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Synthesis and Modification of Polyaniline Nanostructure by Using Various Surfactants

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In this study, polyaniline nanocomposites were prepared in the aqueous media by using ammonium peroxy disulfate as an oxidant in the presence of various surfactants such as sodium dodecylbenzenesulfonate, poly(vinyl pyrrolidone) and hydroxypropylcellulose. Morphology, conductivity and chemical structure of the product were characterized by using scanning electron micrograph, four point probe method and fourier transform infrared spectrometer respectively. The results indicate that the morphology, yield, particle size and conductivity of products are dependent on the type of surfactant. The results also show that the intensity of peaks is dependent on the type of surfactant.

Key Words: Nanocomposite, Surfactant, Chemical structure, Morphology.

INTRODUCTION

Conducting polyaniline is unique among conducting polymers on account of its excellent optical and electronic properties[1,2]. During the last decades, nanostructured (nanoparticles/-rods/-wires) conducting polyaniline with unusual physical and chemical properties have attracted great research interests. Much research has been conducted on the nanostructure of polyaniline because it exhibits enhanced performance in applications where a high surface contact area is needed between the nanostructures and its environment. Recently, various strategies including template synthesis, interfacial polymerization, self-assembly and stepwise electrochemical deposition have been developed for the preparation of polyaniline nanostructures[3-8].

Polyaniline has attracted considerable attention because of its unique electrical, optical and electrooptical properties and its numerous potential applications[9]. 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[10], grafting of polymers to a non-conducting polymer[11], direct polymerization of intractable polymers into the final desired shape, making a composite of blend of conducting polymers[12,13] and copolymerization[14,15]. Foremost among the current commercial ventures are applications of conducting polymers in energy storage devices such as rechargeable batteries[16], electromagnetic interference (EMI) shielding[17], antistatic coatings[18], gas sensors[19] and optical devices[20], *etc.*

In this study, polyaniline nanocomposites were prepared in the aqueous media using ammonium peroxy disulfate as an oxidant.

EXPERIMENTAL

A magnetic mixer model MK20, digital scale model FR 200, scanning electron microscope (SEM) model XL30 and fourier transform infrared (FTIR) spectrometer model Shimadzu 4100 were employed. The four point probe method was used to measure the volume resistivity of conducting polymer films.

Materials used in this work were aniline (extra pure > 99 %, d =1.02 g/cm^3, Merck), hydroxypropylcellulose (HPC, $M_w = 10^6$) from Aldrich, sodium dodecylbenzenesulfonate (DBSNa) from Loba chemie, poly(vinyl pyrrolidone) (PVP, $M_w = 25000$), sulfuric acid and ammonium peroxy disulfate 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.

The reaction was carried out in aqueous media at room temperature for 5 h. The optimal conditions for nanocomposite formation are summarized in Table-1.

TABLE-1
PREPARATION CONDITIONS AND TYPE OF SURFACTANT ON THE CONDUCTIVITY AND YIELD OF PRODUCT

Type of surfactant	Concentration of surfactant (g/L)	Yield of 1 g monomer to polymer (g)	Average particle size (nm)	Electrical conductivity (S/cm)
Dodecyl benzene sulfonate sodium (DBSNa)	5	0.75	174	1.2×10^{-4}
Hydroxypropyl cellulose (HPC)	5	0.83	130	1.3×10^{-8}
Poly(vinyl pyrrolidone) (PVP)	5	0.79	139	7.8×10^{-7}
–	–	0.87	210	8.3×10^{-5}

In a typical experiment (1 mL) aniline monomer was added to stirred aqueous solution (100 mL) of sulfuric acid (1 M) containing 1 g of $[(NH_4)_2S_2O_8]$. After 5 h, the polymer was filtered and in order to separate the oligomers and impurities, the product was washed several times with deionized water. It was then dried at room temperature.

