

Short Communication

Effect of Concentration of Surfactant and Additive on Morphology of Polyaniline Nanocomposites Prepared in Aqueous Solution

M.Mohammadi* and A.A.Rostami

Faculty of Chemical Engineering, Shomal University, Amol, I.R.Iran

(*) Corresponding author: mohammadsm113@gmail.com

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Abstract

In this work polyaniline nanocomposites were synthesized in aqueous media by using ammonium peroxydisulfate (APS) (10g/l) as an oxidant in the presence of hydroxy propyl cellulose (HPC) (2,5,10 g/l) as a surfactant, poly (vinyl chloride) (10,30 g/l) as an additive and sulfuric acid (H₂SO₄). The effects of concentration of surfactant and additive on morphology have been investigated. The characteristics of the products, such as morphology and molecular structure, were investigated. It was found that the concentrations of surfactant and additive have considerable effects on the particle size and morphology of the resulting product. The results indicate that small and spherical nanoparticles can be obtained using HPC (10 g/l). Also, the chemical structure of products was determined by fourier transform infrared spectroscopy (FTIR). The results indicated that the intensities of the peaks were dependent on the concentration of APS, HPC and PVC. FTIR spectra showed that HPC and PVC particles were available in the products.

Keywords: Additive, Chemical structure, Morphology, Nanocomposite, Polyaniline, Surfactant.

1. INTRODUCTION

Conducting polymers possess good tunable electrical conductivity and are organic electrochromic materials with chemically active surface [1]. They are chemically sensitive and have poor mechanical properties and thus pose a processability problem. Thus, nanocomposites formed by combining conducting polymers and oxides nanoparticles possess all the good properties of both the constituents. The properties of nanocomposite of such kind are strongly dependent on concentration of polymer [2-3]. Among the numerous conductive polymers which have been synthesized in recent years, polyaniline (PAn) plays a crucial role. Polyaniline has been known for more than a century, since

the synthesis of the so-called "aniline blacks" that enjoyed an early use as cotton dyes [4]. Polyaniline has attracted considerable attention because of its unique electrical, optical and electro optical properties and its numerous potential applications [5]. One of the key problems related to the potential applications of polyaniline is its processability.

Processability is an important requirement in conducting polymers for their possible commercial use. Since most of the conducting polymers are not processable, much of the efforts made in this field have been directed towards circumventing this problem. To solve this problem, various approaches have been

tried, including addition of side groups to the polymer backbone [6], grafting of polymers to a nonconducting polymer [7], direct polymerization of intractable polymers into the final desired shape, making a composite of blend of conducting polymers [8,9] and copolymerization [10]. Two methods have been used to produce stable dispersions. The first one utilizes a dispersion polymerization route in which macroscopic precipitation is prevented by a thin, physically adsorbed outer layer of a suitable polymeric surfactant which acts as a steric stabilizer. The second one consists of the synthesis of a graft copolymer in which one of the components is the steric stabilizer [11]. Chemical synthesis has the advantage of being a simple process capable of producing bulk quantities of conductive polymer on a batch basis. To date, it has been the major commercial method of producing polyaniline. Several companies produced bulk powders, dispersions and coated products [12]. To improve the properties of polyaniline, one of the methods is its blending with different conventional polymers [13]. The advantages of making a blend of conducting polymers and high performance commercial polymers are to increase the performance of the former [14]. PVC is one of the important commercial polymers and available in powder form. In this work, polyaniline

nanocomposites were prepared in aqueous solution by chemical polymerization of aniline using APS as an oxidizing agent in the presence of HPC as surfactant, PVC as additive and sulfuric acid as a medium. Polyaniline nanocomposites were characterized by fourier transform infrared spectroscopy and scanning electron microscopy. Then the effects of the concentration of surfactant and additive on the colloidal morphology were determined [15-16].

