached 1900 S/Cm. FT-IR data, 3304–3196, 2926–2828, 2200–2022, 1733, 1620 and 1052 cm^{-1} respectively, confirmed the presence of organic intercalates, CMC, quinoid and benzenoid rings of PANI, and the inorganic nanoclay matter in the nanocomposite film. SEM revealed the presence of spine-like nanoflowers with elongated and expanded particle agglomerations. Thermal stability of the prepared nanocomposite thin film reached 700°C. The zone of inhibition ranged from 24-36 mm against S. typhi, E. coli and S. aureus. In conclusion, PANI nanocomposite thin conducting films had robust EC and antibacterial properties. In addition, the In-situ synthesis of PANI on Arginine-modified nanoclay platform aided the electric conductivity of the nanocomposite system.

Keywords: Antibacterial properties; Electric conductivity; Nanocomposite; Organo-nanoclay; Polyaniline.

Introduction

Of the many conducting polymers, polyaniline (PANI) has gained the interest of researchers in the last few decades and now, many researchers have developed renewed interest on PANI especially, on development of new methods for PANI synthesis (Wu et al., 2018; Karbownik et al., 2019) with special attention given to the fabrication of its hybrid composites with many of the inorganic materials with known stable chemical and physical properties such as clay/nanoclay for science/ engineering applications (Boeva & Sergeyev, 2014). PANI has high stability and process ability with tunable conducting and optical properties. It has a metal-like conductivity when the pH is less than 3.0 (Yakhmi et al, 2012) or a pH range of 1-3 (Boeva & Sergeyev, 2014). The different forms of PANI, which have been widely documented are based on the oxidation states (Leucoemeraldine, Emeraldine, and Pernigraniline) (Kalotra & Mehta, 2020). According to Bhandari (2018), only the moderately oxidized form of PANI shows conducting properties while the fully oxidized form of PANI has good insulating properties. The polymer backbone consists of both quinoid and benzenoid rings in differing proportions. The difference in the ratio causes the existence of three oxidized forms of PANI: the fully reduced leucoemeraldine form is in a quinoid state, the fully oxidized Pernigraniline form is in a benzenoid state and the conducting emeraldine form has an

equal ratio of both benzenoid and quinoid rings. The dopant does not change its chemical property and will not create any bond with the main chain; it exists in the close vicinity of the polymer chain (Boeva & Sergeyev, 2014). PANI composites system have been investigated based on different filler contents or solvents and the corresponding effects on the PANI properties investigated (Wu et al., 2018; Karbownik et al., 2019). Karbownik et al. (2019) reported in situ synthesis of PANI/PANI composite with improved thermal and mechanical properties.

Fibrillated Zn/PANI/graphite composites have been designed and used for rechargeable battery with a specific energy of 280 (W h)/kg. However, the drawback in the battery power of about 0.15 % was recorded, and was attributed to the degradation of PANI structure (Boeva & Sergeyev, 2014). A pH range of 1-3 has been reported to play an important role on the conductivity of PANI composites (Ravindrakumar, 2014). Polyaniline has found useful applications in drug delivery; photovoltaic cells; plastic batteries; display devices; super capacitors; microelectronics; chemically modified electrodes; corrosion protection and polymer light-emitting diode (PLED) displays and many other applications such as in water purification, due to its specific properties (Boeva & Sergeyev, 2014; Ravindrakumar, 2014; Ahlatcioglu, Şenkal & Okutan, 2015; Wu et al., 2018; Karbownik et al., 2019) and as an enzyme immobilizing and electrocatalytic material (Ahlatcioglu et al., 2015). Nanoclay and its derivatives are known for their robust performance as fillers in different applications, due to their large surface area, high chemical/thermal stability, ultrafine particle size, high adsorption capacity and ion exchange properties (Ahlatcioglu et al., 2015; Kalotra & Mehta, 2020) and clay ability to enhance PANI electrical conductivity (Boeva & Sergeye, 2014).

The filler used in this study is an organically modified nanoclay which was obtained in aqueous solution. Clay and CMC have high tendency to enhance the electrical conductivity, mechanical and thermal properties of PANI when used in the formulation of its thin films.

In the study we present the results of findings on organically modified nanoclay, denoted as Arginine-modified nanoclay with the arginine intercalates as the reinforcement in an In situ and One-pot matrix reaction to produce an organic-inorganic PANI/Arginine-modified nanoclay dark-green particles (Ternary nanocomposite). The prepared ternary PANI/Arginine-modified nanoclay nanocomposite was further used for the preparation of PANI/Arginine-modified/CMC/EG nanocomposite thin film with conducting and antibacterial properties.

