

Studying the Characteristics of Polypyrrole and its Composites

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Abstract: Polypyrrole and its composites were prepared chemically using FeCl_3 as an oxidant in aqueous and non-aqueous media. The effect of various solutions such as water, ethylacetate, acetonitrile, methylacetate, methanol, ethylmethylketone and surface active agents, poly (ethylene glycol) and poly (vinyl acetate) on the properties of product were studied. The electrically conducting polymer and its composites have been characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) and proton nuclear magnetic resonance (^1H NMR) spectroscopy. The results indicate that the morphology, conductivity and structure of products are dependent on the type of solution and additive.

Key words: Polypyrrole composite . different media . additives . morphology . conductivity . structure

INTRODUCTION

Conducting polymer matrices provide an interesting and useful focus for expansion of the fields of polymeric reagent research and molecular engineering. They are electrically conductive which makes their use as metal replacement materials of some interest.

Conductive electro-active polymers such as polypyrrole (PPy) possess some unique chemical and electrochemical properties. PPy is attractive as an electrically conducting polymer because of its relative ease of synthesis. Bulk quantities of PPy can be obtained as fine powders using the oxidative polymerization of the monomer by selected transition metal ions in water or various other solvents [1-3]. The reaction of pyrrole with aqueous ferric chloride is very rapid and the product is a black powder which is insoluble in all common solvents [4]. Iron (III) salts provide a convenient means for oxidative polymerizing pyrrole and incorporating their anions as dopant ions [4]. PPy⁰ changed to PPy^{+(A?)} spontaneously when it was dipped in an acidic aqueous solution and it changed to PPy^{+(OH?)} when dipped in an alkaline or neutral aqueous solution [5].

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 [6, 7]. Improvement of these material properties can be achieved either by forming copolymers of pyrrole, or by forming PPy composites or blends with commercially available polymers or inorganic materials which offer better mechanical and optical properties, stability and

processability [8, 9]. A general route for creating PPy composites is the in situ polymerization of pyrrole in the presence of organic or inorganic substances. Other useful approach for the improvement of the processability and the mechanical properties of insoluble polymers is the blending with soluble matrix polymers.

A wide range of possible applications have been proposed for conducting polymers such as conductive paint [10], removal of heavy metals [11, 12], gas separations [13], membrane [14]. Deposition of nanometer-scale metal particles into PPy is interesting for making biosensors, which detect peroxide produced by enzymatic reactions [15]. Low ppm detection limits have been demonstrated for toxic gases such as ammonia and nitrogen dioxide [16]. PPy coated glass fiber fabrics have also been used to construct a Salisbury screen absorber and showed promising characteristics for their possible use as radar absorbing materials [17].

In recent years much research was concerned with their composites with conventional polymers. This approach has been successful in producing electrical conductive composites with a wide range of interesting mechanical and electrical properties. In this study, conductivity, morphology and structure of PPy and its composites are investigated using various solutions and additives.

MATERIALS AND METHODS

Instrumentation: A magnetic mixer model MK20, digital scale model FR200, Scanning Electron Microscope (SEM) model LSM50A, Fourier Transform

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Table 1: The optimal conditions for PPy and its composites preparation

Type of sample	Type of additive	Concentration of additive (g L ⁻¹)	Type of solution
PPy	-	-	Water
PPy	-	-	Methylacetate
PPy	-	-	Methanol
PPy	-	-	Water+Ethylacetate
PPy	-	-	Acetonitrile
Composite of PPy and PEG	PEG	20	Water
Composite of PPy and PEG	PEG	6	Ethylacetate+Water
Composite of PPy and PEG	PEG	6	Methylacetate
Composite of PPy and PEG	PEG	20	Acetonitrile
Composite of PPy and PEG	PEG	20	Ethylmethylketon+Water
Composite of PPy and PEG	PEG	20	Methanol
Composite of PPy and PVAc	PVAc	6	Water
Composite of PPy and PVAc	PVAc	6	Methylacetate
Composite of PPy and PVAc	PVAc	6	Ethylacetate+water
Composite of PPy and PVAc	PVAc	6	Acetonitrile
Composite of PPy and PVAc	PVAc	6	Ethylmethylketon+water
Composite of PPy and (PEG+PVAc)	PEG+PVAc	PEG = 6g l ⁻¹ PVAc = 6g l ⁻¹	Ethylmethylketon+Water

Conditions of reaction: (FeCl₃ = 48 g L⁻¹, pyrrole monomer 14.9×10⁻² mol L⁻¹, reaction in environment temperature for 5 hours, volume of solution 100mL and the mixture of solution has been prepared equal volume ratio 50/50% V/V)

Infrared (FTIR) spectrometer model shimadzu4100 were employed. Proton nuclear magnetic resonance (¹H NMR, 400 MHz) spectra were recorded on Avance 400 Bruker spectrometer using deuterated m-cresol and NMP as a solvent. The four point probe is used to measure the volume resistivity of conducting polymer films.

