

PHOTO-INDUCED POLYMERIZATION OF POLYANILINE AND PVA/POLYANILINE COMPOSITE

Thanaphon Kansa-ard^{a*}, Somtop Santibenchakul^{b,c}, Wanichaya Mekprasart^a
and Wisanu Pecharapa^a

^aCollege of Nanotechnology Ladkrabang, King Mongkut's Institute of Technology
Ladkrabang, Bangkok, 10520, Thailand

^bFaculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, 10520,
Thailand

^cFaculty of Science and Technology, Rajmangala University of Technology Tawan-Ok,
Chonburi 20110, Thailand

Received 25 April 2015; Revised 30 April 2015; Accepted 30 April 2015

ABSTRACT

This article represents the preparation of polyaniline (PANI) by photo-induced polymerization method under UV-irradiation. Photo-polymerization based on polyaniline was initially prepared from aniline monomer. Polyvinyl alcohol (PVA) was used as the composite polymer cooperating with PANI. The morphologies, chemical structure, optical properties and electrical conductivity analysis of PANI and PVA/PANI composite polymer were investigated by scanning electron microscope (SEM), FT-IR spectroscopy, UV-Vis spectrometer and four point probe technique. SEM results showed that particle-like PANI was formed via photopolymerization under UVA irradiation, meanwhile, flake-shape and dense aggregation was occurred under UVB irradiation. UV-vis and FT-IR spectra indicated that the polymerization of PANI and the formation of silver metal were carried out via photo-induced polymerization method. Moreover, the conductivity of PVA/PANI composite was obtained when comparing to PANI due to the influence of PVA co-polymer.

KEYWORDS: Composite, Photo-induced polymerization, Polyaniline and PVA

*

Corresponding authors; e-mail: tkansaard@gmail.com Tel.: +66875452360

INTRODUCTION

Nowadays, conducting polymers are promising and attractive materials regarding to their exceptional electrical and optical properties that lead them to be feasible for practical applications in advanced technologies. There are various distinctive and charming organic conducting polymer materials for example, polythiophene, polypyrrole and polyaniline under extensive exploration for their opportunities in specific applications [1]. Among the potential conducting polymers, polyaniline (PANI) discovered by Runge in the 19th century is one of the most studied polymers due to its environmental stability, facile synthesis, high conductivity and low monomer cost [1]. Moreover, the unique property of PANI is the switching between a conductor and an insulator under certain experimental conditions. Due to excellent properties, PANI has been utilized in various applications including gas sensor, protein

functional material, supercapacitor and conducting layer in electronic devices [2-3].

There are several processes for the synthesis of conducting PANI material. Polymerization processes have been achieved by chemical polymerization, electrochemical processes, ultrasonic method and photopolymerization. For the unique method, photopolymerization is chosen as the alternative route to the production of PANI material. This reaction can be occurred under Ultraviolet (UV) illumination [4]. Photons in UV light are the key role to the polymerization of aniline monomer in aqueous solution to polyaniline formation relating to the transition metal salt. However, low solubility is the limitation of PANI that can retard its performance. Copolymer in the composite form is one method for overcoming this problem. Poly(vinyl alcohol) (PVA) is chosen as proper material to be incorporated with PANI in composite form due to its biodegradability, hydrophilicity and environmental friendly. In this

work, PANI and PVA/PANI composite were synthesized by simple photopolymerization under different irradiated UV spectrum. For composite materials of PVA/PANI, it is suggested that electrical properties and solubility of PANI are considerably improved.

MATERIALS AND METHODS

Materials

Aniline monomer 99.5% (LOBA Chemie), nitric acid 70% (RCI Labscan), silver nitrate (AgNO_3) purchased from POCH and polyvinyl alcohol (PVA) was chosen as the precursor of PANI and PVA/PANI composite materials. 1-Methyl-2-pyrrolidinone (NMP) supplied from Sigma Aldrich was used as organic solvent to dissolve PANI before the characterization. PANI and PVA/PANI composites were prepared by photo polymerization.

Preparation of PANI and PVA/PANI composite

Firstly, 0.5 M aniline monomer was dissolved in 20 ml of 1.0 M HNO_3 following by the addition of 0.5 M AgNO_3 in the solution. After that, the mixture was irradiated under UVA and UVB illumination from UV lamp for 12 h and kept at room temperature. Finally, the solution was washed by DI water for clear solution and dried at 70 °C for 24 h to evaporate the organic solvent. For PVA/PANI composite, 10 g of PVA flake was dissolved in DI water and stirred at 90 °C for 5 h and cooled at room temperature then loaded 10 ml of PVA solution into the aniline solution mixture. After irradiation for 12 h, the solution was poured into petri dish and dried at 70 °C for 24 h.