RESULTS AND DISCUSSION

It is well established that the charge transport properties of conjugated polymers strongly depend on the processing parameters[21]. The electrical conductivities of various nanocomposites produced under different reaction conditions were measured on pressed pellets of the nanocomposite powders. The electrical conductivity of compressed pellets was measured using four point probe method.

The yield, particle size and electrical conductivity of nanocomposites using various surfactants are listed in Table-1. As can be seen the yield, particle size and electrical conductivity are dependent on the type of surfactant, because the surfactant, influence the rate of polymerization and also surfactants are adsorbed physically or chemically (graft copolymer) by the growing polymer[22,23].

The morphology of nanocomposites was studied, using scanning electron microscope. As shown in Figs. 1-4, the size and homogeneity of particles are dependent on the type of surfactant. Polyaniline particles synthesized without surfactant is shown in Fig. 1. As can be seen in micrographs, the nanocomposites obtained using surfactants (DBSNa, HPC and PVP) exhibits spherical particles. It is apparent that using surfactant decreases the tendency to form agglomerates which leads to more homogeneous distribution, because surfactant prevent from gross aggregation of particles. As can see been in table, particle size decreases using various surfactants. The size of particles also related to the type of surfactant.

The structure of obtained product was determined by FTIR spectrum. The FTIR spectroscopy has provided valuable information regarding the formation of polyaniline composites. FTIR analysis has been done to identify the characteristic peaks of product.

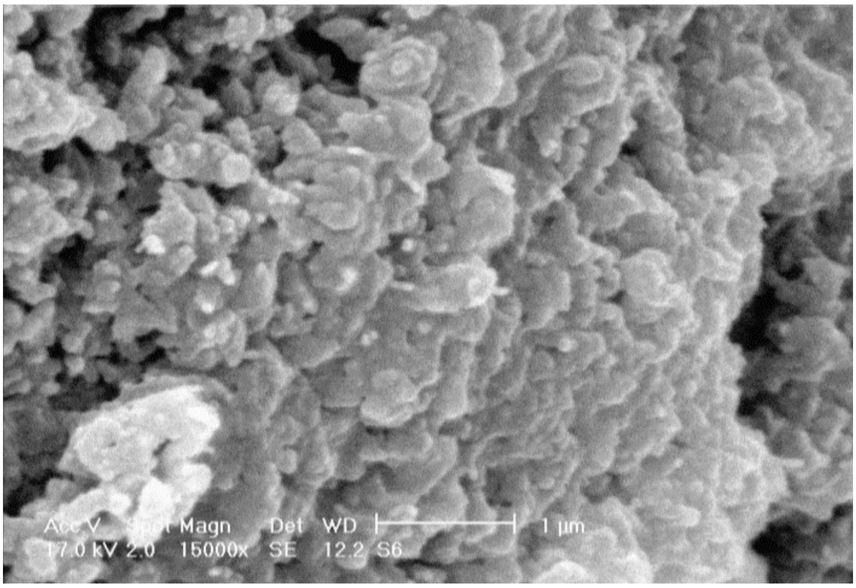


Fig. 1. Scanning electron micrograph of polyaniline in aqueous media. Reaction conditions: (ammonium peroxy disulfate = 10 g/L, aniline monomer 10.75 × 10^{-2} mol/L, volume of solution 100 mL [H_2SO_4 (1M)], reaction time 5 h at room temperature)

