Journal of Engineering Science and Technology
Vol. 3, No. 2 (2008) 146 - 152

PRODUCTION OF POLYANILINE COMPOSITE CONTAINING Fe_2O_3 AND CoO WITH NANOMETER SIZE USING HYDROXYPROPYLCELLULOSE AS A SURFACTANT

HOSSEIN EISAZADEH*, HAMID REZA KHORSHIDI

Faculty of Chemical Engineering, Babol Noshirvani University of Technology,
P.O.Box 484, Babol, Iran
*Corresponding Author: Eisazadeh@hotmail.com

Abstract

In this study, composite of polyaniline containing Fe_2O_3 and CoO with nanometer size was synthesized by a chemical method using hydroxyl-propylcellulose as a surfactant. The characteristics of products such as morphology and conductivity were studied. The results indicate that, the morphology and conductivity of product are dependent on the surfactant, the type and concentration of metallic oxide.

Keywords: Composite, surfactant, metallic oxide, morphology, conductivity

1. Introduction

Polymers are generally used in a wide range of applications often for their low cost, light weight and mechanical properties, or for the three characteristics combined. One of the main characteristics required for electrical and/or optical activities to occur in a polymer is a conjugated backbone which can be subject to oxidation or reduction by electron acceptors or donors. Due to delocalization of the π electrons in conjugated polymers, chain rigidity is very often a predominant property and, as a result of this, an aggregated character of the chains is typical in such material. This results in intractability which has been one of the drawbacks in the field.

Polyaniline (PAn) is unique among the conducting polymers in that it possesses excellent electrical, magnetic and optical properties. Because of its low cost as raw material it is generally regarded as one of the conducting polymers with very high potential in commercial applications. The insolubility in common solvents and infusibility of conducting polymers, in general, make them poorly processable either by solution technique or by melt processing methods [1, 2].

Improvement of these material properties can be achieved either by forming composites of aniline, or by forming PAn composites or blends with commercially available polymers or inorganic materials which offer better mechanical and optical properties, stability and processability [3-6].

A wide range of possible applications have been proposed for conducting polymers such as conductive paint [7], optical devices [8], membrane [9], biomedical applications [10], and removal of heavy metals [11,12] etc. In this study, polyaniline composite was prepared in the aqueous solution using KIO_3 as an oxidant in the presence of metallic oxides such as Fe_2O_3 and CoO as additives, and hydroxypropylcellulose as a surfactant.

2. Experimental

2.1. Instrumentation

A magnetic mixer model MK20, digital scale model FR200, scanning electron microscope (SEM) model XL30 were employed. The four-point probe method was used to measure the volume resistivity of conducting polymer films.

2.2. Reagents and standard solutions

Materials used in this work were aniline and hydroxypropylcellulose (HPC, $M_w=10^6$) from Aldrich, sulfuric acid, potassium iodate from Merck. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Aniline was purified by simple distillation.

2.3. Preparation of nanometer-size Fe_2O_3

A 10 g of $FeSO_4,7H_2O$ was dissolved in 200 mL strong alkaline solution (pH=13-14) at 60°C. The $FeSO_4$ solution was hydrolyzed and after 30 minutes the sedimentation was filtered and then dissolved in 1M sulfuric acid. Then the strong alkaline solution (pH=13-14) was added to the resultant acid solution. The products was filtered and dried at room temperature.

2.4. Preparation of nanometer-size CoO

A 10 g $CoCl_2,6H_2O$ was dissolved in 200 mL strong alkaline solution (pH=13-14) at 60°C. The $CoCl_2$ solution was hydrolyzed and after 30 minutes the resultant sedimentation was filtered and dried at room temperature.

2.5. Preparation of polyaniline composite

The reaction was carried out in aqueous media at room temperature for 20 hours. In a typical experiment 1 mL aniline monomer was added to stirred aqueous solution of 100 mL of 1M sulfuric acid containing 0.8 g of KIO_3, 0.5 g surfactant (HPC) and 0.1-0.5 g metallic oxide respectively. After 20 hours polymer composite was filtered. To separate the oligomers and impurities, the product was washed several times with deionized water and then dried at room temperature.

