

Polyaniline/Silver Chloride 복합체의 표면 특성과 전도도에 미치는 젤라틴 첨가효과

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Effect of Gelatin Incorporation on the Surface Morphology and Conductivity of Polyaniline/Silver Chloride Composites

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초록: 젤라틴에 분산된 염화은 입자를 함유하는 폴리아닐린 복합체를 합성하였다. 합성방법은 질화은과 젤라틴 존재 하에 개시제로 암모늄퍼설페이트를 사용하여 아닐린 하이드로클로라이드를 중합함으로써 얻었다. X-선 회절 실험 결과 함유 젤라틴의 양이 증가할수록 결정성이 증가함을 알 수 있었는데 이는 젤라틴이 구조를 동일방향으로 배열하는데 필요한 핵분 역할을 하고 젤라틴 표면에 폴리아닐린이 배향성을 갖고 성장하도록 도와주기 때문일 것이다. 전도도 연구에 의하면 PANI/AgCl 단순 복합체에 비해 젤라틴이 포함된 복합체의 전도도가 증가하였다. 이는 젤라틴의 함유에 의한 균일한 결정체의 생성에 기인한 것으로 여겨진다. 아울러 젤라틴은 AgCl과 PANI와의 뭉침을 막아 안정화에 도움을 주는 역할을 함과 동시에 결정성이 좋은 균일한 표면성상을 유도하는 것으로 여겨진다.

Abstract: Polyaniline (PANI) composites containing silver chloride (AgCl) embedded on gelatin were prepared via the chemical polymerization of aniline hydrochloride employing ammonium persulfate as an oxidant in the presence of silver nitrate and gelatin. X-ray diffraction patterns showed the crystalline nature of PANI/AgCl was increased by the incorporation of gelatin, where gelatin acts as a structure-directing template and induces a highly oriented growth of PANI over its surface. Conductivity studies showed the enhanced conductivities for PANI/gelatin-AgCl compared to PANI/AgCl. The enhancement of conductivity seems to be due to the formation of uniform crystalline composites by the incorporation of gelatin. The gelatin might act as a stabilizer to inhibit the agglomeration of AgCl and PANI, and therefore resulted in uniform surface morphology with a good crystallinity.

Keywords: polyaniline, gelatin, AgCl, surface morphology, conductivity.

Introduction

The development of organic/inorganic composite materials has been recognized as a potential and cost-effective method for generating new materials with improved mechanical, electrical or catalytic properties, and also with new functions.¹⁻³

Among various organic materials, the composite materials prepared by using conducting polymers have attracted a great concern because of their potential applications in supercapacitors, electrostatic discharge, light-emitting diodes and sen-

sors.⁴⁻⁶ Polyaniline (PANI) belongs to the class of conjugated conducting polymers and has received significant attention because of its interesting redox behavior, processability, environmental stability, and reversible control of electrical properties via charge transfer doping and protonation.⁴⁻⁶ The π -conjugated backbone structure and imine groups of PANI can stabilize other polymer/metal ion in an aqueous medium by π - π interactions, hydrophilic interactions, and steric effects. Several methodologies have been developed for the preparation of nanostructured PANI in the form of dispersions, nanowires, nanofibers and nanotubules.⁷⁻⁹

Among inorganic nanoparticles (NPs), silver halides are photosynthetic materials and are extensively used as source materials in photographic films, photocatalysts, and semicon-

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ductors.¹⁰ The properties of silver chloride (AgCl) and PANI resulted in an increased motivation for the synthesis of composite materials with improved electrical performances and sensing properties.^{11,12} The general synthesis of AgCl results in agglomeration of formed nanoparticles. So the previous studies added polymers during the synthesis of PANI/AgCl, where the added polymer serves as a stabilizer to prevent agglomeration of nanoparticles.¹⁰⁻¹² It is reported that the combination of biodegradable and conducting polymer could enhance the electrical conductivity and biodegradability quite significantly.^{13,14} Gelatin is a high molecular weight water-soluble, biodegradable polymer and is a key hydrocolloid used as a gelling agent in photography, pharmaceuticals, food and cosmetics because of its useful properties such as inherent biodegradability in physiological environments, high melting, gelling point, and thermo-reversibility.^{15,16} Thus the use of gelatin could help to inhibit the agglomeration of AgCl nanoparticles, act as a stabilizer and increase the biodegradable properties of the composite materials.

