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Preparation and characterization of aniline/acrylonitrile nanocomposites using various surfactants in aqueous media

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Abstract−Aniline/acrylonitrile nanocomposites were prepared in aqueous media by using a mixture of $K_2Cr_2O_7/K_2S_2O_8$ as an oxidant in the presence of various surfactants such as poly(vinyl alcohol), hydroxypropylcellulose, and surfactive dopant sodium dodecylbenzenesulfonate. The products were characterized in terms of conductivity, morphology, particle size and chemical structure. The results indicate that the type of surfactant influences the electrical conductivity, size and homogeneity of particles. The FTIR spectra show that the intensity of peaks is related to the type of surfactant.

Key words: Nanocomposite, Morphology, Conductivity, Chemical Structure

INTRODUCTION

Conducting polyaniline (PAni) exhibits extraordinary electronic properties, such as low ionization potential and high electron affinity; as a result, it can be easily reduced or oxidized. Because of this, PAni finds a wide variety of applications in batteries, electromagnetic devices, biosensors, gas-separating membranes, electromagnetic shielding and as an antistatic material [1-5]. However, the common usage of this material has been restricted due to insolubility, infusibility, modest environmental stability and incompatibility with common polymers due to the rigid chain originating from an extended conjugate double bond rendering it unprocessable [6].

To improve the processability of polyaniline various approaches have also been developed: (i) the utilization of a soluble ‘precursor’ method, in which a processable precursor polymer is first prepared in an appropriate form and then chemically converted into the final conducting polymer [7-9]; (ii) formation of conductive blends/composites [10-14]; (iii) formation of PAni filled interpenetrating polymer networks (IPNs) [15-17] and (iv) the copolymerization method, in which graft, block or random conductive copolymers, which are processable were prepared [18-20]. Obviously, materials with relatively high conductivity can be prepared by method (i); however, all the conductive polymers cannot be prepared by this method. Methods (ii) and (iii) provide conductive blends/composites or interpenetrating polymer networks with moderate conductivity and mechanical properties. Method (iv) gives conductive copolymers with increased chemical interaction between the polymers and hence, gives better conductivity and mechanical properties.

Inverse emulsion polymerization consists of an aqueous solution of the monomer, which is emulsified, in a nonpolar solvent and the polymerization is initiated with an oil-soluble initiator. It has several distinct advantages. The reaction carried out in a heterogeneous system takes place in a large number of loci dispersed in a continuous external phase. The physical state of the emulsion makes it easier to control the process. Thermal and viscosity problems are much less significant here than in other polymerization techniques.

On the other hand, polyacrylonitrile (PANr) is an outstanding engineering material generally used in textile applications owing to its good mechanical and thermal properties and is available cheaply. Summan and et al. [21] prepared PANr complexes with copper halides and studied their electrical conductivity at different temperatures. Park and et al. [22] have prepared conducting PAni-PANr composite films by electrochemical polymerization technique. Electrochemical method has the merit of easy control of morphology and electrical properties of the resulting composites, but has a problem in mass production. Whereas, the chemical method is more effective for a mass production of blends/composites or copolymers.

In this study, aniline/acrylonitrile nanocomposites were prepared in aqueous media by using a mixture of $K_2Cr_2O_7/K_2S_2O_8$ as an oxidant, in the presence of various surfactants, respectively.

EXPERIMENTAL

1. Instrumentation

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. A four-point probe method was used to measure the volume resistivity of conducting polymer films.

2. Reagents and Standard Solutions

Materials used in this work were aniline, acrylonitrile, poly(vinyl alcohol) (PVA, M_w=72,000), hydroxypropylcellulose (HPC, M_w=10^6), and sodium dodecylbenzenesulfonate (DBSNa). All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Aniline monomer was purified by simple distillation.

3. Nanocomposite Preparation

The reaction was carried out in an aqueous media at room temperature for 4 hours. The conditions for composite formation are summarized in Table 1.