2. EXPERIMENTAL

2.1. Instrumentation and Materials

All Devices and Materials used in this work are listed in Tables 1 and 2. All reagents were used as received without further purification but aniline monomer was purified by simple distillation

2.2. Synthesis of polyaniline

Polyaniline was synthesized by chemical oxidation of aniline using ammonium peroxydisulfate as an oxidizing agent in acidic medium. The synthesis of polyaniline was carried out by adding slowly 1 ml aniline monomer to a stirred aqueous solution (100 ml) containing 1 g APS as oxidant at room temperature for 5 hours. The polymer was filtered and to separate the oligomers and impurities, product was washed several times with deionized water then dried at room temperature for 3 days.

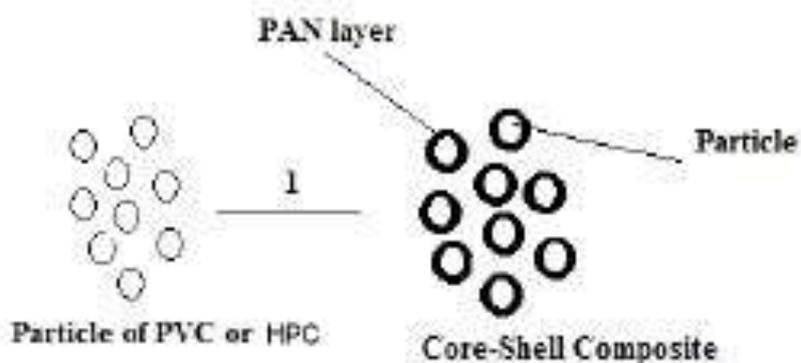


Figure 1. Schematic diagram showing the formation of polyaniline with PVC and HPC nanoparticles [17].

Table1. Devices and equipment

Application	Model	Device
weight	PA214	digital scale
mix	RO 10 p	magnetic mixer
morphology	EM3200	SEM
chemical structure	Shimadzu 4100	FTIR

Table2. Reagents and standard solution

Application	Company	Purity	M _w (g/mol)	Density (g/cm ³)	Viscosity (Pa. s)	Average Particle Size (nm)	Reagent
monomer	Merck	% 99<	93	1.02	0.024	-	Aniline
dopant	Merck	% 95-97	98	1.8	0.0267	-	sulfuric acid
surfactant	Aldrich	% 99<	10 ⁶	-	-	23	HPC
additive	Merck	% 99<	62000	-	-	69	PVC
oxidant	Merck	% 99.5	228.2	-	-	-	APS

Table3: Preparation conditions and some properties of products in aqueous media

Type of nanocomposite	Concentration of oxidant (g/l)	Concentration of surfactant (g/l)	Concentration of additive (g/l)	Average particle size (nm)
PAn	10	0	0	114
PAn/HPC	10	2	0	91
PAn/HPC	10	5	0	86
PAn/HPC	10	10	0	79
PAn/PVC	10	0	10	94
PAn/PVC	10	0	30	89

2.3. Preparation of PAn/PVC nanocomposite

1 ml of aniline monomer was added to a stirred aqueous solution (100 ml) containing 1 gr of APS, (1, 3) gr of PVC

for 5 hours at room temperature. The nanocomposites were collected by filtration, and washed several times with deionized water. It was then dried at room temperature for 3 days.

3. RESULT AND DISCUSSION

The chemical method can be a general and useful procedure to prepare conductive polymer and its nanocomposites. It is well established that the charge transport properties of conjugated polymers strongly

depend on the processing parameters. Polyaniline has a reactive N-H group in a polymer chain flanked on either side by a phenylene ring, imparting a very high chemical flexibility