In the present work, we report the synthesis of PANI composites with AgCl-gelatin, wherein the aniline is polymerized in the presence of AgCl embedded on the gelatin surface using ammonium persulfate as an oxidizing agent. The materials were characterized by Fourier transform infrared (FTIR) and UV-visible spectroscopy, and X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses. The temperature-dependent direct current (DC) conductivity of the synthesized composites was measured in the range of 300-500 K.

Experimental

Materials. Aniline hydrochloride (99%, $C_6H_7N \cdot HCl$), silver nitrate ($AgNO_3$), ammonium persulfate (99%) (APS), gelatin from porcine skin (gel strength 300, Type A) and other reagents were purchased from Sigma-Aldrich, USA and used as received.

Preparation PANI/Gelatin-AgCl Composites. In a typical synthesis, calculated amount of $AgNO_3$ and 300 mg of gelatin were taken in 50 mL of deionized water and stirred for 1 h to obtain uniform solution. To this solution, 1.29 g of $C_6H_7N \cdot HCl$ was slowly added and stirred for 30 min. Then the APS solution in 50 mL of deionized water was slowly added to the above mixture for a period of 30 min. After complete addition, the reaction was performed for 5 h at ambient temperature. The reaction mixture was filtered and washed with an excess of hot deionized water and acetone to remove unreacted mate-

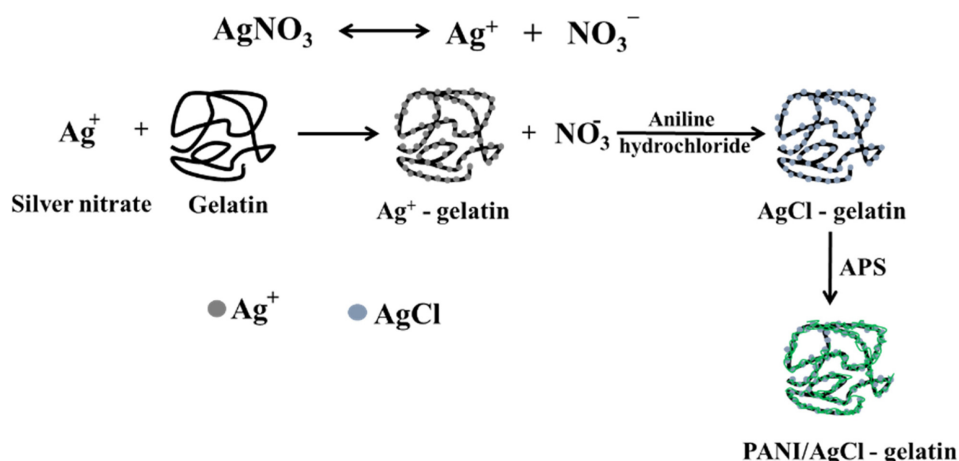
rials and oligomers. The resultant PANI/gelatin-AgCl powder was dried until constant weight in a vacuum oven at 60 °C.

In the present work 0.1, 0.2 and 0.3 M concentration of $AgNO_3$ were used to prepare PANI/gelatin-AgCl composites, and they are hereafter denoted for the simplicity as PANI/gel-AgCl-1, PANI/gel-AgCl-2 and PANI/gel-AgCl-3, respectively. For comparison, PANI/AgCl composite with 0.1 M $AgNO_3$ was prepared by a similar procedure without use of gelatin.