In a typical experiment 5 mL of acrylonitrile monomer was added to a stirred aqueous solution of 50 mL of sulfuric acid (1 M) containing 1.5 g $K_2S_2O_8$ and heated 70 °C for 2 hr. The solution was

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Table 1. Effect of preparation conditions on the conductivity and particle size of nanocomposites

Type and concentration of surfactant (g/L)	Type and concentration of oxidant (g/L)	Average particle size (nm)	Reaction time of acrylonitrile (hr)	Electrical conductivity (S/cm)	Yield of 5.045 g monomers (acrylonitrile+aniline) to nanocomposite (g)
Sodium dodecylbenzenesulfonate=2.5	$K_2Cr_2O_7$=10 $K_2S_2O_8$=15	88	2	10^{-4}	4.18
Hydroxypropylcellulose=2.5	$K_2Cr_2O_7$=10 $K_2S_2O_8$=15	76	2	1.6×10^{-5}	3.92
Poly(vinyl alcohol)=2.5	$K_2Cr_2O_7$=10 $K_2S_2O_8$=15	72	2	3.6×10^{-5}	4.10
Sodium dodecylbenzenesulfonate=5	$K_2Cr_2O_7$=10 $K_2S_2O_8$=15	76	2	1.8×10^{-3}	4.14
Hydroxypropylcellulose=5	$K_2Cr_2O_7$=10 $K_2S_2O_8$=15	91	2	20×10^{-2}	3.66
Poly(vinyl alcohol)=5	$K_2Cr_2O_7$=10 $K_2S_2O_8$=15	86	2	3.3×10^{-4}	3.98
Sodium dodecylbenzenesulfonate=7.5	$K_2Cr_2O_7$=10 $K_2S_2O_8$=15	96	2	2.1×10^{-3}	3.95
Hydroxypropylcellulose=7.5	$K_2Cr_2O_7$=10 $K_2S_2O_8$=15	72	2	2×10^{-4}	3.55
Poly(vinyl alcohol)=7.5	$K_2Cr_2O_7$=10 $K_2S_2O_8$=15	82	2	2.1×10^{-3}	3.94
Without surfactant	$K_2Cr_2O_7$=10 $K_2S_2O_8$=15	87	2	1.1×10^{-4}	4.10
Without surfactant	$K_2Cr_2O_7$=10 $K_2S_2O_8$=15	77	0.5	1.66×10^{-4}	3.28
Without surfactant	$K_2Cr_2O_7$=10 $K_2S_2O_8$=15	51	4	10^{-4}	4.15

cooled using cold water for ten minutes. Then 50 mL of sulfuric acid (1 M) containing 1 g $K_2Cr_2O_7$ and 0.25 g of one of the surfactants was added to stirred aqueous solution, respectively. After a few minutes 1 mL aniline monomer was injected to the stirred solution at room temperature and the reaction continued for 4 hr. The product was filtered using filter paper, and in order to separate the impurities and oligomers, the resultant product was washed several times with deionized water. It was then dried at room temperature.

RESULTS AND DISCUSSION

1. Effect of Surfactant Type on the Conductivity of Aniline/Acrylonitrile Nanocomposite

As PAni is molecular composite containing a cationic polymer

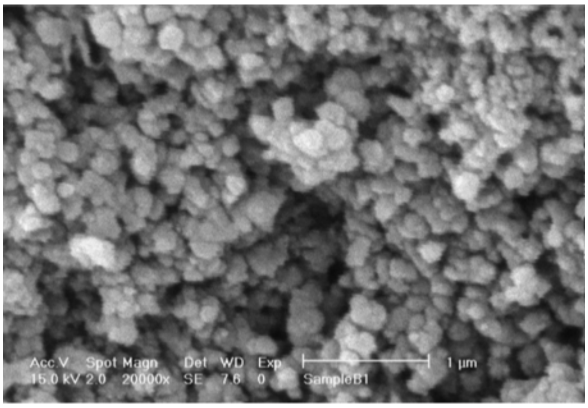


Fig. 1. Scanning electron micrograph of pure PAni generated in aqueous media. Reaction conditions: ($K_2Cr_2O_7$=10 g/L, aniline monomer 10.75×10^{-2} mol/L, volume of solution 100 mL, reaction time 4 hr at room temperature).