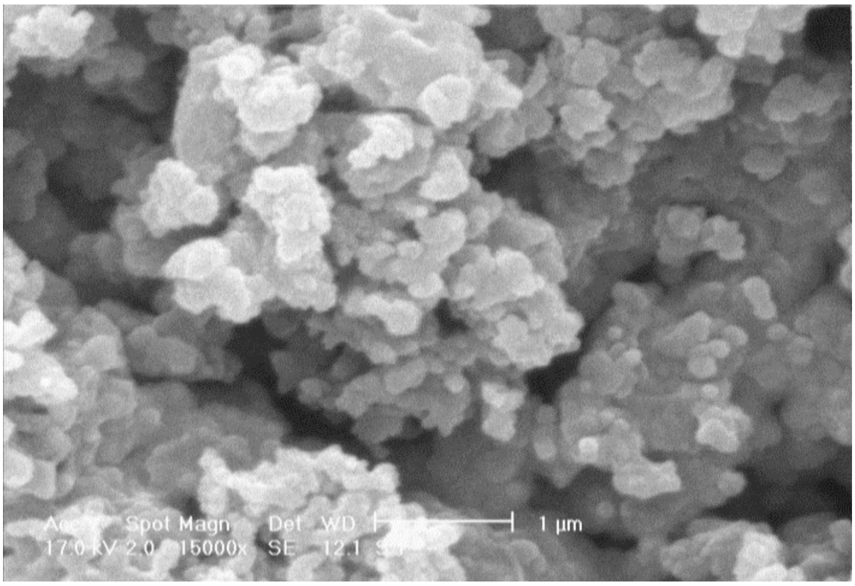


Fig. 2. Scanning electron micrograph of polyaniline in aqueous media. Reaction conditions: (ammonium peroxy disulfate =10 g/L, aniline monomer 10.75 × 10^{-2} mol/L, sodium dodecylbenzenesulfonate = 5 g/L, volume of solution 100 mL (H_2SO_4 (1M)), reaction time 5 h at room temperature)

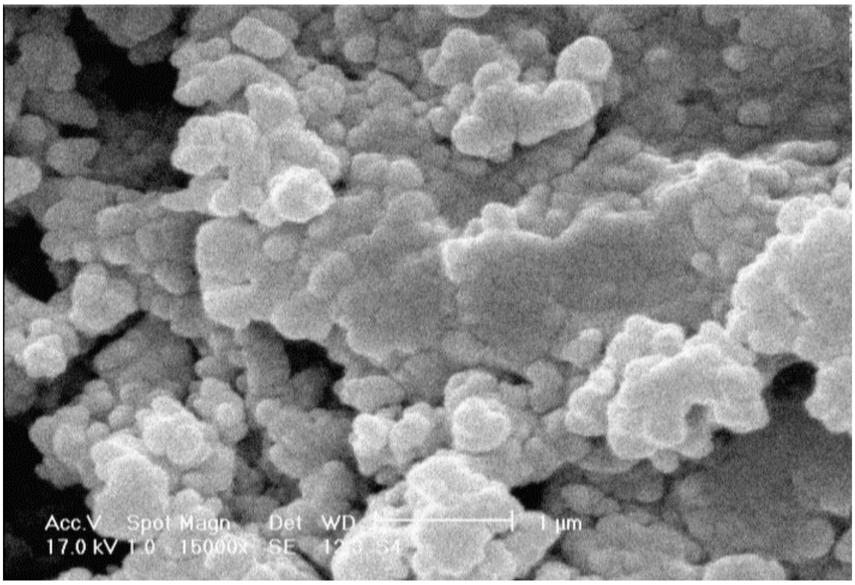


Fig. 3. Scanning electron micrograph of polyaniline in aqueous media. Reaction conditions: (ammonium peroxy disulfate = 10 g/L, aniline monomer 10.75 × 10^{-2} mol/L, hydroxypropylcellulose = 5 g/L, volume of solution 100 mL (H_2SO_4 (1M)), reaction time 5 h at room temperature)