Materials and Methods

Materials

Arginine ($C_6H_{14}N_4O_2$), Aniline (C_6H_7N) with (99.5% pure) and molecular mass 93.13 g/mol, and density, 1.02 g/mL, potassium dichromate ($K_2Cr_2O_7$) of molecular mass 294.185 g/mol and HCl of molecular mass 36.46 g/mol and density 1.2 g/mL were BDH chemicals, purchased from reliable chemical vendors, Nahson and Panlac enterprises, Nig. Ltd. All reagents used in this study were of analytical grade. All reagents were used as received except, aniline, which was vacuum distilled before used.

Synthesis of PANI using $K_2Cr_2O_7$ as an oxidizer and HCl as dopant

Polyaniline (PANI) was synthesized by chemical oxidation polymerization method using $K_2Cr_2O_7$ as oxidizer while HCl as dopant in aqueous solution (Wu et al., 2018). In a typical experiment, 0.1 M of aniline was prepared and 50 mL of the prepared solution was measured and transferred into a beaker 500 mL beaker and placed in an ice-bath. Into this solution was gradually added 20 mL HCl, the mixture was vigorously stirred for one hour and there was a colour change from brown to colourless. 50 mL of aqueous solution of $K_2Cr_2O_7$ (Oxidant) was added drop-wise while the solution being vigorously stirred on a mechanical stirrer equipped with a stirring bar until a purple colour was observed indicating the formation of polyaniline (Pernigraniline) base (PANI-PB), and from purple to dark green, indicating the transformation of Pernigraniline to emeraldine salt (PANI-ES). After vigorous stirring for 2h it was kept at room temperature for 24 h for complete polymerization. Filtration was achieved by vacuum using a 0.004 µm cellulose acetate membrane filter while dilute solution of HCl acid was used for repeated washing of the final product (Plate I). Afterwards, it was dried in an oven at 60 °C for 12h. The synthesized PANI was grind and stored in sample bottles for further analysis.

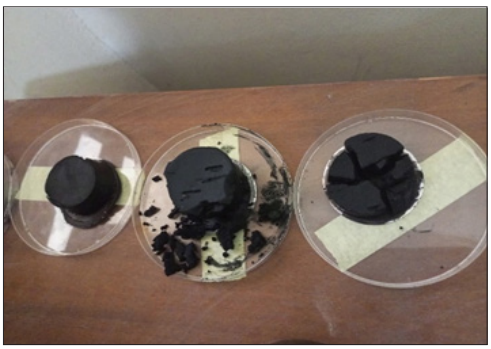


Plate I: PANI product obtained after filtration

In situ Synthesis of PANI/Arg-Modified-Nanoclay Composite: PANI was synthesized in situ in arginine-modified nanoclay suspension. 0.1 moldm^{-3} of aniline was dissolved in 20mL of HCl to form the hydrochloride. Arginine-Modified nanoclay powder was added as weight percent (0.001, 0.002, 0.04, 0.006, 0.008 and 0.01 wt%) respectively to the aniline hydrochloride solution coupled with vigorous stirring for 1 h in order to keep the C_6H_7N.HCl/Arg-Modified nanoclay composite mixture in suspension. Into this reaction mixture was slowly introduced 50 mL of $K_2Cr_2O_7$ (Oxidant) with continuous stirring for 2h using a magnetic stirring bar in an ice-bath. Precipitation occurred and the precipitate formed was allowed to stand for 24h to settle. It was then, filtered to separate the precipitate (Ternary nanocomposite) from the supernatant. The precipitate recovered was washed with 20 mL dilute HCl. Finally, the

sample was dried in an oven at 60°C for 6-8 h until constant weight. The In situ synthesized PANI-Arg-Modified nanoclay (Ternary nanocomposite) was powdered into fine particles and stored in polyethylene bags for further analysis. This procedure was repeated using five different weight percent (wt%): 0.002, 0.04, 0.006, 0.008 and 0.01 wt% respectively of the Arg-Modified Nanoclay powder using $K_2Cr_2O_7$ as the oxidant and HCl (Dopant) to obtain PANI/Arg-Modified Nanoclay composites (Plate II).