Reagents and standard solutions: All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Pyrrole monomer was purified by simple distillation. Materials used in this work were Pyrrole (Aldrich), ethylacetate (RdH), Poly (vinyl acetate) (PVAc, M_w = 25000), Poly (ethylene glycol) (PEG, M_w = 35000), acetonitrile, methylacetate, methanol, ethylmethylketone all obtained from Merck.

Polypyrrole and its composites preparation: Chemical method was used for the preparation of PPy and its composites in the various solutions. FeCl₃ was used as the oxidant, with PVAc and PEG as the surface active agents. The reaction was carried out in aqueous and non-aqueous media such as water, ethylacetate, acetonitrile, methylacetate, methanol, ethylmethylketone at the room temperature for 5 hours. The optimal conditions for PPy and its composites preparation are summarized in Table 1.

In a typical experiment 1 mL of pyrrole monomer was added to stirred aqueous or non-aqueous solutions 100 mL containing 4.8 g of ferric chloride and 0.6-2 g one of the PEG or PVAc. After 5 hours product was filtered and to separate the oligomers and impurities, product was washed several times with deionized water and dried at room temperature.

It should be mentioned that in the preparation of PPy composites, when the amount of surface active agents such as PEG or PVAc are low, the stabilization is inefficient and so the macroscopic precipitation of polymer occurs.

RESULTS AND DISCUSSION

The chemical method can be a general and useful procedure to prepare conductive polymer and its composites. PPy is attractive as an electrically conducting polymer because of its relative ease of synthesis. In order to exploit this material in some potential commercial applications, it will be necessary to synthesize it at low cost.

The electrical conductivities of various composites produced under different reaction conditions were measured on pressed pellets of the composite powders. The results show that conductivities of the pressed pellets were in the range of (2.2×10⁻³ - 4.4×10⁻¹ S cm⁻¹) without additive, (2.1×10⁻⁴ - 17.8×10⁻² S cm⁻¹) with

Table 2: Conductivity of PPy and its composites in various solutions and additives

Type of solution	Conductivity (S cm ⁻¹)	Type of additive	Concentration of additive (g L ⁻¹)	Conductivity (S cm ⁻¹)	Type of additive	Concentration of additive (g L ⁻¹)	Conductivity (S cm ⁻¹)
Water 100mL	4.4×10^{-1}	PEG	20	17.8×10^{-2}	PVAc	6	8.2×10^{-2}
Methylacetate 100mL	2.2×10^{-3}	PEG	6	9.5×10^{-4}	PVAc	6	1.7×10^{-4}
Ethylacetate+water (50/50% v/v)	3.6×10^{-1}	PEG	6	13.5×10^{-2}	PVAc	6	3.22×10^{-2}
Acetonitrile 100 mL	6×10^{-2}	PEG	20	2.4×10^{-2}	PVAc	6	1.36×10^{-2}
Ethylmethylketon+ water (50/50% v/v)	4.2×10^{-2}	PEG	20	2.1×10^{-4}	PVAc	6	4.1×10^{-3}
Methanol 100 mL	3.1×10^{-2}	PEG	20	2×10^{-2}	PVAc	6	1.2×10^{-2}
Ethylmethylketon+ water (50/50% v/v)	-	-	-	-	PVAc+PEG	PVAc = 6 g L ⁻¹ PEG = 6 g L ⁻¹	3.9×10^{-3}

PEG and (1.7×10^{-4} - 8.2×10^{-2} S cm⁻¹) with PVAc respectively.