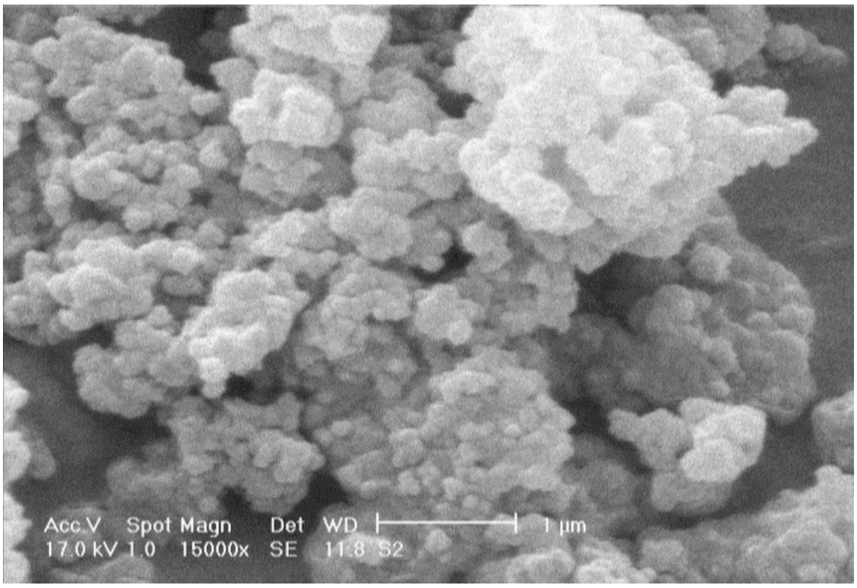
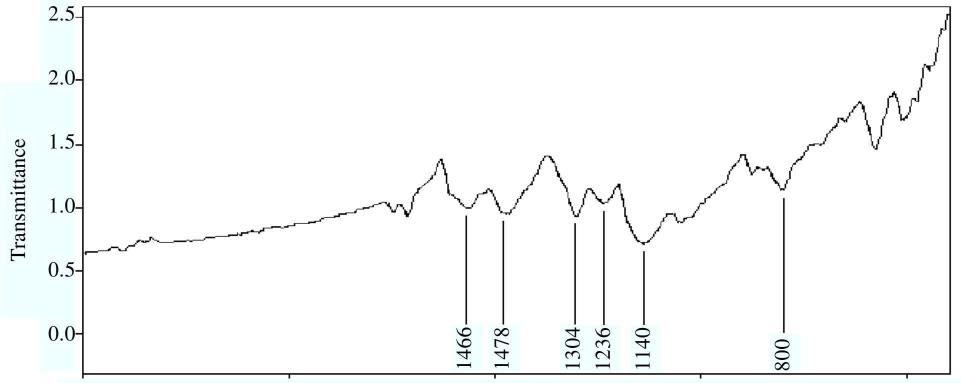
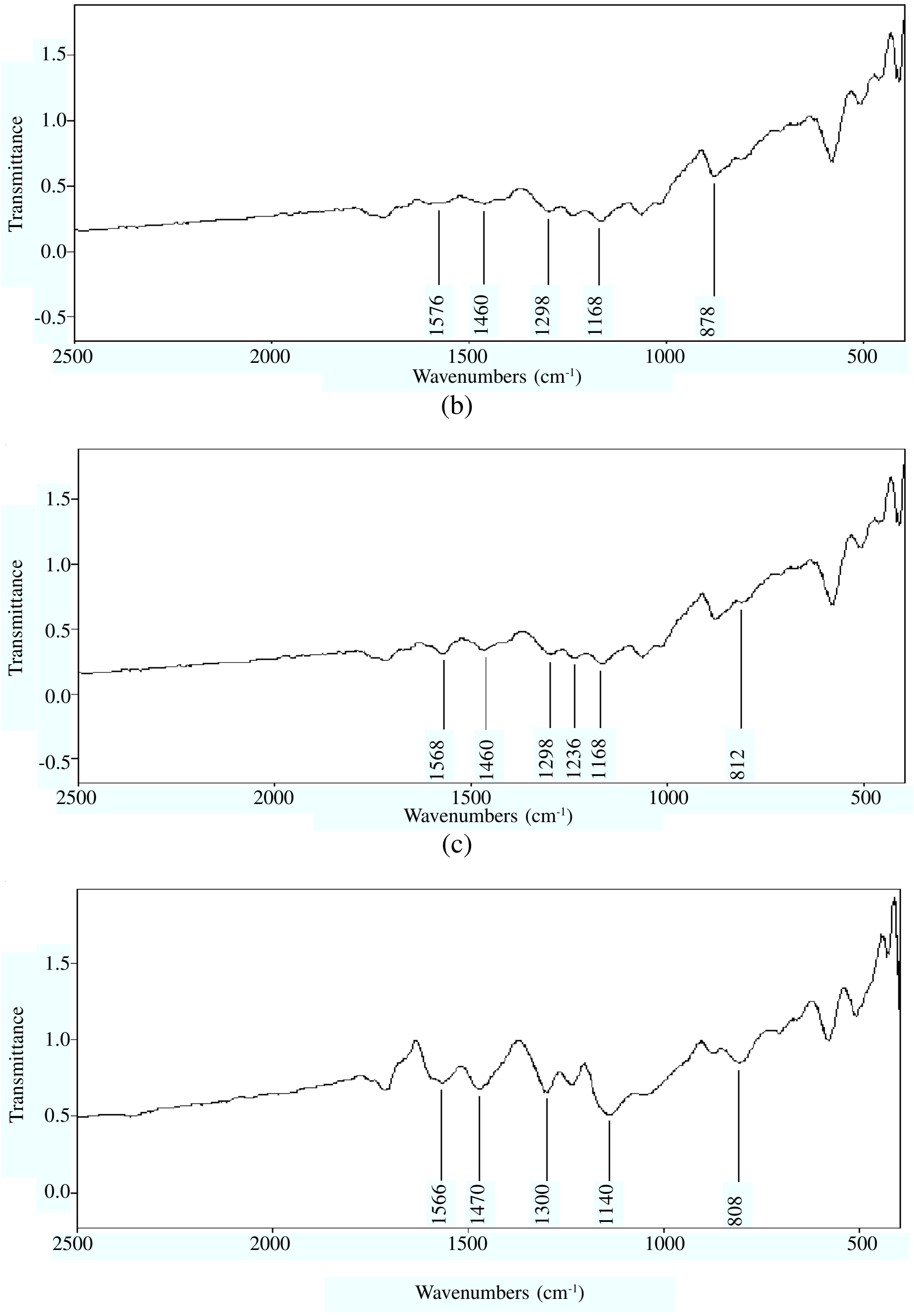