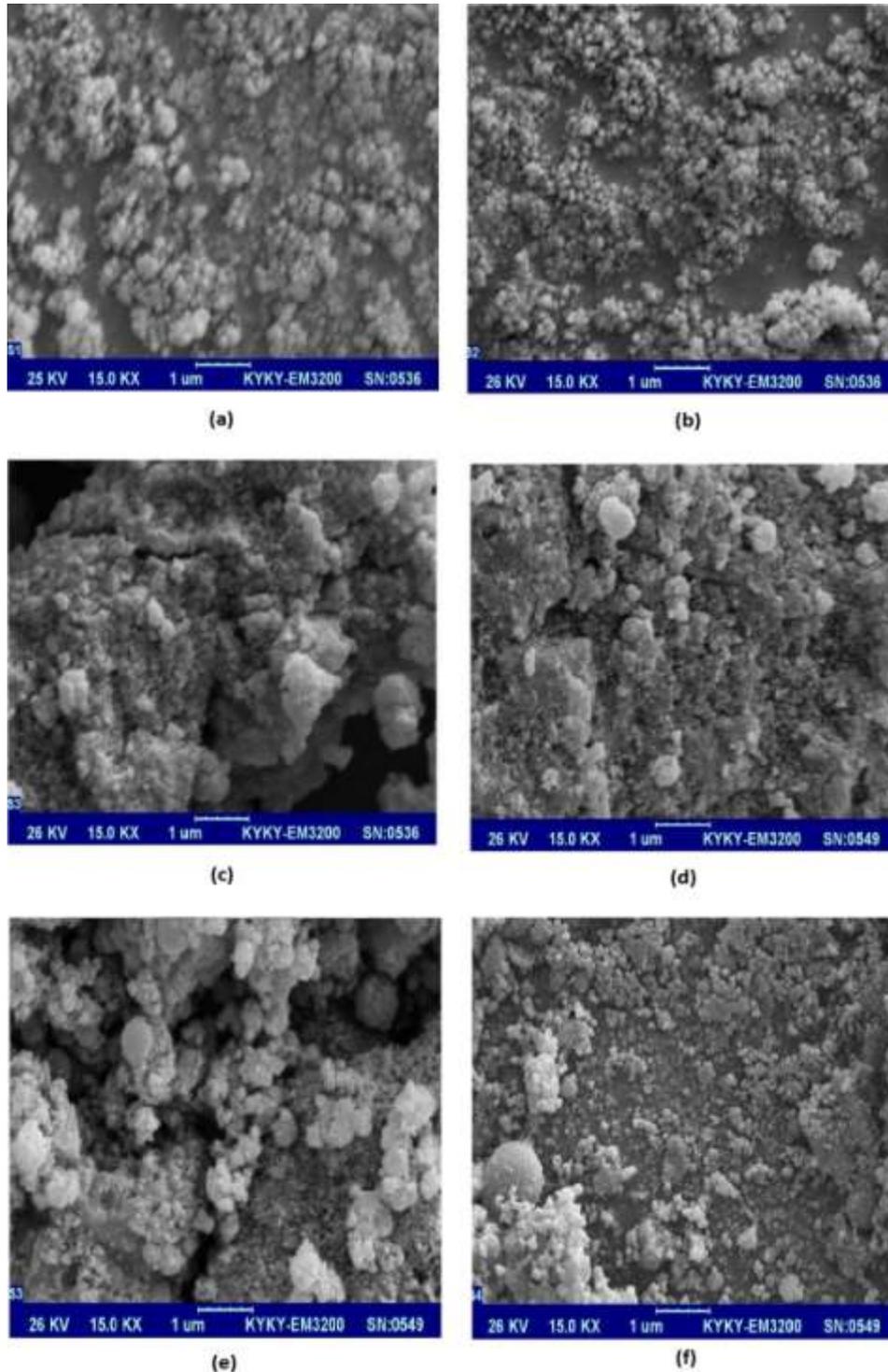


Figure2: SEM of (a) PAn, (b) PAn-(HPC 2g/l), (c) PAn-(HPC 5g/l), (d) PAn-(HPC 10g/l), (e) PAn-(PVC 10g/l), (f) PAn-(PVC 30g/l)