Compressed pellets were obtained under 2 ton cm⁻² pressure in the environment temperature. The average thickness of the compressed pellets was 250µm. The electrical conductivity of compressed pellets was measured using four point probe method. The results are shown in Table 2. As can be seen in Table 2, the electrical conductivity is dependent on type of solutions and additives. PEG and PVAc are stabilizing agents and could affect the size, morphology and the homogeneity of particles [18, 19], because the surfactants are adsorbed physically to the polymer by the growing polymer. It is well established that the charge transport properties of conjugated polymers strongly depend on the processing parameters [20]. The use of specific solvents during the processing plays an important role in the conductive properties of prepared films [21].

The conductivity increased with increasing polarizability of the carrier solvents, because this became increasingly compatible with pyrrole as polarizability increased [22]. The conductivity decreases in non-aqueous media due to increase stabilizer adsorption, but as a result of an increase in the polymerization rate in the polar organic media, polydispersed particles are formed. As shown in Table 2, the conductivity of composites is dependent on the type of surfactant. Poly (ethylene glycol) and poly (vinyl acetate) are polymeric surfactants, which influence the viscosity of solution and can react with monomer droplet of emulsion.

As shown in Table, by comparison between PVAc and PEG at the same concentration, in general, the lower conductivity measured for the PVAc compared to PEG. This is probably due to the increased amount of

adsorbed physically insulating surfactant relative to the conductive component. It is found that the conductivity decreases by increasing stabilizer concentration for a given solvent. A probable explanation for these observations is that the polymeric surfactant chains are physically adsorbed onto the polypyrrole particles at a faster rate and therefore in larger relative amounts. So, this is related to the mass of insulating steric stabilizer adsorbed [23].

Among the solvents used in this oxidative polymerization, a more polar character of solvent such as water gave higher conductivities. Water seems to be the best solvent from the conductivity observed for PPy powders and the range of surfactant concentrations that may be employed. Moreover, in view of a possible application to synthesis on a large scale, the cost, handling and safety characteristics, water seem more attractive than those of any other solvents.

It has been clearly shown that surface active agents are usually employed to influence the morphology of conducting polymers during chemical polymerization. Morphology plays an important role in determining conductivity and mechanical properties of the materials because electrical conductivity related to surface morphology [22, 24].

The role of stabilizer on the surface of the PPy particles has to be studied so as to clarify its influence on the structural arrangement of the particles in the matrix [25]. Adsorption of the stabilizer on the PPy particles is primarily due to the hydrophobic component in the stabilizers, probably via a hydrogen bonding mechanism with the pyrrole NH group. The type and concentration of additive are known to influence the rate of polymer formation, particle size, size distribution, morphology, homogeneity and structure [18, 23, 26-30].

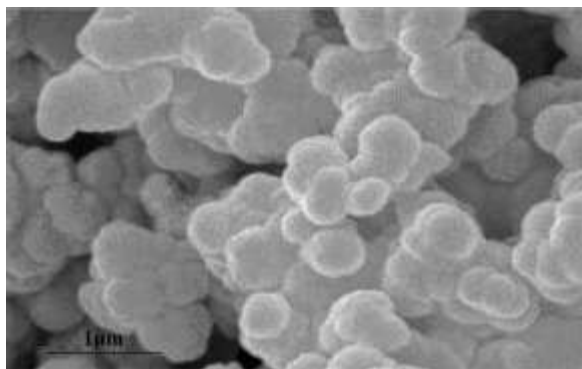


Fig. 1: Scanning electron micrograph of pure PPy in aqueous media. Reaction conditions: ($\text{FeCl}_3 = 48 \text{ g L}^{-1}$, Pyrrole monomer $14.9 \times 10^{-2} \text{ mol L}^{-1}$, volume of solution 100 mL, reaction time 5 hours at room temperature)

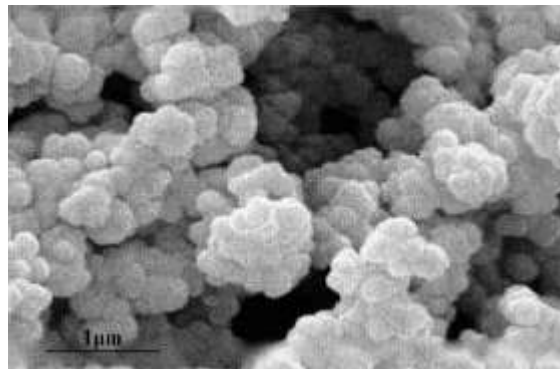


Fig. 3: Scanning electron micrograph of pure PPy in non-aqueous media (methanol). Reaction conditions: ($\text{FeCl}_3 = 48 \text{ g L}^{-1}$, Pyrrole monomer $14.9 \times 10^{-2} \text{ mol L}^{-1}$, volume of solution 100 mL, reaction time 5 hours at room temperature)