3. Results and Discussion

The chemical method can be a general and useful procedure to prepare conductive polymer and its composites. It is well established that the charge transport properties of conjugated polymers strongly depend on the processing parameters [13]. Polyaniline (PAn) has a reactive N-H group in a polymer chain flanked on either side by a phenylene ring, imparting a very high chemical flexibility. It undergoes protonation and deprotonation in addition to adsorption through nitrogen, which having alone pair of electrons, is responsible for the technologically interesting chemistry and physics.

The electrical conductivity of various composites produced under different reaction conditions was measured on pressed pellets of the composite powders. The average thickness of the compressed pellets was 250 μm. The electrical conductivity of compressed pellets was measured using four-point probe method. The results are shown in Table 1. As it can be seen the electrical conductivity is dependent on the type and concentration of metallic oxides, because the conductivity increases with increasing polarizability of the carrier solvents [14]. As PAn is molecular composite containing a cationic polymer backbone, dopant must be incorporated for maintenance of charge neutrality. As a result, it is expected that the chemical and physical properties of the doped PAn will be affected by dopant [15]. Also as shown in Table 1 the conductivity of products is related to the surfactant.

The morphology of composites was studied using scanning electron microscope. As shown in Figs. 1-5, the size and homogeneity of particles are dependent on the type of metallic oxides and surfactant. This is presumably due to the amount of adsorbed chemically surfactant (grafting copolymer) to the polyaniline particles. Surface active agents affect the physical and chemical properties of the solutions. The type of surfactant is known to influence the rate of polymer formation, particle size, size distribution, morphology and homogeneity [16-21]. Adsorption of the surface active agent on the PAn particles is primarily due to the hydrophobic component in the surfactants, probably via a hydrogen bonding mechanism with the aniline N-H group. As can be seen in Fig. 1, the polyaniline obtained using HPC exhibits spherical particles, because surfactants prevent from gross aggregation of particles. Figs. 2 and 4 show the morphology of pure Fe_2O_3 and CoO which have been prepared in this research. As shown in Figs. 3 and 5, the composites obtained using Fe_2O_3 and CoO as additives in the presence of HPC as a surfactant are composed of small spherical particles. As can be seen, the type of additive has a considerable effect on the size and homogeneity of particles.

4. Conclusion

In this work, the characteristics of PAn composites such as conductivity and morphology were investigated using HPC as a surfactant in the presence of nanometer-size metallic oxides as additives. It was found that, the type of additive has a considerable effect on the conductivity and morphology of resultant products. The SEM micrographs show that the type of metallic oxide plays a major role on the surface morphology of products. Also the surfactant decreases

the tendency to form agglomerate which leads to more homogeneous distribution in the particles, because the surfactant prevents from gross aggregation of particles. As shown in figures, the surfactant has a considerable effect on the size and homogeneity of particles, because surfactant adsorbed chemically to the polyaniline (grafting copolymer).

Table 1. The Effect of Additive and Surfactant Type on the Conductivity of Polyaniline Composite.

Type of sample	Concentration of oxidant (g/L)	Concentration of Fe_2O_3 (g/L)	Concentration of CoO (g/L)	Concentration of HPC (g/L)	Electrical conductivity (S/cm)
Pure polyaniline	KIO_3=8	-	-	-	4.5×10^{-6}
Polyaniline and HPC	KIO_3=8	-	-	5	1.2×10^{-8}
Polyaniline and Fe_2O_3	KIO_3=8	5	-	-	1.1×10^{-8}
Polyaniline and Fe_2O_3	KIO_3=8	1	-	-	6.8×10^{-6}
Polyaniline + Fe_2O_3 + HPC	KIO_3=8	5	-	5	1.6×10^{-8}
Polyaniline + Fe_2O_3 + HPC	KIO_3=8	1	-	5	1.2×10^{-8}
Polyaniline and CoO	KIO_3=8	-	5	-	1.2×10^{-8}
Polyaniline + CoO + HPC	KIO_3=8	-	5	5	1.6×10^{-6}
Polyaniline + CoO + HPC	KIO_3=8	-	1	5	0.7×10^{-8}

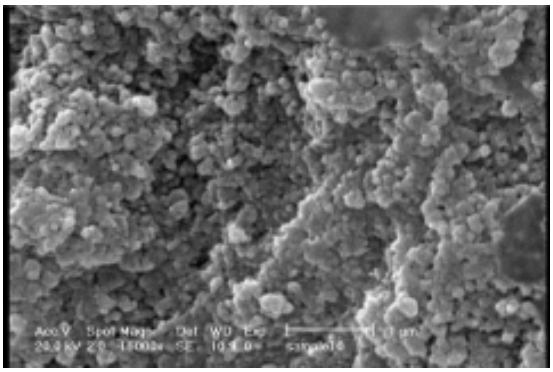

Fig. 1. Scanning Electron Micrograph of PAn in an Aqueous Media Using HPC (M_w= 10^6, 5 g/L as a Surfactant). Reaction Conditions: (KIO_3= 8 g/L, PAn Monomer= 10.7×10^{-2} mol/L, Volume of solution = 100 mL, Reaction time 20 hours at room temperature).