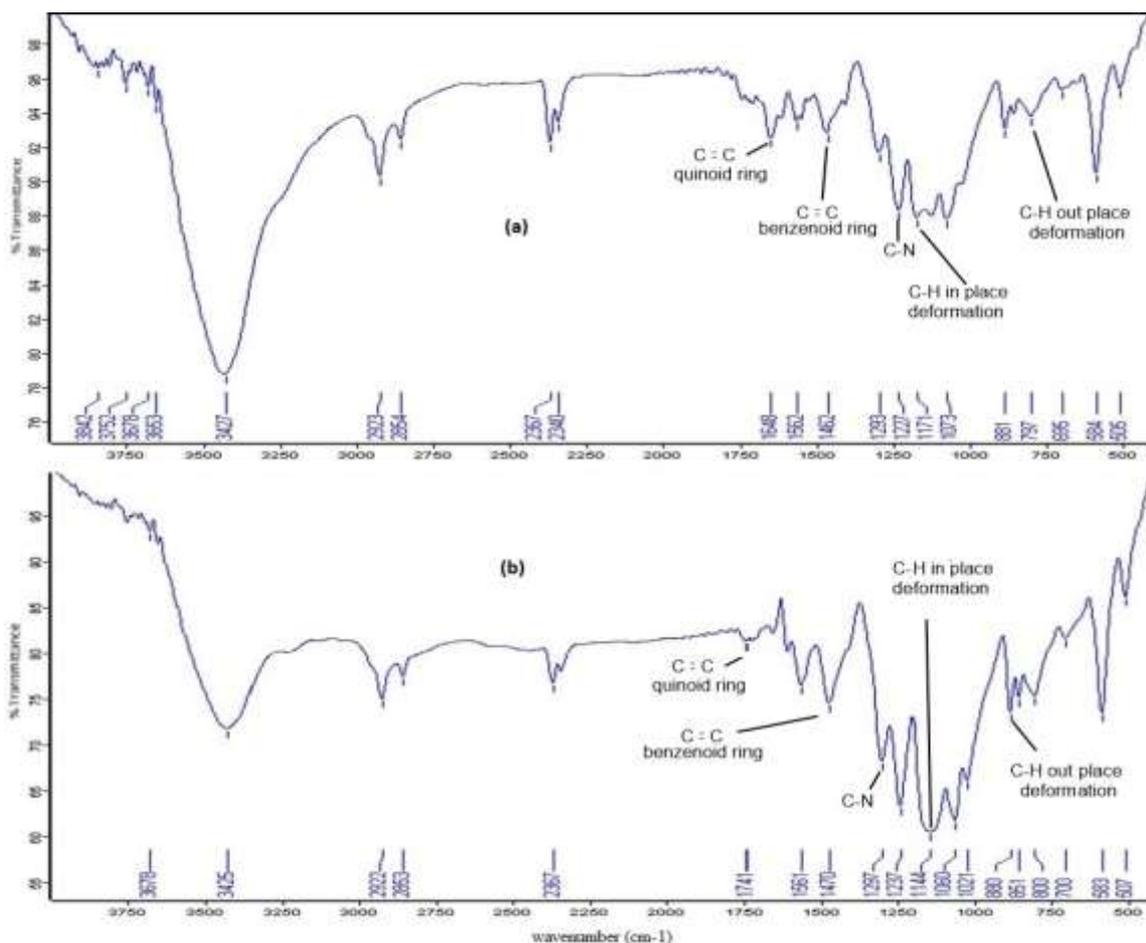


Figure3: FTIR spectra of (a) PAn, (b) PAn-HPC

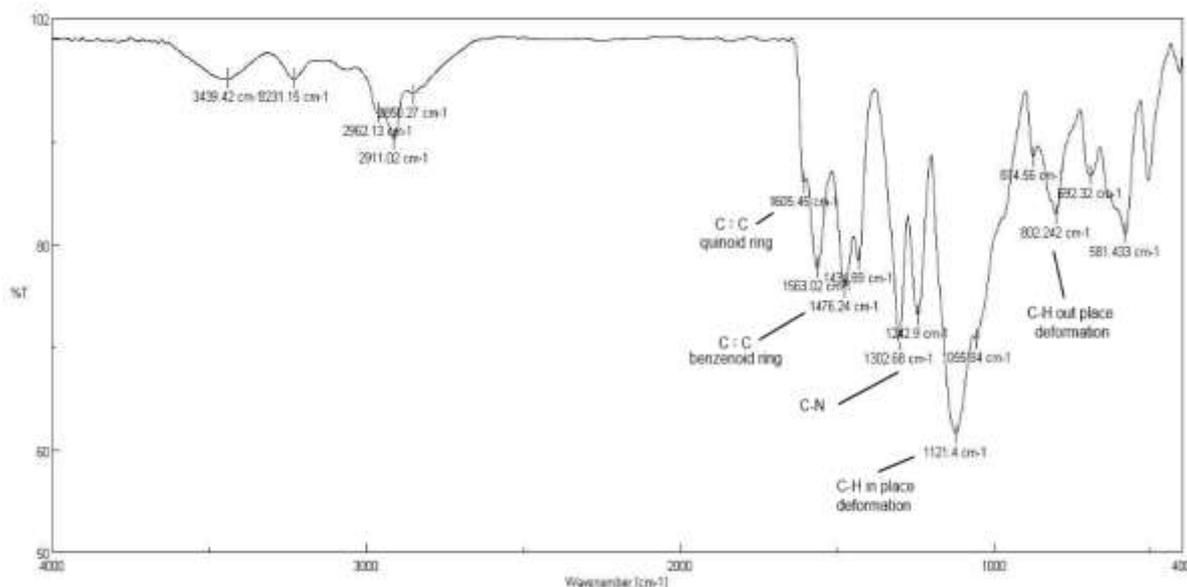


Figure4: FTIR spectra of PAn/PVC in aqueous media

It undergoes protonation and deprotonation in addition to adsorption through nitrogen, which having lone pair

of electrons. The product containing mineral acid group as a dopant, PVC as an additive and HPC as a surfactant, HPC acts as the surfactant

as well as dopant for polyaniline. Preparation conditions and some properties of nanocomposites are listed in Table 3. As can be seen, the size of particles decreases when surfactant and additive are added to solution. The morphology of the polymer was studied using scanning electron microscope. As shown in Figs 2(a-f) the size and homogeneity of the particles are dependent on the concentration of surfactant and additive. Also, as shown in these figures, the surfactant has a considerable effect on the size and homogeneity of particles, because surfactant adsorbed chemically to polyaniline. The chemical structures of the obtained products were determined by FTIR spectroscopy, which has provided valuable