Characterization

Morphologies of PANI synthesized under different UV light sources were investigated by scanning electron microscope (SEM). Meanwhile, the formation of PANI powder was confirmed by UV-Vis spectroscopy. Chemical bonding structure of PANI and PVA/PANI composite polymer was characterized by FTIR spectroscopy. Electrical conductivity was observed by four point probe technique.

RESULTS AND DISCUSSION

The color of precursor solution composed of aniline, nitric acid and Ag ions was changed from light yellow solution to dark green colloid after UV irradiation for 12 h. After that the dark green precipitate was characterized to confirm PANI formation by mean of SEM image and its absorption by UV-vis spectrometer. For the affirmation of PANI product by photopolymerization, the precipitate was dissolved in NMP for absorbance analysis. The absorption of aniline monomer, precursor without illumination and PANI powder under UVA and UVB illumination is depicted in Fig. 1. The absorption spectrum of the sample in dark condition (non-irradiation) was similar to aniline absorbance showing unobservable absorption region. This result indicates that the polymerization of PANI product with the precursor materials of nitric acid and Ag ions may be obtained by the assistance of UV irradiation. Under UVA and UVB illumination, two absorption region in range of 400-450 and 500-900 nm are clearly observed attributing to the absorbance of π - π^* transition in benzenoid structure of PANI [5]. Moreover, higher absorption in 400-450 nm in visible region was obtained due to the characteristic absorption of silver atom after the synthesis. This feature suggests that the excitation of the aniline monomer by UV light can be occurred through photopolymerization. Assisted Ag^+ ions are the key role to oxidize the monomer and consequently reduce its charge to a metal, Ag^0 [6]. These results indicate that PANI polymerization can be completely formed under both UV illumination. The amount of PANI from UVA light is greater than the product synthesized under UVB light interpreting from higher absorbance of the sample spectra. Therefore, UVA irradiation was chosen as UV light source for the production of composite polymer of PVA/PANI.

The morphologies of PANI under different UV irradiation investigated by SEM images are shown in Fig. 2. The morphology of PANI under UVA irradiation (Fig. 2(a)) appears in spherical nanoparticles whose diameters are less than 100 nm. Meanwhile, PANI powder obtained under UVB irradiation as seen in Fig. 2(b) was changed from particle form to flake-like structure and dense layer. Due to high activated energy in UVB region, the agglomeration of PANI in dense morphology and high packing area could be obtained.

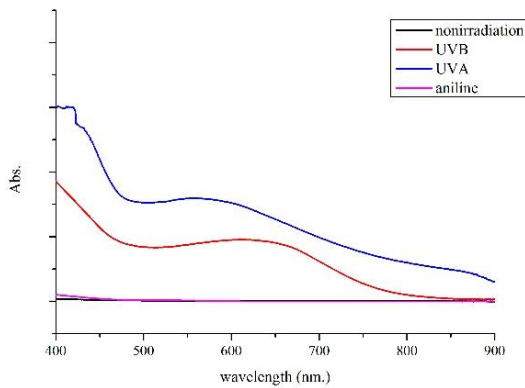


Fig. 1. UV-visible spectra of aniline, non-irradiation of pre-cursor and PANI under UVA and UVB irradiation.

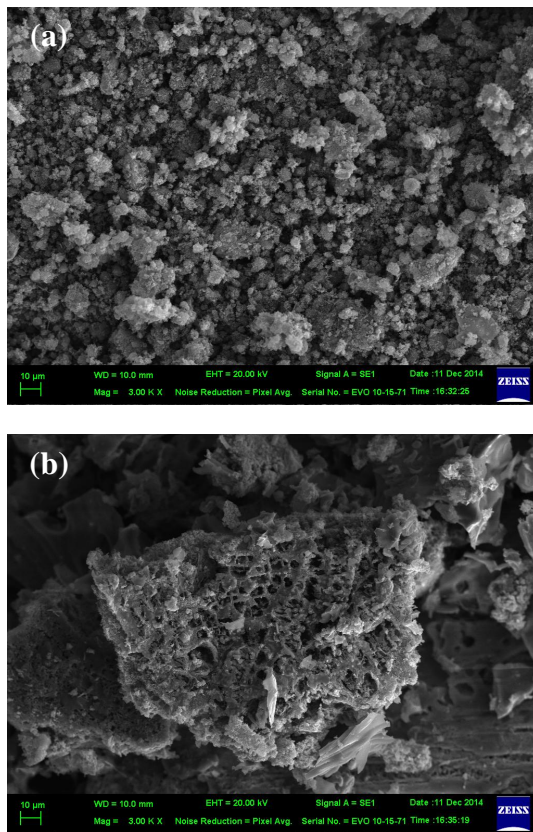


Fig. 2. SEM images of PANI powder obtained under (a) UVA and (b) UAB irradiation.