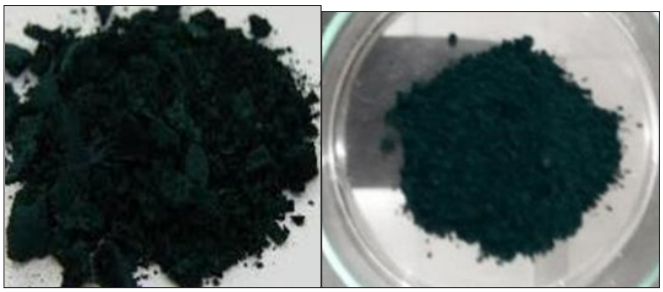


Plate II: PANI/Arg-Modified Nanoclay Composite (Ternary Nanocomposite)

Preparation of PANI/Arg-Modified Nanoclay/CMC/EG Thin Film Nanocomposite

One gram (1.00 g) of carboxyl methylcellulose (CMC) was weighed and placed into a 250 mL beaker followed by the addition of 30 mL (NaOH), 20 mL (H_2O), 10 mL (Dilute acetic acid) and 2.5 mL (Ethylene glycol). The mixture was stirred until complete dissolution of CMC was observed. Into this homogenous solution was introduced 0.001, 0.002, 0.003, 0.004, and 0.005 w% of the fine dark-green powder of PANI/Arg-Modified nanoclay (Ternary nanocomposite) and then, stirred continuously until a dark-green gel mixture was obtained. The gel product was then, cast on a smooth surface and was allowed to dry at room temperature for 24 h. Afterwards, it was peeled-off the surface to afford a PANI/Arg-Modified-Nanoclay/CMC/EG transparent and flexible thin film nanocomposite (Plate III). This procedure was repeated using different gram of PANI/Arg-Modified-Nanoclay composite powder to prepare PANI/Arg-Modified-Nanoclay/CMC/EG.

Plate III: Prepared Flexible PANI/Arg-Modified-Nanoclay/CMC/EG Thin Film Nanocomposite

Anti-Bacterial Evaluation

A non-synthetic medium was used. Nutrient agar was prepared by dissolving 28.0g of the powdered medium in a liter of distilled water and the agar, sterilized at 121 °C for 15 min at a pressure of 1.5 Nm^{-2}. The sterilized medium was allowed to attain a dispersing temperature (45 °C – 50 °C) and then, dispersed into a sterilized petri-dish and allowed to solidify before holes were made inside, using a sterilized cork borer of 6.0 mm in diameter. Nutrient broth was prepared by dissolving 13.0g of the powder in 1L of distilled water then, 10mL of the broth was dispersed into a test-tube and sterilized, cool before use.

Reconstitution

The biofilm was reconstituted to liquid form by weighing 0.3g (300 mg) and was dissolved in 5 mL of Dimethyl Sulphur Oxide (DMSO). This was further distilled with 3 mL sterile distilled water. Therefore, the concentration of each biofilm was 300 mg/8 mL (37.50 mg/mL). This served as dilate used for the antibacterial activity.

Inoculation

The test bacterial was inoculated into broth medium (Nutrient broth) and was incubated for 30 min at 37 °C. The broth was sub-cultured into another free sterile broth using a loopful of the wire-loop. The sub-cultured broth was incubated for 3 h at 37 °C. The turbidity of the incubated sub-culture was compared with McFarland's turbidity standard before use. The above compared culture after attaining turbidity standard was inoculated unto nutrient agar petri-dish using swab sticks.

Dispersing the Liquid Biofilm

After inoculation of the plate holes with the test organism (Bacteria), followed by the introduction of 2 mL of the biofilm into the inoculated plate holes and allowed to stand for 2 h for effective diffusion into the wells. The plates containing the test bacteria and the diffused biofilm were incubated in the incubator at 37 °C for 24 h.

Characterization

Electrical Conductivity

Electrical conductivity for PANI/Arg-Modified-Nanoclay/CMC/EG (0.10, 0.30, and 0.5 g) for the nanocomposite films of both modified and control were measured using CT-3030 hand-held conductivity meter in wet-phase. The electrical conductivity of the distilled water was first measured after, which the nanocomposite films were each immersed in distilled water and conductivity values obtained for each sample. Distilled water is a very poor conductor of electricity, so the more swellable the film in water, the higher the conductivity values obtained.

Fourier Transform Infrared Synthesized Nanocelluloses (FT-IR)

The FT-IR spectra of nanocomposite thin film were determined using FT-IR-8400S Fourier Transform Infrared Spectrometer in the spectra range of 4000-400 cm^{-1}. Nanocomposite thin film samples were run as (KBr) pellets.