information regarding the formation of Polyaniline nanocomposite. The FTIR spectra analysis has been done to identify the characteristic peaks of the product. The FTIR spectra in the 450-4000 cm^{-1} region for PAn in aqueous media is shown in Fig 3(a). Absorption bands at 1648 cm^{-1} (C=C stretching vibration of the quinoid ring), 1462 cm^{-1} (stretching vibration of C=C of the benzenoid ring), 1293 cm^{-1} (C-N stretching vibration), 1171 cm^{-1} (CH in-plane deformation) and 797 cm^{-1} (C-H out-of-plane deformation) are present in PAn polymer. As can be seen in Figure 3(b), the bands at 1648, 1462, 1293, 1171 and 797 cm^{-1} were shifted to 1741, 1470, 1297, 1144 and 851 cm^{-1} , in Fig 4, the bands at 1648, 1462, 1293, 1171 and 797 cm^{-1} were shifted to 1605, 1476, 1302, 1121 and 802 cm^{-1} , in PAn/HPC and

PAn/PVC nanocomposites, respectively, and it proves the interaction of antimony oxide nanoparticles with different reaction sites of polyaniline. The possible interaction between antimony oxide nanoparticles and the nitrogen side of polyaniline in the composite may be the reason for the band shift at 1562-1648 cm^{-1} .