Fig. 4. Scanning electron micrograph of polyaniline in aqueous media. Reaction conditions: (ammonium peroxy disulfate = 10 g/L, aniline monomer 10.75 × 10^{-2} mol/L, poly(vinyl pyrrolidone) = 5 g/L, volume of solution 100 mL (H_2SO_4 (1M)), reaction time 5 h at room temperature)

FTIR spectra in the 2500-400 cm^{-1} region, for polyaniline nanocomposite is shown in Fig. 5. As can be seen, the FTIR spectrum changes greatly and gradually as the composite is formed using various surfactants. For instance, pure polyaniline (Fig. 5a) shows the presence of characteristic absorption bands at 1566 cm^{-1} (C=C stretching vibration of the quinoid ring), 1478 cm^{-1} (stretching vibration of C=C of the benzenoid ring), 1304 cm^{-1} (C-N stretching vibration), 1140 cm^{-1} (C-H in-plane deformation), 800 cm^{-1} (C-H out-of-plane deformation).



(a)



(b)

(c)

(d)

Fig. 5. FTIR spectra of a) pure polyaniline, b) DBSNa, c) HPC and d) PVP used as surfactant in aqueous media

Conclusion

In this work the characteristics of polyaniline nanocomposites such as conductivity, yield, morphology, particle size and structure were investigated using various surfactants in aqueous media. It was apparent that the type of surfactant has a considerable effect on the conductivity, morphology and particle size of resultant product which is probably due to the adsorption of surfactant. The SEM micrographs show that the type of surface active agent plays a major role on the surface morphology of products. As shown in Fig. 5 the intensity of peaks is related to the type of surfactant.

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