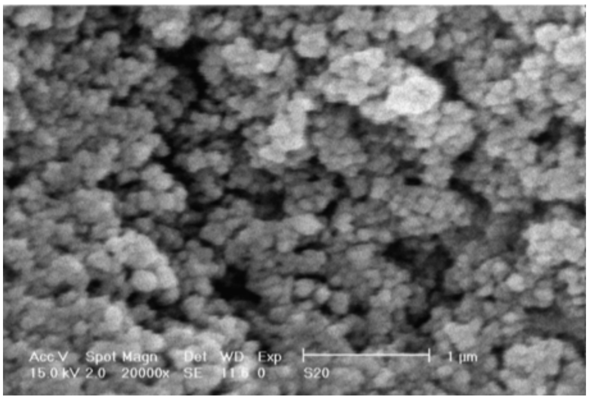
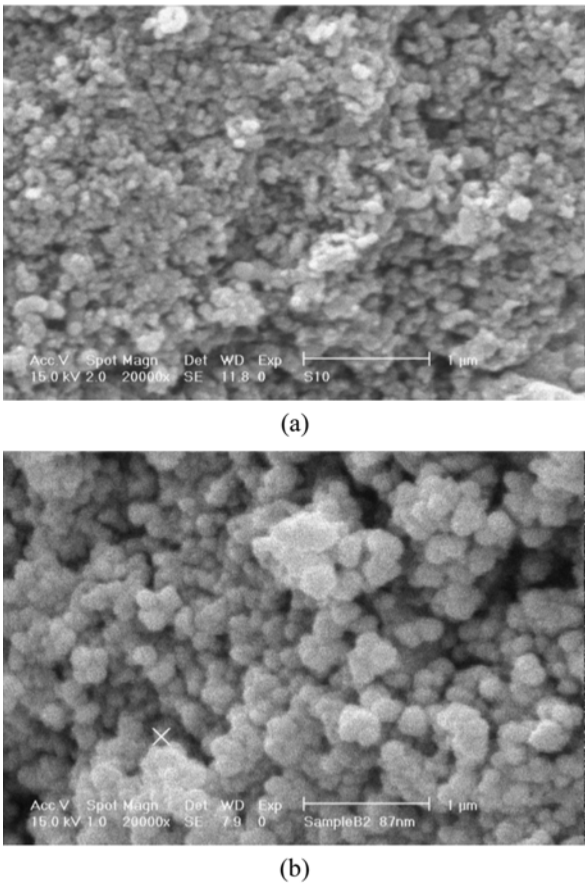


Fig. 2. Scanning electron micrograph of pure PANr generated in aqueous media. Reaction conditions: ($K_2S_2O_8$=15 g/L, acrylonitrile monomer 7.58×10^{-2} mol/L, volume of solution 100 mL, reaction time 4 hr at 70 °C temperature).



(a)

(b)

Fig. 3. Scanning electron micrograph of Ani/ANr nanocomposite without surfactant in aqueous media. Reaction conditions: ($K_2Cr_2O_7$=10 g/L, $K_2S_2O_8$=15 g/L, aniline monomer 10.75×10^{-2} mol/L, acrylonitrile monomer 7.58×10^{-2} mol/L, volume of solution 100 mL. Acrylonitrile monomer was added to solution and heated for (a) 4 hr and (b) 2 hr at 70 °C. Then aniline monomer was injected into the solution at room temperature and reaction continued for 4 hr).