4. CONCLUSIONS

In this study Polyaniline nanocomposites were prepared by chemical oxidative polymerization of aniline using APS = 10 g/L as an oxidant in the presence of hydroxyl propyl cellulose (HPC) as a surfactant and poly(vinyl chloride) (PVC) as an additive in aqueous media. The characteristics of the products, such as morphology and molecular structure, were investigated. It was found that the concentrations of surfactant and additive have considerable effects on the particle size and morphology of the resulting product. Particle size decreases by adding surfactant and additive, because surfactant and additive influence the physical and chemical properties of solution, adsorbed chemically to the polymer, and prevent from gross aggregation of the particles. The molecular structures of the products were determined by FTIR spectroscopy. The results indicated that the intensities of the peaks were dependent on the concentrations of APS, HPC and PVC. FTIR spectra showed that HPC and PVC particles were available in the products.

REFERENCES

1. Eun-Mi, K., Chan-Keun, J. and Chunji, G. (2011), "Highly Conductive Polyaniline Copolymers with dual-functional hydrophilic dioxyethylene Side Chains." *Polymer*, Volume 52, Issue 20, pp. 4451-4455.
2. Hans, G. (2005), "Plastics, General Survey, Ullmann's Encyclopedia of Industrial Chemistry." Wiley-VCH, Weinheim, pp. 102-109.
3. Kavitha, K. and Kumar, K. (2013), "Synthesis and Characterization of Polyaniline Nano-Fibers, *Indian Journal of Pure and Applied Physics*." Vol. 51, pp. 207-209.
4. Madani, S.M. and Ehteshamzadeh, M. (2010), "The Effect of Calcination on the Corrosion Performance of TiO_2 sol-gel Coatings Doped with Benzotriazole on Steel CK45." *Materials & Corrosion*, Vol. 61, No. 4, pp. 318-323.
5. Morat, A. and Tolga, K. (2012), "Conducting Polymers and Their Applications." *Current Physical Chemistry*, 2, pp. 224-240.

6. Parsa, A. (2009), "Studies on Electrochemically Synthesized Polyaniline and its Copolymers." University Sains Malaysia.
7. Prati, S., Joseph, E. and Sciutto, G. (2010), "New Advances in the Application of FTIR Microscopy and Spectroscopy for the Characterization of Artistic Materials." *Acc. Chem. Res.* 43 (6), pp. 792–801.
8. Pud, A. (2003), "Some Aspects of Preparation Methods and Properties of Polyaniline Blends and Composites with Organic Polymers." *Polymer, Sc.* 28, pp. 1701 -1753.
9. William, F. and Javad, H. (2010), "Polymerization Techniques." 4th edition, pp. 1024-1053.
10. Christopher, M. (2005), "Manufacturing Processes for Advanced Materials." *Nanocomposites, AeonClad Coatings*, pp. 778-792.
11. Coroporation & Seiko Electronic Components patent number, 4865932, pp.1 -11.
12. Yuetao, Y., Zhiming, J. and Dawei, F. (2013), "The Use of Conducting Polyaniline as Corrosion Inhibitor for Mild Steel in Hydrochloride Acid." *Int. J. Electrochem. Sci.*, 8, pp. 3540–3550.
13. Chin, M. and Joana, P. (2014), "Surface-Initiated Polymerization." *Chem. Mater.* 26(1), pp. 745-762.
14. Pud, A. (2003), "Some Aspects of Preparation Methods and Properties of Polyaniline Blends and Composites with Organic Polymers." *Prog .Polym, Sc.* 28, pp. 1701 -1753.
15. Ghafouri, H., AleAhmad, A. and Eisazadeh. H. (2010), "Effect of Surfactant on Morphology and Conductivity of Polyaniline Nanoparticles Prepared in Water/Tetrahydrofuran Solution." *Asian Journal of Chemistry*, Vol. 22, No. 9, pp. 6897-6905.
16. Naarmann, H. (2000), "Synthesis an Electroactive Polymer." *Encyclopedia of Industrial Chemistry*, 18, pp. 125-146.
17. Vatani, Z. and Eisazadeh, H. (2012), "Synthesis of Polyaniline/Polystyrene and Polyaniline/Poly(vinyl chloride) Nanocomposite using Hydroxypropylcellulose as a Surfactant." 4th International Conference on Nanostructures, Kish Island, pp. 129-131.