Characterization. Fourier transform infrared (FTIR) analyses were obtained using Varian 1000 FTIR spectrometer (Scimitar series, Varian Inc., USA) at a resolution of 4 cm^{-1} and 40 scans were signal averaged in the range of $600\text{-}4000\text{ cm}^{-1}$. For FTIR analysis, about 2 mg of sample was mixed with ~20 mg KBr powder and made into pellets, in which the sample was distributed uniformly in KBr. The UV-Vis spectra of the samples were obtained by Evolution 201 spectrophotometer with a path length of 1 cm (Thermo Scientific, USA) in NMP solution using a sample concentration of 2 mg mL^{-1} . X-ray diffraction (XRD) profiles of powder samples were registered on a D8 Advance X-ray diffractometer (Bruker AXS, Germany) with $CuK\alpha$ radiation ($\lambda=1.54\text{ \AA}$) at a scan speed of $0.045^\circ\text{ min}^{-1}$. The morphologies of samples were carried out using SEM (COXEM, CX-100 model). The powder sample was sputtered on a carbon disk with the help of double-sided adhesive tape and sputtered with gold to minimize charging problems. TEM measurement for polymer samples was carried out with JEOL JEM-2010 instrument. DC electrical measurements were obtained by four-point probe technique using Keithley 6220 constant current source and Keithley 2182A digital electrometer. For conductivity measurements, the powder samples were pressed to pellets of 1-2 mm thickness and 10 mm diameter by applying a pressure of 90 MPa using a hydraulic press. The thickness of pellets was measured using a micrometer screw gauge. The pellets were coated with silver paste on either side of the surfaces to reduce contact resistance. The copper electrodes are used to obtain better electrical contacts.

Results and Discussion

Schematic representation for the synthesis of PANI/gel-AgCl polymer composites was shown in Scheme 1. Briefly, $AgNO_3$ and gelatin were dissolved in aqueous media and stirred for 1 h. $AgNO_3$ in water is dissociated into Ag^+ and NO_3^- ions, the formed Ag^+ ions are adsorbed onto the surface of gelatin nanofibers. By the addition of aniline hydrochloride,



Scheme 1. Overall process for the synthesis of PANI/gel-AgCl polymer composites.

the Ag^+ ions on gelatin react with Cl^- in aniline hydrochloride to form AgCl. The formed AgCl and aniline is adsorbed on the surface of gelatin nanofibers. Thus the gelatin act as a stabilizer and nucleating surface for AgCl and aniline, thus inhibit agglomeration of composite materials. Then the initiator APS was slowly added to the reaction mixture to initiate the polymerization of aniline to form PANI. During the polymerization, PANI grows on the surface of AgCl embedded gelatin nanofibers to form nanocomposites of PANI/gel-AgCl.

Figure 1 shows the FTIR spectra of gelatin, PANI/AgCl and PANI/gel-AgCl-1 composites. The FTIR spectra of all the PANI/gel-AgCl composites are similar, so PANI/gel-AgCl-1 is shown as a representative spectrum. The FTIR spectrum of gelatin shows the prominent peaks at 3320 and 2850 cm^{-1} , characteristic of the amide group of gelatin. The presence of amide group in gelatin is also further evidenced by the presence of peaks at 1650 and 1450 cm^{-1} .¹⁷ Besides these prominent peaks, it also shows many peaks in 621-1248 cm^{-1} , characteristic to that of gelatin. The FTIR spectrum of PANI/AgCl shows a broad peak at 3469 cm^{-1} corresponding to the N-H stretching of the benzenoid ring, whereas the bands at 1580 and 1500 cm^{-1} are attributed to C=N and C=C stretching for the quinonoid and benzenoid units. The peak at 1140 cm^{-1} is due to the combination modes of benzenoid and quinonoid units. The C-N stretching in the quinoid system of the oxidized or protonated polyaniline is observed at 1300 cm^{-1} . A sharp peak at 810 cm^{-1} is assigned to C-H out of the plane bending of the para di-substituted benzene rings.¹⁸ Thus the presence of these prominent peaks of polyaniline confirms the formation of PANI/AgCl. The spectrum of PANI/gel-AgCl-1 shows the transmission bands originated from both PANI/AgCl and gel-