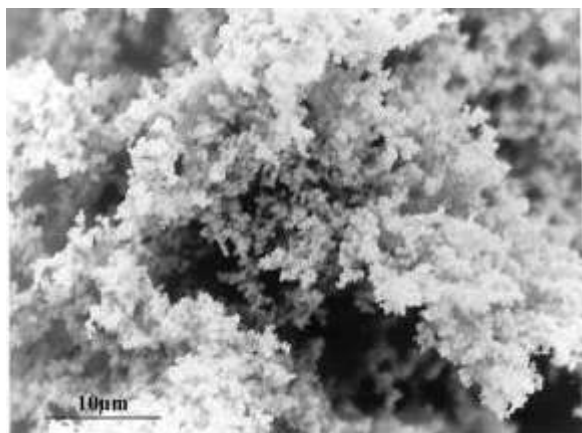


Fig. 2: Scanning electron micrograph of PPy and PEG composite in aqueous media using PEG ($M_w = 35000$, 6 g L^{-1}). Reaction conditions: ($\text{FeCl}_3 = 48 \text{ g L}^{-1}$, Pyrrole monomer $14.9 \times 10^{-2} \text{ mol L}^{-1}$, volume of solution 100 mL, reaction time 5 hours at room temperature)

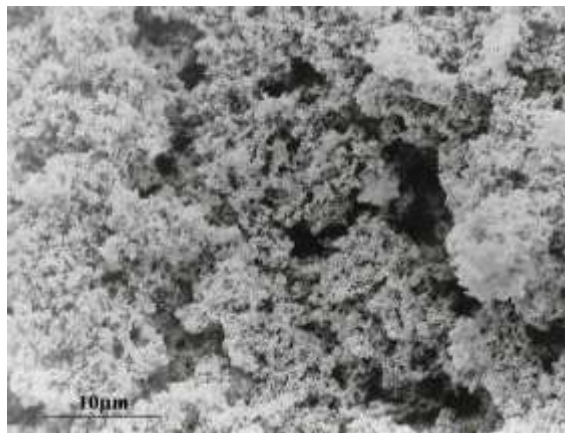


Fig. 4: Scanning electron micrograph of PPy and PEG composite in non-aqueous media (methanol) using PEG ($M_w = 35000$, 6 g L^{-1}). Reaction conditions: ($\text{FeCl}_3 = 48 \text{ g L}^{-1}$, Pyrrole monomer $14.9 \times 10^{-2} \text{ mol L}^{-1}$, volume of solution 100 mL, reaction time 5 hours at room temperature)

The morphology of PPy and its composites were studied, using scanning electron microscope. The results are shown in Fig. 1-5. As shown in Fig. 1 the bulk polymer tends to aggregate in large particles in the form of large globules. This is probably due to an increased inter-chain interaction compared to its stabilized particles in which the polymeric surfactant chains act as a limiting factor for such an interaction. As can be seen in Fig. 1 and 3, the type of solution affects the homogeneity, particle size and size distribution, because solvent may influence the rate of polymerization. In the organic solvent the rate should decrease with decreasing polarity of the medium [31].

Also solvent plays an important role in electrical conductivity and surface morphology [32, 33].

As shown in Fig. 5, when co-surfactants (PEG and PVAc) were employed for the preparation of composites, good spherical particles resulted. The polydisperse spherical morphology could be due to an increase of the polymerization rate in the aqueous/non-aqueous media (water and ethylmethylketone). By comparison between Fig. 1 and 2 (aqueous media) and also between Fig. 3 and 4 (non-aqueous media), the use of surfactant leads to average particle size decreases, because polymeric surfactant influences the viscosity of solution and presumably adsorbs onto the