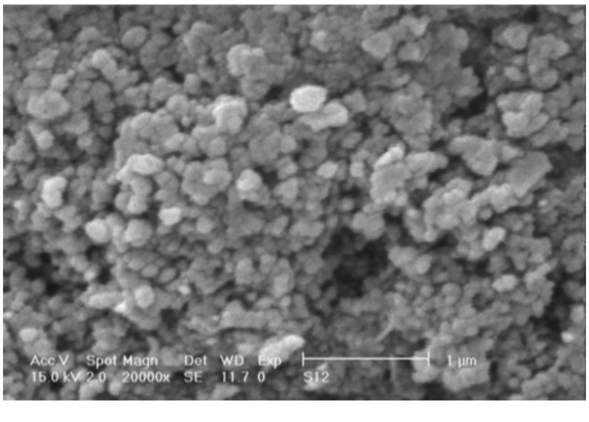


Fig. 4. Scanning electron micrograph of Ani/ANr nanocomposite without surfactant in aqueous media. Reaction conditions: ($K_2Cr_2O_7$=10 g/L, $K_2S_2O_8$=15 g/L, aniline monomer 10.75×10^{-2} mol/L, acrylonitrile monomer 7.58×10^{-2} mol/L, volume of solution 100 mL. Acrylonitrile monomer was added to solution and heated for 0.5 hr at 70 °C. Then aniline monomer was injected into the solution at room temperature and reaction continued for 4 hr).

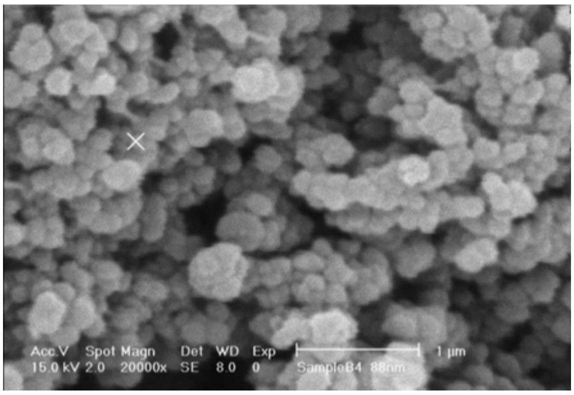
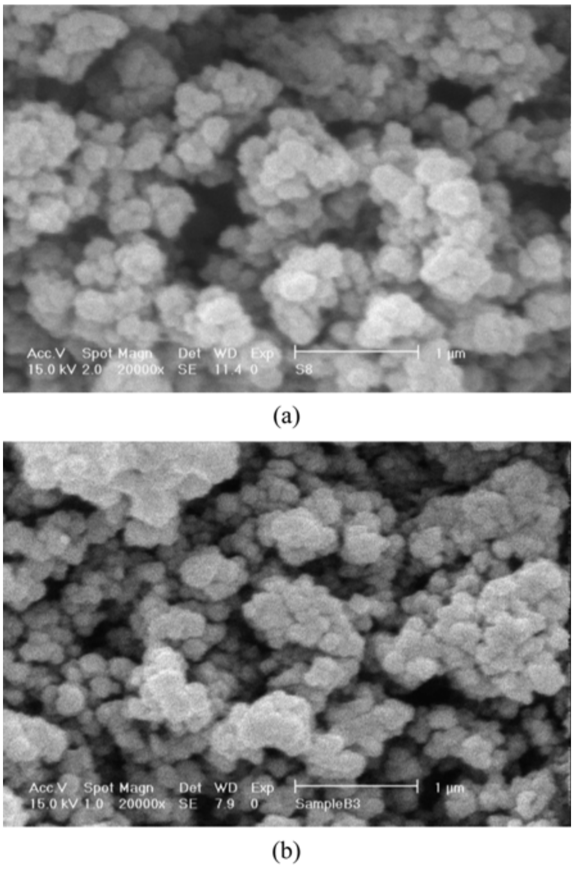


Fig. 5. Scanning electron micrograph of Ani/ANr nanocomposite, DBSNa, used as surfactants in aqueous media. Reaction conditions: ($K_2Cr_2O_7$=10 g/L, $K_2S_2O_8$=15 g/L, aniline monomer 10.75×10^{-2} mol/L, acrylonitrile monomer 7.58×10^{-2} mol/L, DBSNa=2.5 g/L, volume of solution 100 mL. Acrylonitrile monomer was added to solution and heated for 2 hr at 70 °C. Then aniline monomer was injected into the solution at room temperature and reaction continued for 4 hr).