Scanning Electron Microscope (SEM)

The morphology of the surface was observed using a scanning electron microscope, TESCAN, VEGA SEM, Czech Republic. The PANI/CMC/EG/Arg-modified nanocomposite thin film

samples were prepared by fracturing small pieces of the monolithic PANI/CMC/EG/Arg-modified nanocomposite in order to investigate the surface morphology of these PANI/CMC/EG/Arg-modified nanocomposite samples. The samples were coated with gold under a vacuum using TESCAN sputtering before imaging in order to increase the image resolution. All SEM images were taken at an acceleration voltage of 5.0 keV.

Thermal Stability

The thermal stability of the native, nanoclay and modified derivatives were characterized by a simultaneous thermal analyzer (Metler, Toledo, TGA/SDTA 851e instrument with the heating rate of 10 °C/minutes from 30 °C to 900 °C under a nitrogen atmosphere with a flow rate of 30 mL/minute. The percentage of the weight loss was reported as a function of the temperature.

Results

Results obtained for the various characterization techniques employed for sample studies are as presented in Tables 1-3 and Figures 1-4 respectively.

S/No	PANI/ Arg-Nanoclay/ CMC/EG Film (g)	PANI/ Arg-Nanoclay/ CMC/EG Film (g)	Film: Distilled Water Ratio	Electric Conductivity (S/cm)
1	0.1	0.1	1:50	$8.3x10^2$
		0.3	1:50	$1.9 x10^3$
		0.5	1:40	$1.8x10^3$
2	0.2	0.1	1:20	$1.4 x10^3$
		0.3	1:40	$1.9 x10^3$
		0.5	1:50	$1.9 x10^3$
3	0.4	0.1	1:50	$1.7 x10^3$
		0.3	1:50	$1.5 x10^3$
		0.5	1:60	$1.6 x10^3$
4	0.6	0.1	1:50	$1.8 x10^3$
		0.3	1:50	$1.6 x10^3$
		0.5	1:80	$1.8 x10^3$
5	0.8	0.1	1:40	$1.8 x10^3$
		0.3	1:60	$1.7 x10^3$
		0.5	1:80	$1.8 x10^3$
6	1.0	0.1	1:30	$1.9 x10^3$
		0.3	1:30	$1.9 x10^3$
		0.5	1:70	$1.9 x10^3$

Table 1: Electrical Conductivity of PANI/Arg-Nanoclay/ CMC/EG Nanocomposite Film

S/No	PANI/ CMC/ Modified Nanoclay film (g)	PANI/ CMC/ Unmodified Nanoclay film (g)	Film: Distilled water ratio	Electric conductivity (S/cm)
1	0.0	0.1	1:20	$8.8x10^1$
		0.3	1:20	$1.5x10^3$
		0.5	1:50	$1.9x10^3$
2	0.2	0.1	1:50	$1.1x10^2$
		0.3	1:30	$1.9x10^3$
		0.5	1:30	$1.8x10^4$
3	0.4	0.1	1:20	$2.7x10^2$
		0.3	1:80	$1.8x10^3$
		0.5	1:80	$1.6x10^3$
4	0.6	0.1	1:50	$4.2x10^2$
		0.3	1:50	$6.5x10^2$
		0.5	1:60	$8.7x10^2$
5	0.8	0.1	1:20	$6.6x10^2$
		0.3	1:50	$1.8x10^3$
		0.5	1:40	$1.2x10^3$
6	1.0	0.1	1:40	$1.7x10^4$
		0.3	1:40	$1.8x10^3$
		0.5	1:20	$8.7x10^2$

Table 2: Electrical Conductivity of PANI/CMC/EG Unmodified Nanoclay Composite Film

S/No.	Sample Code	Sample Composition (g)	Sample Composition (PANI/CMC/Arg-nanoclay)(%)	*S. typhi* Zone of inhibition (mm)	*E-coli* (mm)	*S. aureus* (mm)
1	PANI/CMC/Arg/modified nanoclay	1.0/1.0/1.0	33.3/33.3/33.3	36	24.00	32.00
2	PANI/CMC/Arg/modified nanoclay	0.2/1.0/0.2	14.3/71.4/14.3	34	29.00	30.00
3	PANI/CMC/Unmodified nanoclay	1.0/1.0/1.0	33.3/33.3/33.3	36.00	26.00	32.00
4	PANI/CMC/Unmodified nanoclay	0.2/1.0/0.2	14.3/71.4/14.3	0.00	0.00	0.00