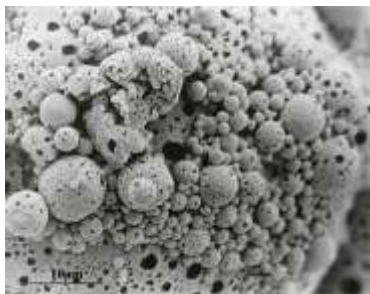


Fig. 5: Scanning electron micrograph of PPy and PVAc+PEG composite in an aqueous/non-aqueous media (water+ethylmethyleketon) using PVAc ($M_w = 25000$, 6 g L^{-1}) and PEG ($M_w = 35000$, 6 g L^{-1}). Reaction conditions: ($\text{FeCl}_3 = 48 \text{ g L}^{-1}$, Pyrrole monomer $14.9 \times 10^{-2} \text{ mol L}^{-1}$, volume of solution 100 mL (50/50% V/V), reaction time 5 hours at room temperature)

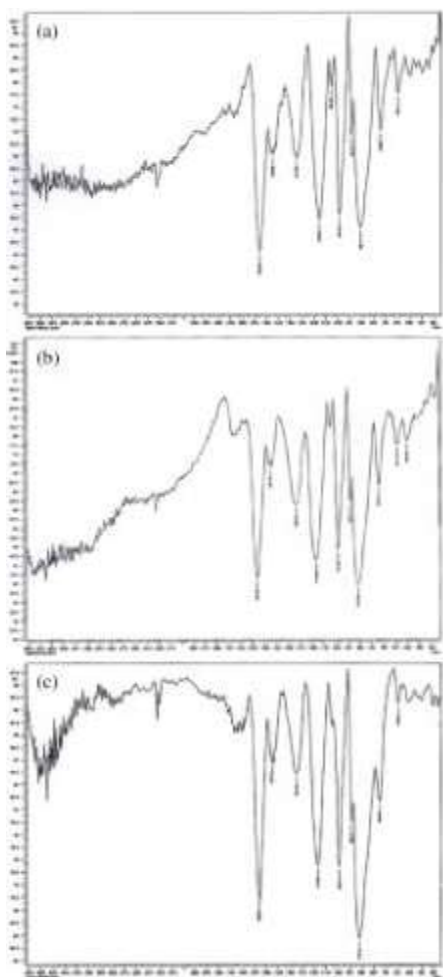


Fig. 6: FTIR spectra of polypyrrole prepared in aqueous and non-aqueous media: (a) water, (b) methanol, (c) acetonitrile

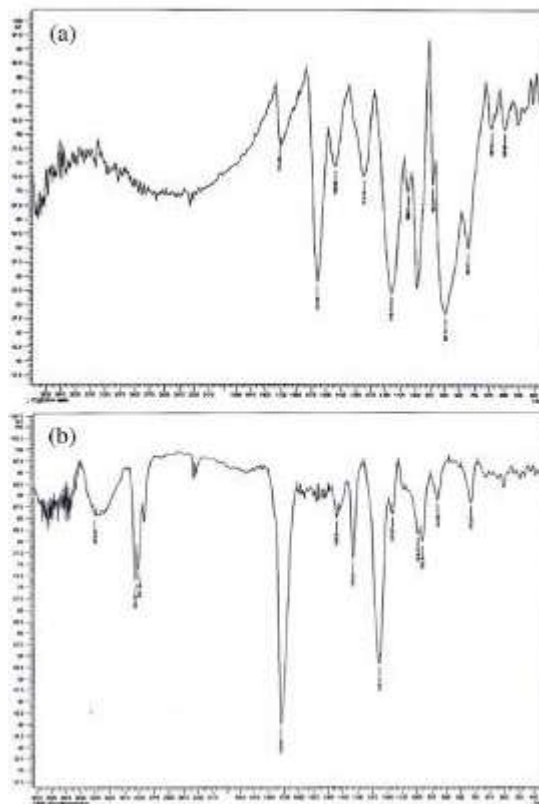


Fig. 7: FTIR spectra of polypyrrole prepared in aqueous and non-aqueous media using PVAc as additive: (a) water, (b) ethylmethyleketone

growing polypyrrole chain/particle and prevents further aggregation by a steric stabilization mechanism. In electrically conducting polymers, the conductivity is similarly affected by the chemical structure and morphology [34].

The structure of obtained product was determined by FTIR and ^1H NMR spectrum. FTIR spectra in the $4000\text{-}500 \text{ cm}^{-1}$ regions are shown in Fig. 6-8. One can notice in the spectra, the peaks related to type of solutions and additives. As can be seen in Figures the FTIR spectrum of the polymer changes greatly and gradually as the solution changes. In Fig. 6-8, the FTIR spectrum of the grafted polypyrrole onto PVAc and PEG has been shown. As shown in Figures the FTIR spectrum of the polymer and its composites strongly depends on the type of solution and additive.