(a)

(b)

Fig. 6. Scanning electron micrograph of Ani/ANr nanocomposite, (a) PVA and (b) HPC used as surfactants in aqueous media. Reaction conditions: ($K_2Cr_2O_7$=10 g/L, $K_2S_2O_8$=15 g/L, aniline monomer 10.75×10^{-2} mol/L, acrylonitrile monomer 7.58 $\times10^{-2}$ mol/L, PVA=2.5 g/L, HPC=2.5 g/L, volume of solution 100 mL. Acrylonitrile monomer was added to solution and heated for 2 hr at 70 °C. Then aniline monomer was injected into the solution at room temperature and reaction continued for 4 hr).

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 PAni will be affected by dopant [23]. Particle size and electrical conductivity of nanocomposite are listed in Table 1. As can be seen, particle size and electrical conductivity are dependent on the type of surfactant, because the surfactants are adsorbed physically or bonded chemically (graft copolymer) to the growing polymer [24].

The electrical conductivities of various nanocomposites produced under different reaction conditions were measured on pressed pellets of the nanocomposite powders. The electrical conductivity of the compressed pellets was measured using four point probe method. As can be seen in table, the electrical conductivity of resultant products is related to the type of surfactant.

By comparison between DBSNa and (HPC, PVA), conductivity increased using DBSNa, because DBSNa simultaneously acts as emulsifier and dopant. Also, particle size is related to the type of surfactant, due to surfactant preventing from gross aggregation of particles.

Usually in conductive polymers, electrical conductivity increases, when particle size decreases, because total surface area is related to the size of particles. But in this work, at first a non-conductive polymer (polyacrylonitrile) was generated and then the resultant con-

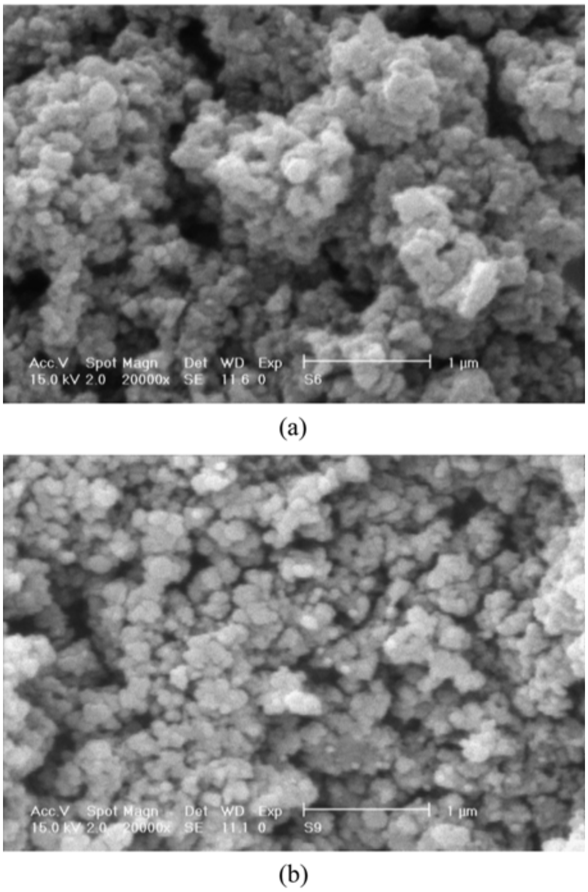


Fig. 7. Scanning electron micrograph of Ani/ANr nanocomposite, (a) DBSNa and (b) PVA used as surfactants in aqueous media. Reaction conditions: ($K_2Cr_2O_7$=10 g/L, $K_2S_2O_8$=15 g/L, aniline monomer 10.75×10^{-2} mol/L, acrylonitrile monomer 7.58×10^{-2} mol/L, DBSNa=7.5 g/L, PVA=7.5 g/L, volume of solution 100 mL. Acrylonitrile monomer was added to solution and heated for 2 hr at 70 °C. Then aniline monomer was injected into the solution at room temperature and reaction continued for 4 hr).