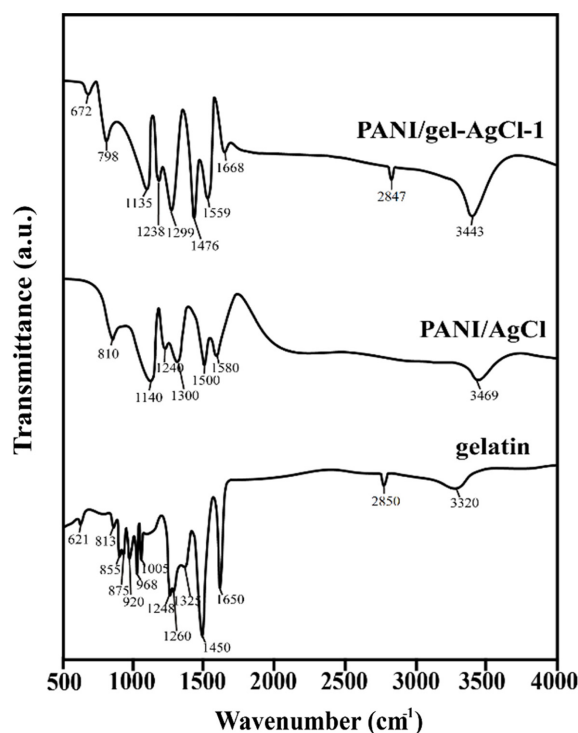


Figure 1. The FTIR spectra of gelatin, PANI/AgCl and PANI/gel-AgCl-1 composites.

atin. The exact differentiation of peaks of gelatin and polyaniline is not possible because of the presence of prominent absorption bands at similar wavenumbers. Shifting of absorption peaks is observed in ternary composites compared to PANI/AgCl suggests the formation of composites.

Figure 2 shows the UV-Vis spectra for PANI/AgCl and PANI/gel-AgCl composites. The absorption spectra of PANI/AgCl and PANI/gel-AgCl composites show two peaks; one

appears between 260-350 nm and the other between 600-700 nm. The broad peak observed at 260-350 nm corresponds to both AgCl and polyaniline. The PANI shows peaks at 200-300 nm ($\pi \rightarrow \pi^*$ transition) and 250-320 nm (polaron- π transition), whereas silver salts show an absorption peak at 330-360 nm. Also PANI shows a peak at 600-700 nm corresponding to the formation of an intermolecular charge-transfer exciton.¹⁹

Figure 3 shows the SEM images of PANI/AgCl and PANI/

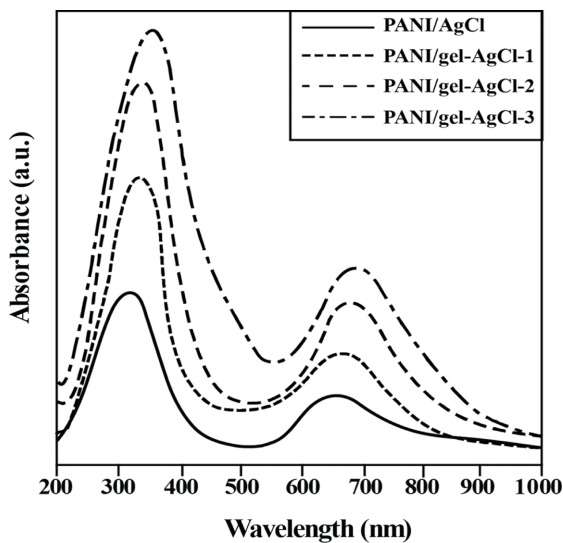


Figure 2. UV-vis spectra for PANI/AgCl and PANI/gel-AgCl.