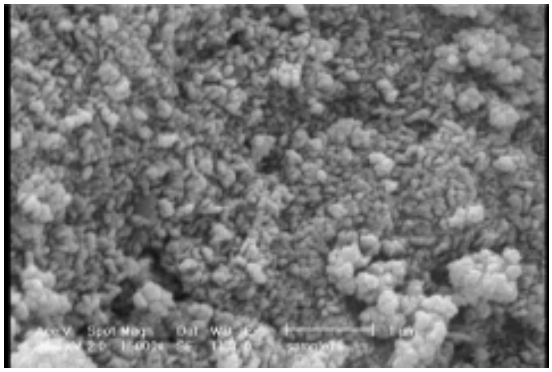

Fig. 2. Scanning Electron Micrograph of Pure Fe_2O_3 (The method of preparation has been explained in the text).

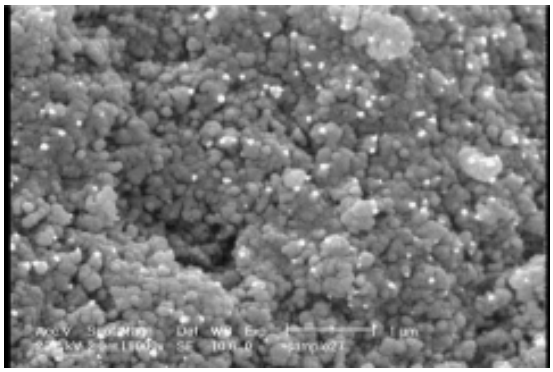

Fig. 3. Scanning Electron Micrograph of PAn and Fe_2O_3 Composite in an Aqueous Media Using HPC (M_w= 10^6, 5 g/L as a Surfactant). Reaction Conditions: (KIO_3= 8 g/L, PAn Monomer= 10.7×10^{-2} mol/L, Fe_2O_3= 5 g/L, Volume of solution= 100 mL, Reaction time 20 hours at room temperature).

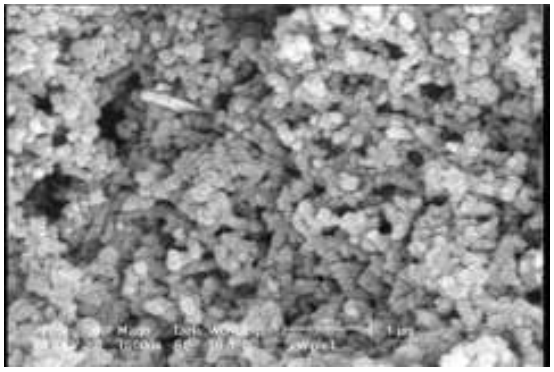

Fig. 4. Scanning Electron Micrograph of Pure CoO (The method of preparation has been explained in the text).

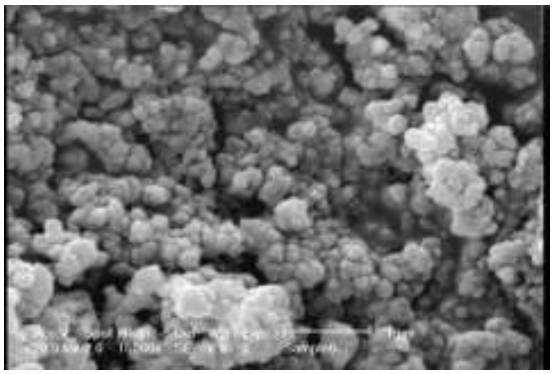

Fig. 5. Scanning Electron Micrograph of PAn and CoO Composite in an Aqueous Media Using HPC ($M_w = 10^6$, 5 g/L as a Surfactant). Reaction Conditions: (KIO_3=8 g/L, PAn Monomer = 10.7×10^{-2} mol/L, CoO = 5 g/L, Volume of solution = 100 mL, Reaction time 20 hours at room temperature).