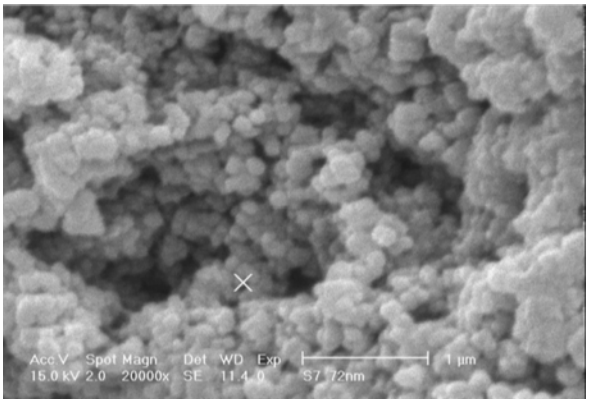


Fig. 8. Scanning electron micrograph of Ani/ANr nanocomposite, HPC used as surfactant in aqueous media. Reaction conditions: ($K_2Cr_2O_7$=10 g/L, $K_2S_2O_8$=15 g/L, aniline monomer 10.75×10^{-2} mol/L, acrylonitrile monomer 7.58×10^{-2} mol/L, HPC=7.5 g/L, volume of solution 100 mL. Acrylonitrile monomer was added to solution and heated for 2 hr at 70 °C. Then aniline monomer was injected into the solution at room temperature and reaction continued for 4 hr).

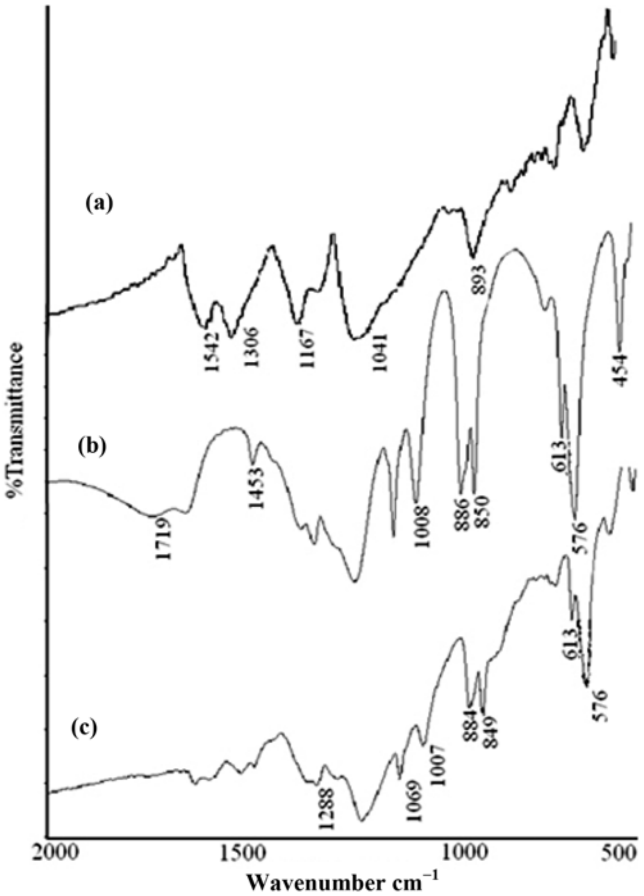


Fig. 9. FT-IR spectra of (a) pure PAni, (b) pure PANr and (c) surfactant free Ani/ANr nanocomposite.

ductive polymer (polyaniline) coated the surface of non-conductive polymers. Therefore, electrical conductivity is related to amount of polyaniline coated or probably grafted to polyacrylonitrile particles.

2. Characterization of the Aniline/Acrylonitrile Nanocomposite

Morphology plays an important role in determining conductivity and mechanical properties of the materials, because electrical conductivity is related to surface morphology. Figs. 1 and 2 show scanning electron micrographs of pure polyaniline, pure polyacrylonitrile and Figs. 3 and 4 show scanning electron micrographs of Ani/ANr nanocomposite synthesized without surfactant in different reaction times in aqueous media, respectively. As shown in Figs. 5-8 the size, homogeneity and size distribution of particles are dependent on the type and concentration of surfactant. The type of surfactant is known to influence the rate of polymer formation, particle size, size distribution, morphology and homogeneity [25-28]. As can be seen in the figures the type of additive affects the homogeneity and size of particles, because ionic and non-ionic additives influence the physical and chemical properties of solution and rate of polymerization. Adsorption of the surface active agent on the Ani/ANr particles is primarily due to the hydrophobic component in the surfactants, probably via a hydrogen bonding mechanism with the aniline N-H group [29].