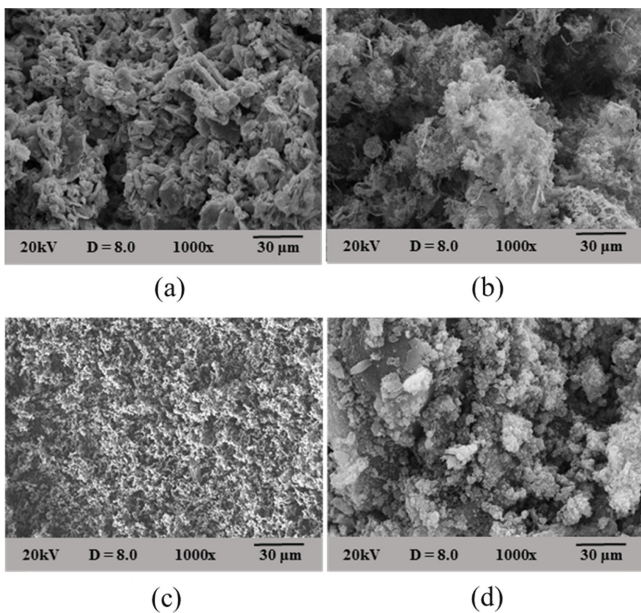


Figure 3. SEM images of (a) PANI/AgCl; (b) PANI/gel-AgCl-1; (c) PANI/gel-AgCl-2; (d) PANI/gel-AgCl-3 composites.

gel-AgCl composites. The SEM image of PANI/AgCl shows agglomerated lump like structures. During the polymerization process, the polymerized PANI particles appeared to be coated on the surface of AgCl resulting into such morphology of PANI/AgCl. PANI/gel-AgCl-1 shows nanofibrous morphology. The inclusion of gelatin during the polymerization resulted in the fibrous morphology of the composite materials because the gelatin acted as a stabilizer and provides the nucleating sites for AgCl and aniline, where the polymerization of PANI took place and led to more uniform morphologies. Similar observations were observed by the use of PVP in the synthesis of PANI/AgCl in previous reports.¹⁰⁻¹² The surface morphology of PANI/gel-AgCl-2 and PANI/gel-AgCl-3 composites shows similar morphology as that of PANI/gel-AgCl-1. The SEM results support that the incorporation of gelatin prevents the agglomeration of AgCl and PANI and forms uniform nanofibrous morphology.

Figure 4(a-d) shows the TEM images of PANI/AgCl, PANI/gel-AgCl-1, PANI/gel-AgCl-2, and PANI/gel-AgCl-3 composites. The TEM image of PANI/AgCl in Figure 4(a) shows spherical-particle like structures with dark and gray regions. The diameters of these dark and gray spherical structures are between 10-20 nm. The TEM image of Figure 4(b-d) also show particle like morphologies with a particle diameter of 30-50 nm. The TEM images of PANI/gel-AgCl-2 composite contain agglomerated particles along with fiber like structures (the left corner of the Figure 4(c)) on which it appears as though some small nanoparticles have attached on the surface of the fiber and these smaller nanoparticles are probably AgCl. Similarly, the TEM images of PANI/gel-AgCl-3 is also similar to PANI/gel-AgCl-2 composite. The dark colored regions are

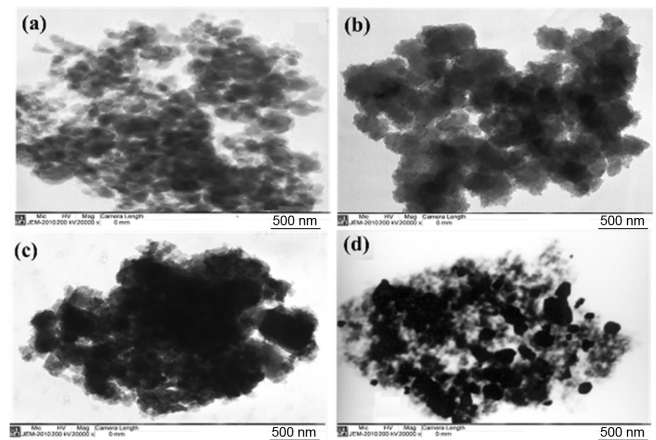


Figure 4. TEM images of (a) PANI/AgCl; (b) PANI/gel-AgCl-1; (c) PANI/gel-AgCl-2; (d) PANI/gel-AgCl-3 composites.