Table 3: Diameter of Zone of Inhibition for Anti-bacterial Activity of the Films

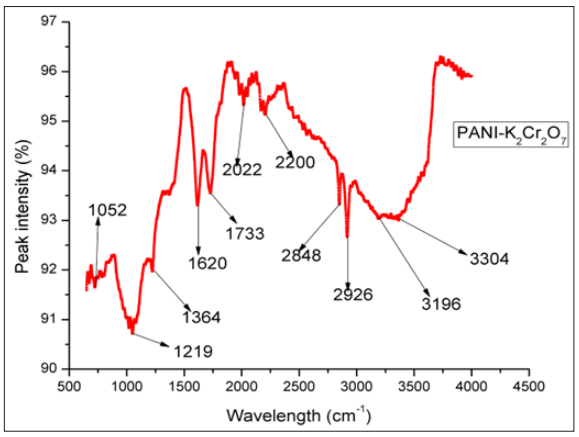


Figure 1: FTIR Spectra of PANI/CMC/Arg-Modified Nanoclay

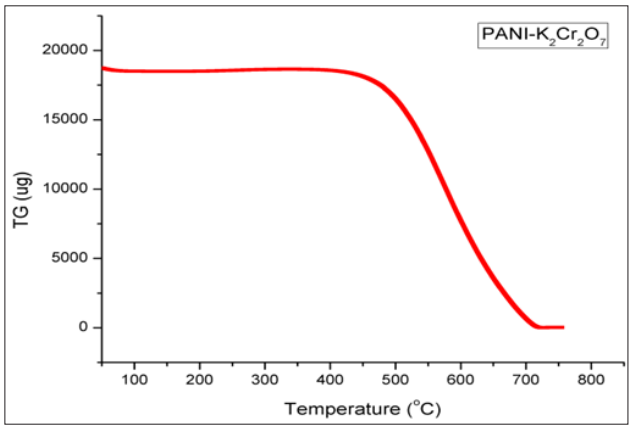


Figure 2: TGA Spectra of PANI/CMC/Arg-Nanoclay Composite Thin Film

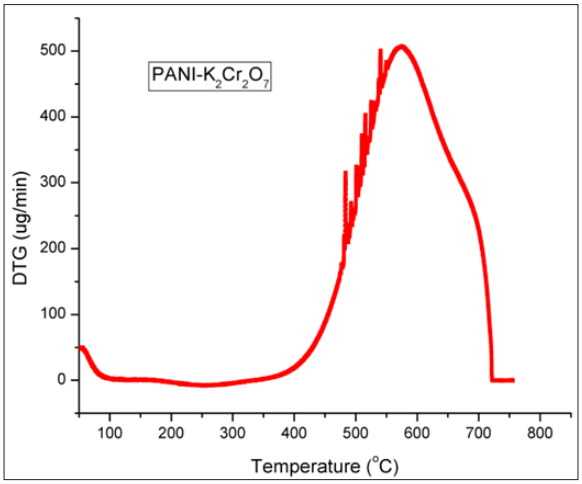
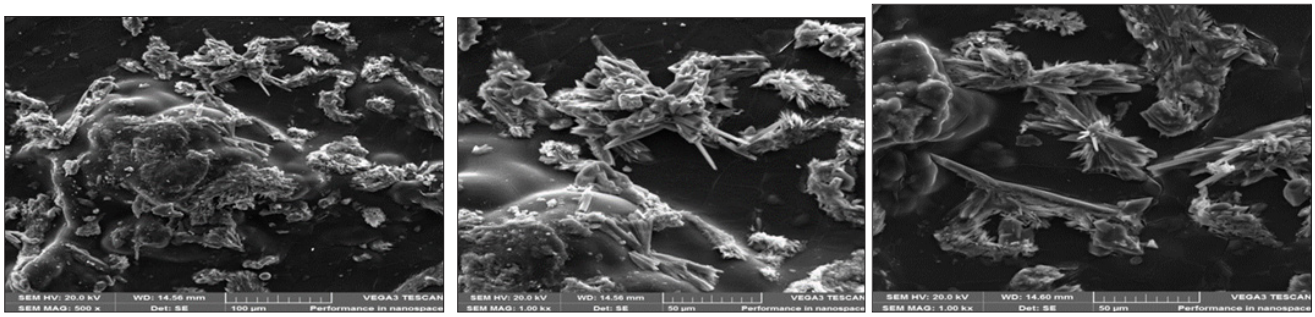
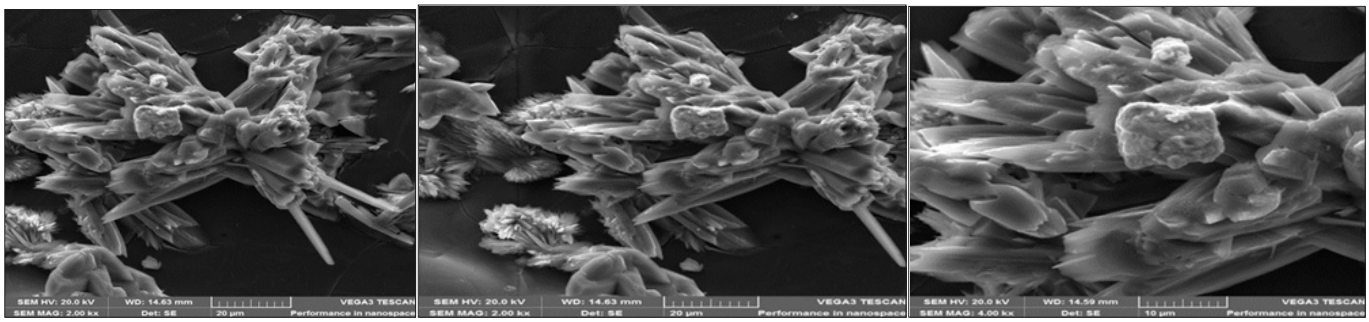