FTIR spectra of PANI and PVA/PANI composite obtained via photo-induced polymerization are shown in Fig. 3. In pure PANI spectrum, the vibration stretching at 3218 cm^{-1} corresponds to N-H stretching from amine functional group in PANI structure. Meanwhile, the characteristic peaks situated at 1283, 1485 and 1559 cm^{-1} are ascribed to secondary aromatic

amine of C-H stretching, benzinoid ring (B) and quinoid ring (Q) stretching modes [5]. The strong broad band located at 1141 cm^{-1} is assigned to the vibration mode of $-\text{NH}^+$ structure [4]. After adding PVA in the composite, the infrared spectra showed the similar pattern comparing to bare PANI. Meanwhile, co-polymer PVA is still in same structure in the composite interpreting form the presence of the bonding of O-H stretching vibration at board band $3100\text{-}3400\text{ cm}^{-1}$ [7].

Table 1. Comparing resistivity of PANI and PVA/PANI composite

Specimen	Resistivity ($\Omega\text{-cm}$)
commercial PANI	128.47
as-synthesized PANI	0.35
PVA/PANI composite	4.61

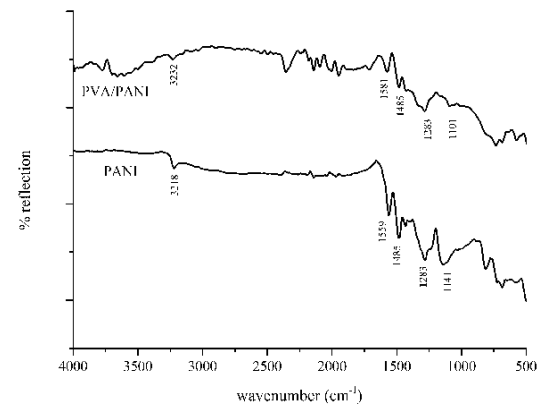


Fig. 3. FTIR spectra of (a) PANI and (b) PVA/PANI powder.

The electrical conductivities of individual product is expressed in Table 1. The resistivity of commercial grade PANI was found to be $128.47\ \Omega\text{-cm}$ while that values of as-synthesized PANI and PVA/PANI composite are $0.35\ \Omega\text{-cm}$ and $4.61\ \Omega\text{-cm}$, respectively. The synthesized product has lower resistivity than the commercial grade because of the emeraldine salt (ES) structure of the synthesized product but emeraldine base (EB) for the commercial product. For PAV/PANI composite, its resistivity exhibits slight increase comparing to the bare ES-PANI due to the incorporation of PVA co-polymer with high electrical resistivity.

CONCLUSION

In the summary, PANI and PVA/PANI composites were successfully synthesized via photo-induced polymerization. Good production and high yield of PANI material are suitably acquired under UVA irradiation resulting to complete polymerization between aniline monomer and AgNO₃ solution in spherical structure. Meanwhile, no transformation of monomer was noticed accompanying the absence of light irradiation. The formation of PANI can be completely obtained by UV illumination interpreting from UV-vis absorbance. Particle-like PANI is obtained by polymerization under UVA irradiation meanwhile flake-shape and dense aggregation is occurred under UVB irradiation. The formation of PANI by aniline monomer is affirmed by chemical bonding of FTIR spectra and UV-Vis absorption in visible range. Moreover, the presence of Ag phase is investigated by the absorption data due to final product from pre-cursor material. For PANI polymer composite with PVA, its FTIR spectrum is identical to those of pure PANI whilst the intensity of each peak is reduced due to the incorporation with PVA phase.

[7] Z. Zhang, M. Wan: *Synthetic Met.* 128, **2002** 83-89.

ACKNOWLEDGEMENTS

This work has been supported by King Mongkut's Institute of Technology Ladkrabang (KMITL) research fund and the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, through its program of Center of Excellence Network.

REFERENCES

- [1] K.M. Molapo, P.M. Ndangili, R.F. Ajayi, G. Mbambisa, S.M. Mailu, N. Njomo, M. Masikini, P. Baker and E.I. Iwuoha: *J. Electrochem. Sci.* 7, **2012** 11859-11875
- [2] G.D. Khuspe, D.K. Bandgar, S. Sen, V.B. Patil: *Synthetic Met.* 162, **2012** 1822-1827.
- [3] L. Di, L.P. Wang, Y.N. Lu, L. He, Z.X. Lin, K.J. Wu, Q.S. Ren, J.Y. Wang: *Acta Biomater.* 7, **2011** 3738-3745.
- [4] Z. Shi, V.K. Johns, C. Alber, Y. Liao: *Synthetic Met.* 161, **2011** 1420-1423.
- [5] P. Bober, M. Trchová, J. Prokeš, M. Varga, J. Stejskal: *Electrochim. Acta.* 56, **2011** 3580-3585.
- [6] R.A. Barros, W.M. Azevedo, F.M. Aguiar: *Synthetic Met.* 160, **2010** 61-61.