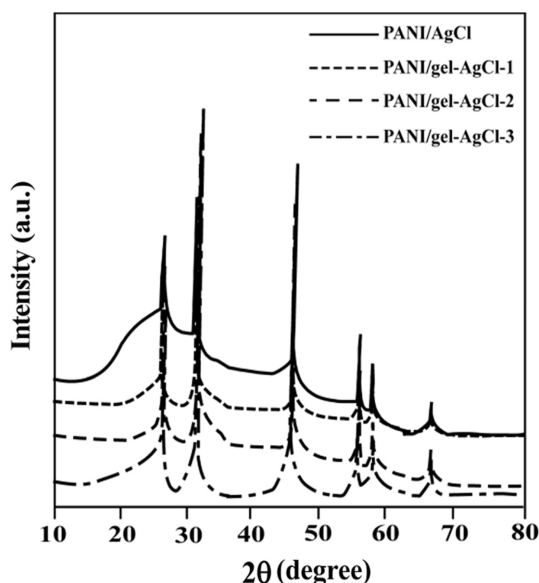


Figure 5. X-ray diffraction patterns for PANI/AgCl and PANI/gel-AgCl composites.

AgCl nanoparticles embedded on the gelatin polymers during the synthesis of the polymer composites.

Figure 5 shows the X-ray diffraction patterns for PANI/AgCl and PANI/gel-AgCl composites. The diffraction pattern of PANI/AgCl shows a broad peak at 2θ values of 25° corresponding to the polymer chain of PANI. It also shows peaks at 2θ values of 27° , 31° , 46° , 55° , 57° and 67° corresponding to the characteristic diffraction peaks of (111), (200), (220), (311), (222), and (400) planes, respectively. These diffraction patterns confirm the presence of AgCl and are in good agreement with JCPDS No. 06-0480. By incorporation of gelatin, the peaks become more intense because the gelatin acts as template for the nucleation of aniline and induces the formation of ordered PANI.^{20,21} With increasing the concentration of AgCl, the diffraction patterns of PANI/gel-AgCl-2 and PANI/gel-AgCl-3 composites becomes narrower because of predomination effect of AgCl and the relative intensity of PANI diffraction peaks decreases. The result of the diffraction studies shows that the crystalline nature was increased by incorporation of gelatin to the PANI/AgCl composites.

Figure 6(a) represents the variation of electrical conductivity with temperature for PANI/AgCl and PANI/gel-AgCl composites. The room-temperature electrical conductivities of PANI/AgCl, PANI/gel-AgCl-1, PANI/gel-AgCl-2 and PANI/gel-AgCl-3 were found to be 0.22, 0.33, 0.82 and 2.04 S cm^{-1} , respectively. The conductivities of PANI/gel-AgCl composites were much higher compared to PANI/AgCl. The incorporation