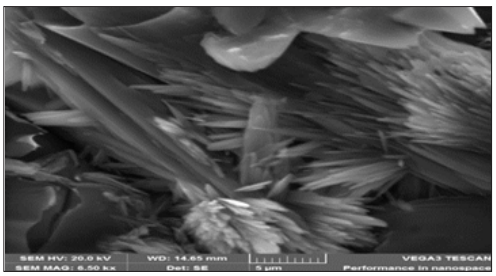
Figure 3: DTG Spectra of PANI/Arg-Modified-Nanoclay/CMC/EG Nanocomposite Thin Film



(a) (b) (c)



(d) (e) (f)



(g)

Figure 4: SEM Image of PANI/Arg-Modified-Nanoclay/CMC/EG Nanocomposite Thin Film

Discussion

Electric Conductivity of Nanocomposite Film

Results for the PANI/Arg-Modified-Nanoclay/CMC/EG thin film nanocomposite formulated in this study are presented in Table 1. PANI as a conductive polymer has found various applications in electronics (Bia et al., 2021). In this study, the electric conductivity of the PANI/Arg-Modified-Nanoclay/CMC/EG nanocomposite thin film was studied using the wet-phase method in distilled water, taking advantage of the swellability of the CMC film matrix in water. The highest EC recorded in this study was 1900 Scm^{-1} while the least recorded value of EC was 830 Scm^{-1}. The highest EC recorded in our study far exceeded 1.2 Scm^{-1}, the EC value reported for pure PANI (Boeva & Sergeyev, 2014). The values in our study are also, higher than those reported by Olad and Rashidzadeh (2008) on PANI/Na-MMT and PANI/O-MMT composite, where pure PANI films had 1.275 Scm^{-1} whereas, PANI/5 % Na-MMT and PANI/5 % O-MMT had EC values of 1.201 and 1.650 Scm^{-1} respectively. However, the EC values recorded in our study are low compared to 4000 Scm^{-1}, the highest ever recorded EC value for PANI composite (PANI/SWCNTs) reported by Wu et al. (2018). This method is believed to enhance ion mobility of nanoclay and PANI crystals in the film, making them available to conduct and as well, enhanced the electrical conductivity of PANI (Tables 1 and 2). This, the researchers attributed the enhanced electric conductivity of the thin films to the occluded water in the clay pores as suggested by Usmani et al. (2016). The presence of rod-like crystals/flakes of PANI nanoflowers on the film morphology further, supports the high EC values obtained with the film in wet-phase, corresponding to the large surface area of nanoflowers (Hossein & Rahi, 2016; Zhang et al., 2017; Shende et al., 2018; Shcharbin et al., 2019; Dangare et al., 2020). EC of the thin films may also, be attributed to the expanded PANI molecular layers caused by the intercalation of organo nanoclay plates into the PANI matrix. It is worthy to note that nanoclay layers as potential templates for synthesis could enhance the In situ synthesis of expanded-elongated PANI-Arg-Nanoclay-CMC-EG nanocomposite (Organic-Inorganic hybrid nanoflowers) coils with high EC. This finding is similar to that proposed by Wu et al. (2018) on PANI/CNTs composites. Thermoelectric and electrical conductivity of various PANI composites have been reviewed by Singh and Shukla (2019).