3. FT-IR Spectra

The chemical structures of the obtained products were determined by FTIR spectroscopy. The FTIR spectra analysis has been done to identify the characteristic peaks of product.

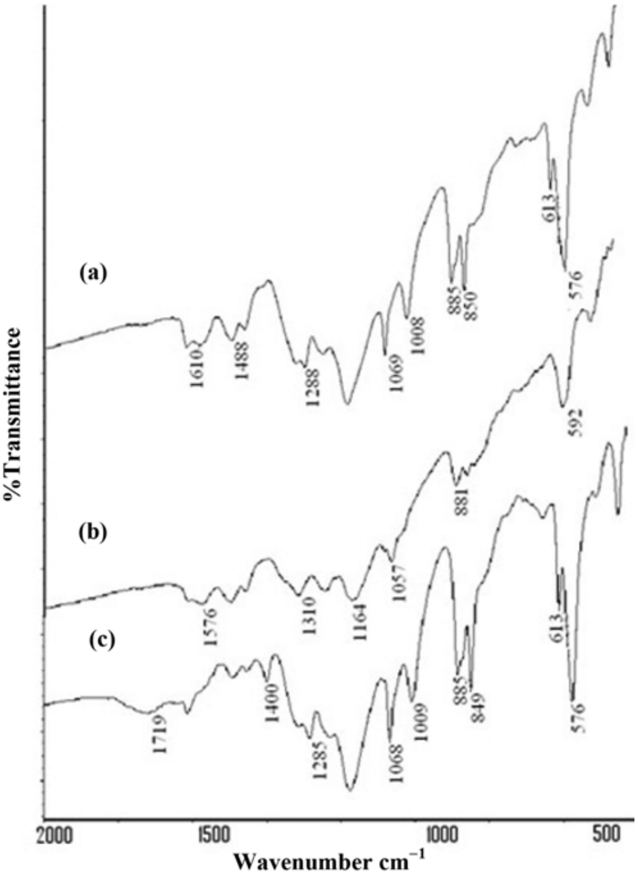


Fig. 10. FTIR spectra of Ani/ANr nanocomposite. (a) DBSNa, (b) HPC and (c) PVA used as surfactant, concentration of surfactant=2.5 g/L.