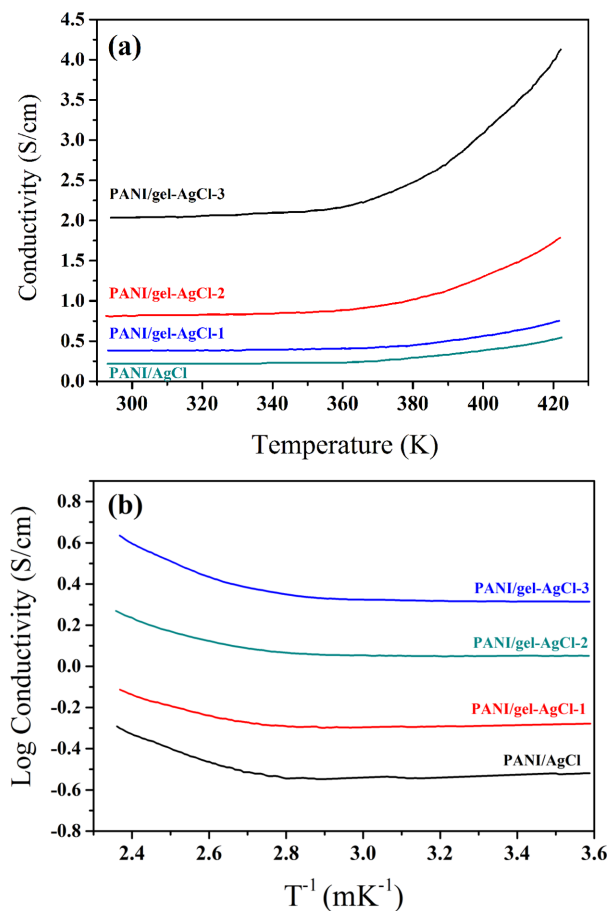


Figure 6. Variation of (a) electrical conductivity with temperature; (b) log conductivity with inverse temperature for PANI/AgCl and PANI/gel-AgCl composites.

of gelatin induced the more oriented growth of PANI over AgCl-embedded gelatin and increased its crystallinity and also inhibited the agglomeration of AgCl and PANI for a more uniform composite, further it also facilitated the contact and transport of electronic charges between PANI and AgCl nanoparticles embedded on its surface their-by improved electrical properties of gelatin incorporated PANI/AgCl composites. The conductivity was also increased by the increase of AgCl concentration in the PANI/gel-AgCl composites due to supplementary effect of AgCl for transport of electronic charge. The increase in the conductivity among PANI/gel-AgCl composites was due to the increase of AgCl concentration, while the increase in the conductivity among PANI/gel-AgCl and PANI/AgCl is due to the more template effect of gelatin which will induce the more oriented and crystalline growth of PANI, their-by increased conductivity.^{20,21} By increasing the temperature from room temperature to 425 K, the conductivity of PANI/AgCl and

PANI/gel-AgCl composites was also increased as 0.47, 0.705, 1.76 and 4.41 S cm⁻¹ for PANI/AgCl, PANI/gel-AgCl-1, PANI/gel-AgCl-2, and PANI/gel-AgCl-3 composites, respectively. The increase in conductivity with temperature is the property of semiconducting materials. The conductivities of the PANI/AgCl and PANI/gel-AgCl composites increased by temperature confirm the semiconducting behavior of the composite materials, characteristic of PANI. The increase of temperature assists the flow of charge carriers, inducing an enhancement of the conductivity.

Figure 6(b) shows log conductivity with inverse temperature for PANI/AgCl and PANI/gel-AgCl composites. In general, σ can be expressed as: $\sigma = \sigma_0 \exp(-E_a/kT)$; where σ_0 is the maximum conductivity and E_a is the activation energy. The slope of the curve was obtained using the plot of logarithmic conductivity vs. inverse temperature of polymer composites to obtain the activation energy (E_a) values as shown in Figure 6(b). The graph shows a nearly linear plot in the range of 2.4-2.8 which corresponding to 450 to 350 K. The calculated activation energy (E_a) values in the range for PANI/AgCl, PANI/gel-AgCl-1, PANI/gel-AgCl-2, and PANI/gel-AgCl-3 composites were 9.13, 7.69, 6.32, and 5.89 kJ mol⁻¹, respectively. The variation of conductivity with temperature depends on the chain length of polymer and E_a values. Higher E_a values implies higher potential barrier and lower E_a values implies lower potential barrier in the conduction process.