Antibacterial Evaluation

The antibacterial activity of PANI/Arg-Modified-Nanoclay/CMC/EG nanocomposite thin film was investigated using susceptibility studies. The results for diameter zone of inhibition for *Salmonella typhi*, *E. coli* (Gram negative) and *Staphylococcus aureus* (Gram positive) as test organisms are presented in Table 3. The films with different formulation compositions exhibited appreciably and interestingly good antibacterial activity against the test organisms. This could be due to the organic intercalates (Arginine molecules), expanded nanoclay interlayer (Increased d-spacing) and the hybrid PANI crystallite nanoflowers on the film surface might have enhanced the surface reactivity of the hybrid films (Shende et al., 2018; Shcharbin et al., 2019; Dangare et al., 2020). PANI/Arg-Modified-Nanoclay/CMC/EG nanocomposite thin film with a composition of 0.01/0.01 wt% and 0.002g/0.002 wt% respectively, had zone of inhibition of 36 and 34 mm, 24 and 29 mm and 32 and 30 mm for *Salmonella typhi*, *E. coli* and *Staphylococcus aureus*. PANI/Arg-Modified-Nanoclay/CMC/EG nanocomposite thin film with a composition of 1g/1g showed comparable antibacterial activity against *Salmonella typhi* (36 mm), *E. coli* (26 mm) and *S. aureus* (32 mm) respectively. Whereas no activity was recorded for the PANI/Arg-Modified-Nanoclay/CMC/EG nanocomposite film with a 0.002/0.002 wt% composition. Results indicate that modification of nanoclay with the ammonium ion of the amino acid, arginine and its use in conjunction with PANI in formulating thin film nanocomposites could enhance the antibacterial properties of thin film, which may find useful medical applications such as, for surface wound healing, and for active food packaging applications (Fasihnia et al., 2017). In addition, the antibacterial properties of the thin films have been attributed to the presence of nanoclay hybrid layers, CMC and their ability to remove water molecules from the environment thus, leaving the organisms dehydrated and/or disabling them and eventual death. Other researchers have reported the antibacterial properties of different clay matrices. A study by Elele et al. (2020) show that Arginine-modified nanoclay could inhibit the growth of *E. coli* and *Staphylococcus aureus*, where both hybrid clay materials respectively had 18 mm and 19 mm zone of inhibition. In another study, Azeh et al. (2021) demonstrated the ability of nanoclay modified with the amino acid (arginine) to inhibit the growth of *E. coli* with zone of inhibition of 16 mm and 18 mm as well as, 14 mm recorded against Pseudomonas aeruginosa while *Staphylococcus aureus* and *Proteus Sp*. respectively, had 19mm zone of inhibition. In the present study, zone of inhibitions recorded against *E. coli* and *S. aureus* were higher compared to those earlier reported by Elele and Co-workers (2020) and Azeh and Co-workers (2021). Caitlin and Shelley, (2013) reported a broad-spectrum antibacterial potential of native clay by In vitro studies. They show that the clay mixtures inhibited growth of Escherichia coli and methicillin-resistant *Staphylococcus aureus* (MRSA). Chitosan-clay nanocomposites coupled with antimicrobial agents have been used as active packaging materials in different food applications (Bai and Yangchao, 2021). Chitosan-Kaolinite (Neji et al., 2020) and Chitosan-Sapiolite composites showed enhanced antibacterial properties

due to the presence of clay particles as reinforcement (Tekin et al., 2019; Li et al., 2020). Other properties like, the antioxidant potentials were reported to improve in Chitosan-clay composite (Bai & Yangchao, 2021). Other mechanisms for the inhibition of microbes could be the widely accepted mechanisms of ammonium ion ($R\text{-}NH_3^+$), Fe, Cu and Zn metal ions in clay and their ability to react with the negative charges in the cell membrane of the microorganisms (Caitlin & Shelley, 2013; Jiwook et al., 2018). CMC/gelatin/TiO_2/Ag composite were shown to have antioxidant/antibacterial properties (Sajad et al., 2020). In the present study, nanoflowers (Shende et al., 2018; Shcharbin et al., 2019; Dangare et al., 2020) were seen on the surface of the organic-inorganic hybrid nanomaterials. This the researchers attributed to the enhanced antibacterial properties of the nanocomposite thin films.