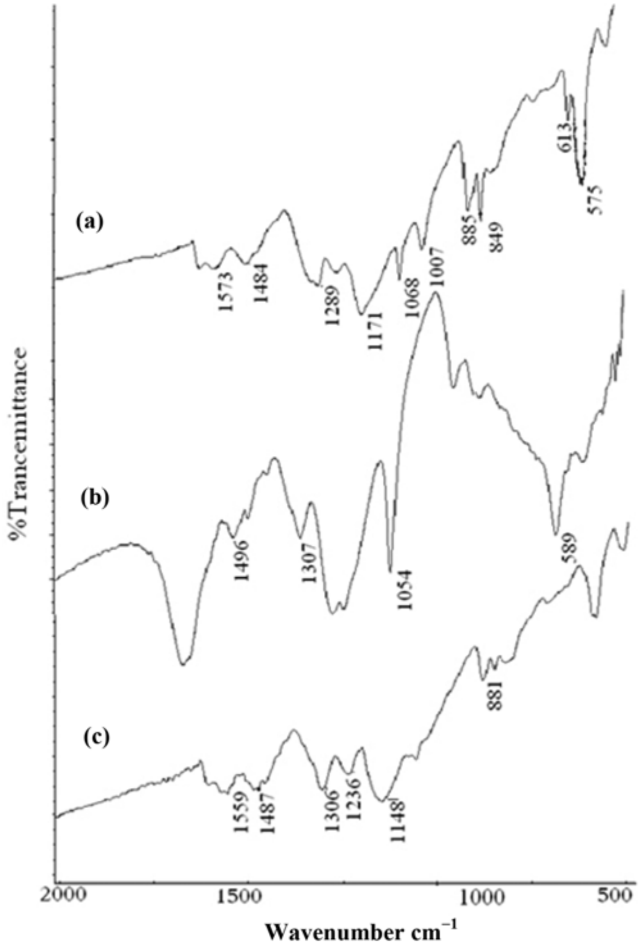


Fig. 11. FTIR spectra of Ani/ANr nanocomposite. (a) DBSNa, (b) HPC and (c) PVA used as surfactant, concentration of surfactant=7.5 g/L.

The FTIR spectra in the 2,000-400 cm^{-1} region for various polymers are shown in Figs. 7-10. As can be seen, the FTIR spectrum changes when the composite is formed by compositization. As shown in Fig. 7(a), one characteristic of the aniline unit at 1,542 cm^{-1}, the peaks are at 1,306 cm^{-1} (C-N stretching vibration), 1,167 cm^{-1} (C-H in-plane deformation), 1,041 cm^{-1} (N-H in-plane deformation) and 893 cm^{-1} (C-H out-of-plane deformation).

CONCLUSIONS

The characteristics of Ani/ANr nanocomposites such as morphology, electrical conductivity, chemical structure and particle size were investigated using various surfactants with various concentration and in various reaction time of acrylonitrile. It was found that the type of surfactant has considerable effect on the conductivity, size, homogeneity, size distribution and morphology of the resultant product, which is probably due to additive absorption. Spherical nanoparticles were obtained using DBSNa, PVA and HPC as surfactant. The structure of products was determined by FTIR spectrum. The results indicate that the intensity of peaks is related to the type of surfactant.

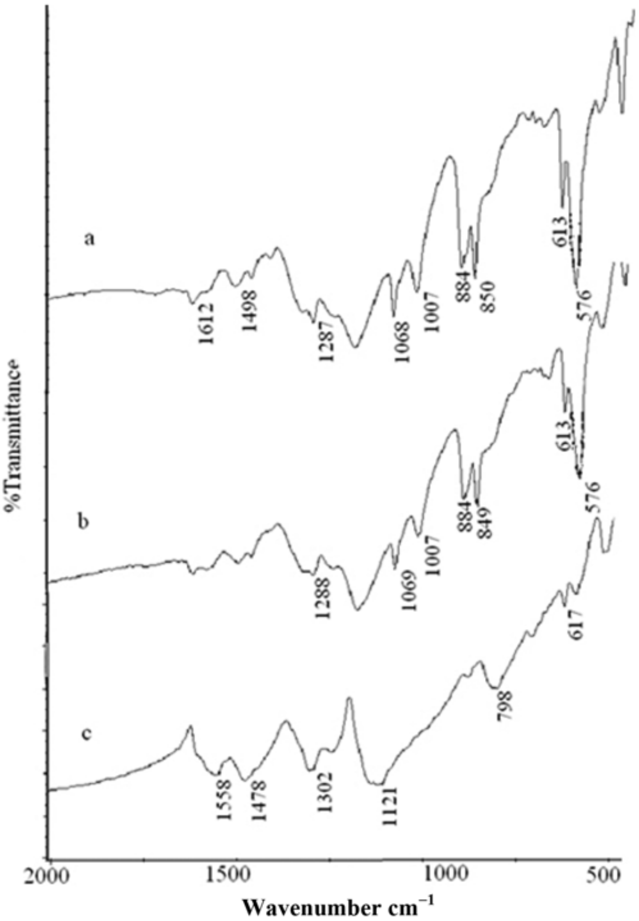


Fig. 12. FTIR spectra of Ani/ANr nanocomposite in different resident time of acrylonitrile monomer. (a) 0.5 hr, (b) 2 hr and (c) 4 hr.

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