Conclusions

PANI/gel-AgCl composites were successfully synthesized by *in-situ* polymerization of aniline hydrochloride using ammonium persulfate as an oxidant in the presence of gelatin and silver nitrate. PANI/gel-AgCl composites were formed with uniform morphologies without agglomeration and good crystallinity. Surface morphological studies suggested that there is a conjugation between the PANI polymer and AgCl embedded on the surface of gelatin fibers. Conductivity of PANI/AgCl was increased by the incorporation of gelatin resulting in enhanced conductivity for PANI/gel-AgCl compared to PANI/AgCl. The results show that gelatin has an active role in the enhancement of the conductance of the PANI/gel-AgCl composites because the gelatin enhances the inter-connection between PANI and AgCl. The synthetic approaches discussed here may be expanded to create more versatile nanocomposites with a broad selection of other inorganic nanoparticles for obtaining better and wider ranges of applications. The

new composites may also benefit the development of new applications for biomaterials in molecular electronics and other fields.

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References

1. C. Sanchez, B. Lebeau, F. Chaput, and J. Boilot, *Adv. Mater.*, **15**, 1969 (2003).
2. S. Li, M. M. Lin, M. S. Toprak, D. K. Kim, and M. Muhammed, *Nano Rev.*, **1**, 1 (2010).
3. T. W. Kim, Y. Yang, F. Li, and W. L. Kwan, *NPG Asia Mater.*, **4**, 18 (2012).
4. S. Bhadra, D. Khastgir, N. K. Singha, and J. H. Lee, *Prog. Polym. Sci.*, **34**, 783 (2009).
5. U. Male and P. Srinivasan, *RSC Adv.*, **5**, 70675 (2015).
6. U. Male, P. Srinivasan, and B. S. Singu, *Int. Nano Lett.*, **5**, 231 (2015).
7. G. Ciric-Marjanovic, *Synth. Met.*, **177**, 1 (2013).
8. R. Ansari, M. Arvand, and L. Heydari, *J. Chem. Sci.*, **126**, 41 (2014).
9. S. K. Martha and B. Hariprakash, *J. Chem. Sci.*, **118**, 93 (2006).
10. S. Vohra, M. Kumar, S. K. Mittal, and M. L. Singla, *J. Mater. Sci. Mater. Electron.*, **24**, 1354 (2013).
11. C. Ozdemir, F. Yeni, D. Odaci, and S. Timur, *Food Chem.*, **119**, 380 (2010).
12. A. Manzoli, F. M. Shimizu, L. A. Mercante, E. C. Paris, O. N. Oliveira, D. S. Correa, and L. H. C. Mattoso, *Phys. Chem. Chem. Phys.*, **16**, 24275 (2014).
13. C. Basavaraja, Y. Veeranagouda, K. Lee, R. Pierson, and D. S. Huh, *J. Polym. Sci.; Part B: Polym. Phys.*, **47**, 36 (2009).
14. C. Basavaraja, J. K. Kim, P. X. Thinh, and D. S. Huh, *Polym. Compos.*, **33**, 1541 (2012).
15. P. Rujitanaroj, N. Pimpha, and P. Supaphol, *Polymer*, **49**, 4723 (2008).
16. M. Sarmah, A. Hussain, A. Ramteke, and T. K. Maji, *J. Chem. Sci.*, **128**, 1291 (2016).
17. Y. C. Lim, J. Johnson, Z. Fei, Y. Wu, D. F. Farson, J. J. Lannutti, H. W. Choi, and L. J. Lee, *Biotechnol. Bioeng.*, **108**, 116 (2011).
18. U. Male, S. Uppugalla, and P. Srinivasan, *J. Solid State Electrochem.*, **19**, 3381 (2015).
19. U. Male, E. J. Jo, J. Y. Park, and D. S. Huh, *Polymer*, **99**, 623 (2016).
20. L. Pan, H. Qiu, C. Dou, Y. Li, L. Pu, J. Xu, and Y. Shi, *Int. J. Mol. Sci.*, **11**, 2636 (2010).
21. S. J. Varma, F. Xavier, S. Varghese, and S. Jayalekshmi, *Polym. Int.*, **61**, 743 (2012).