FT-IR Analysis

In Figure 1 below the FT-IR bands found around 3304 cm^{-1} and 3196 cm^{-1} are due to the N–H of amine (NH_2) group in nanoclay modified with the arginine and the PANI ring imine respectively (Olad & Rashidzadeh, 2008; Oraon et al., 2015; Oraon et al., 2017; Karbownik et al., 2019). The peak at 2926 cm^{-1} and 2828 cm^{-1} have been attributed to the stretching vibration of Sp^3 C-H vibration in CMC and arginine respectively (Oraon et al., 2015). The aromatic overtones for the C=C were found around 2022 cm^{-1} and 2200 cm^{-1} respectively, indicating the presence of quinoid and benzenoid structure in the nanocomposite, mainly due to the PANI polymer chains (Wu et al., 2018; Karbownik et al., 2019). The band at 1733 cm^{-1} is due to C=O and –COO- vibrations, resulting from amide bond in modified nanoclay (Karbownik et al., 2019). The band at and 1620 cm^{-1} has been assigned to C=C of the PANI polymer chains (Olad & Rashidzadeh, 2008). Kalotra and Mehta, (2020) reported this peak at 1556 and 1485 cm^{-1} in PANI-MMT composites at different MMT loading while Karbownik et al. (2019) observed the peak at 1588 cm^{-1}. The band observed at 1364 cm^{-1} is due to C-H bending vibration in CMC film matrix and PANI composite. The peak at 1219 cm^{-1} was due to C-N+ polymer chains similar to the findings by Ahlatciogu et al. (2015); Oraon et al. (2017) and Karbownik et al., (2019) on PAN/PANI composite fibers. The peak at 1052 cm^{-1} in the composite have been assigned to Si-O-Si and C-O-C, which confirms that the nanoclay and the CMC structures were not destroyed (Ahlatcioğlu et al., 2015; John et al., 2015; Oraon et al., 2017).

Thermogravimetric Analysis (TGA and DTGA)

The TGA curve of PANI/Arg-Modified-Nanoclay/CMC/EG nanocomposite film is depicted in Figure 2. The minima were observed which revealed the majority weight loss of the particular steps. The one-stage thermal degradation observed around 450 °C to 750 °C maybe attributed to the loss of absorbed water in the film (Zeng & Ko, 1998; Nithyaprakash et al., 2014) and decomposition of dopant and dehydroxylation of the inner -OHs in nanoclay and the CMC skeleton (Nobrega et al., 2012). The remarkable stability observed could be linked to the nanoclay matrix. The differential thermogravimetry analysis (DTG) of the sample (Figure 4.3) revealed a two-step decomposition pattern. The first step occurred slightly below 100 °C and may be due to loss of CO, CO_2, NH_3, etc. The maximum stability of the film reached 600 °C, which was due to the presence of clay nanolayers in the thin film.

Scanning Electron Microscopy (SEM)

The morphology of the synthesized PANI/Arg-Modified-Nanoclay/CMC/EG nanocomposite thin film was investigated by SEM at different magnifications. Figure 4 showed the morphology of PANI/Arg-Modified-Nanoclay/CMC/EG nanocomposite showing several features ranging from flower-like, platelet-like, rod-like, spine-like and fibrous-like particles (Perera et al., 2014; Samzadeh et al., 2016) on the film surface and in the matrix of the film forming agent, CMC. Prominent particles observed were the agglomerations of rod-like/spine-like crystals of PANI nanoflowers seen on the topology of the film. The observed film topology may be responsible for the high EC and the robust antibacterial properties exhibited by the nanocomposite films. The nanocomposite films also, showed good evidence of strong interactions between the reinforcement and the matrix material as revealed by their smoothness, cellular web, nanoflower-like and stacking morphological and a tridimensional network (Fernando et al., 2012). The presence of silicate layers and their intercalation in the CMC and PANI matrices were evidenced by SEM. This, probably, was due to the tendency of hydrogen bonding between the amino acid modified nanoclay, CMC and PANI imine groups of the polymer chains.

Acknowledgement

The authors wish to acknowledge the laboratory technologists of the department of chemistry, IBB University for their immense support. Dr. Oluwaseyi Damilare Saliu is appreciated for assisting in running the SEM, TGA and FT-IR analyses while he was a PhD student there in SA. This work was sponsored by the authors and No conflict of interest there exists.

Conclusion

PANI hybrid nanocomposite have been prepared using potassium dichromate as the oxidant. Results indicate that the surface of the film was loaded with nanoflowers, which probably, enhanced the EC and antibacterial properties of the prepared film. The formation of PANI/Arg-Modified-Nanoclay/CMC/EG nanocomposite film was successful, and analysis of the films' EC revealed high values (1900 Scm^{-1}). The film was thermally stable up to 700 °C. Moreover, the inclusion of sodium carboxymethyl cellulose (Na-CMC), dopant HCl, and nanoclay all had a substantial impact on the EC of the films. The formulated PANI/Arg-Modified-Nanoclay/CMC/EG nanocomposite could be utilized for a variety of purposes including, drug delivery, photonic cells, diodes for electrical appliances, and active packaging, tissue engineering, and scaffold wound healing etc.

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