References

1. Yin, W., Li, J., Li, Y., Wu, J. and Gu, T. (2001). Conducting composite film based on polypyrrole and crossliked cellulose. *J. Appl. Polym. Sci*., 80(9), 1368-1373.
2. Machado, J. M., Karasz, F. E. and Lenz, R. W. (1988). Electrically conducting polymer blends. *Polymer*, 29(8), 1412-1417.
3. Paoli, M. A. D., Waltman, R. J., Diaz, A. F. and Bargon, J. (1984). Conductive composites from poly(vinyl chloride) and polypyrrole. *J. chem .Soc. Chem. Commun*., 15, 1015-1016.
4. Lindsey, S. E. and Street, G. B. (1984/85). Conductive composites from poly (vinyl alcohol) and polypyrrole. *Synth. Met*., 10(1), 67-69.
5. Cassignol, C., Cavarero, M., Boudet, A. and Ricard, A. (1999). Microstructure conductivity relationship in conducting polypyrrole/epoxy composites. *Polymer*, 40(5), 1139-1151.
6. Bhat, N. V., Gadre, A. P. and Bambole, V. A. (2001). Structural and electrical properties of electropolymerized polypyrrole composite film. *J. Appl. Polym. Sci.*, 80(13), 2511-2517.
7. Eisazadeh, H., Spinks, G. and Wallace, G. G. (1993). Conductive electroactive paint containing polypyrrole colloids. *Mater. Forum*, 17, 241-245.
8. Falco, E. H. L. and Azevedo, W. M. (2002). Polyaniline-poly (vinyl alcohol) composite as an optical recording material. *Synth. Met*., 128, 149-154.
9. Misoska, V., Ding, J., Davey, J. M., Price, W. E., Ralph, S. F. and Wallace, G. G. (2001). Polypyrrole membranes containing chelating ligands: synthesis characterization and transport studies. *Polymer*, 42, 8571-8579.
10. Benabderrahmane, S., Bousalem, S., Mangeney, C., Azioune, A., Vaulay, M. J. and Chehimi, M. M. (2005). Interfacial physicochemical properties of functionalized conducting polypyrrole particles. *Polymer*, 46, 1339-1346.

11. Eisazadeh, H. (2007). Removal of mercury from water using polypyrrole and its composites. *Chinese Journal of Polymer Science*, 25(4), 393-397.
12. Eisazadeh, H. (2007). Removal of chromium from waste water using polyaniline. *J. App. Polym. Sci*., 104, 1964-1967.
13. Cao, Y., Qiu J. and Smith, P. (1995). Effect of solvents and co-solvents on the processability of polyaniline: solubility and conductivity studies. *Synth. Met*., 69, 187-190.
14. Son, S. H., Lee, H. J., Park, Y. J. and Kim, J. H. (1998). Preparation of conducting polymer composites: effects of porosity on electrical conductivity. *Polym. Inter*., 46, 308-312.
15. Liu, L. and Wan, M. (2001). Polypyrrole doped with 1,5-naphtahalenedi-sulfonic acid. *Synth. Met*., 124, 317-321.
16. Aldissi, M. and Armes, S. P. (1991). Colloidal dispersion of conducting polymers. *Prog. Org. Coat*., 19(1), 21-58.
17. Eisazadeh, H., Spinks, G. and Wallace, G. G. (1992). Electrochemical properties of conductive electroactive polymeric colloids. *Mater Forum*, 16, 341-344.
18. Armes, S. P. and Aldissi, M. (1990). Preparation and characterization of colloidal dispersions of polypyrrole using poly(2-vinyl pyridine) based steric stabilizers. *Polymer*, 31, 569-574.
19. Aldissi, M. (1993). Is there a colloid in every solution processable conducting polymer. *Advance mater*, 5(1), 60-62.
20. Eisazadeh, H., Wallace, G. G. and Spinks, G. (1994). Influence of steric stabilizers on the electropolymerization and properties of polypyrrole. *Polymer*, 35(8), 1754-1758.
21. Dipankar, C., Mukut, C. and Broja, M. M. (2001). Dispersion polymerization of aniline using hydroxypropylcellulose as stabilizer. *Polym. Inter*., 50, 538-544.