The FTIR spectrum obtained for PPy in aqueous media (Fig. 6) shows the presence of characteristic absorption bands at 1542.95 , 1458.08 cm^{-1} (C = C stretching of pyrrole ring), 1311.50 cm^{-1} (C-N stretching vibration in the ring), 1166.85 cm^{-1} (C-H in-plane deformation), 1041.49 cm^{-1} (N-H in-plane deformation), 908.41 cm^{-1} (C-H out-of-plane

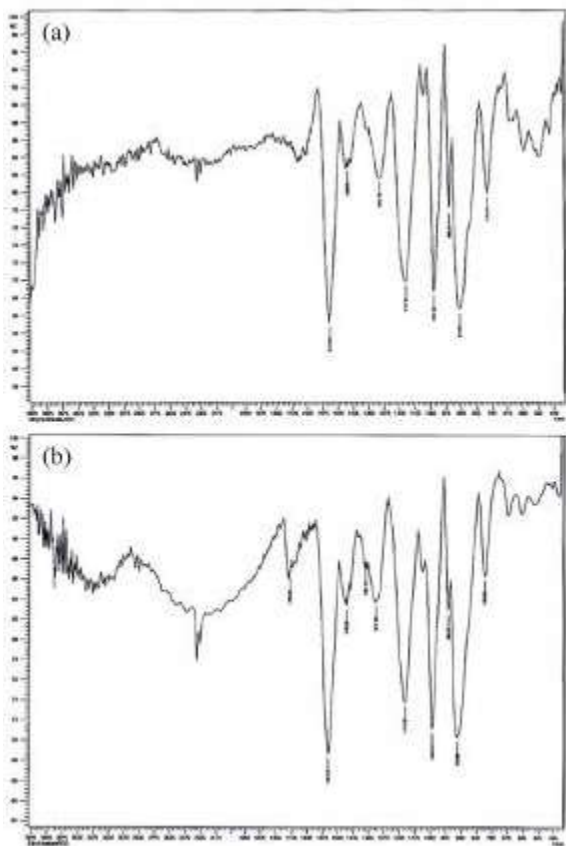


Fig. 8: FTIR spectra of polypyrrole prepared in ethylacetate using: (a) pure polypyrrole, (b) PEG as additive

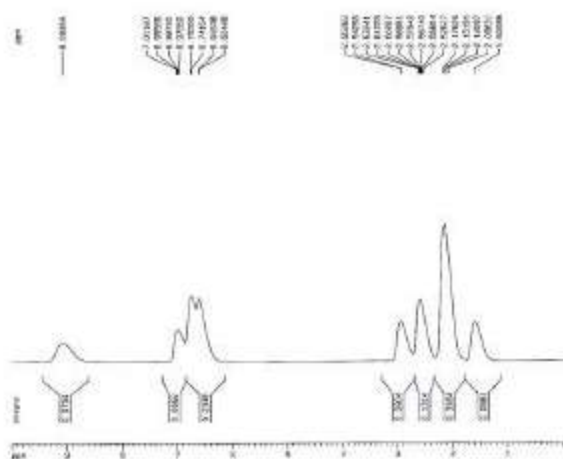


Fig. 9: ^1H NMR spectra of PPy/PVAc composite prepared in an aqueous media using FeCl_3 as an oxidant (deuterated m-cresol and NMP were used as a solvent)

deformation), 783.05 cm^{-1} (C-H out-of-plane ring deformation) and 673.11 cm^{-1} (C-C out-of-plane ring deformation or C-H rocking).

The FTIR spectrum obtained for PPy/PVAc composite in aqueous media (Fig. 7) shows the presence of characteristic absorption bands at 1733.89 cm^{-1} (C=O stretching vibration), $1544.88, 1458.08\text{ cm}^{-1}$ (C=C stretching of pyrrole ring) respectively. The peaks are at 1313.43 cm^{-1} (C-N stretching vibration in the ring), 1170.71 cm^{-1} (C-H in-plane deformation), 1040 cm^{-1} (N-H in-plane deformation), 898.77 cm^{-1} (C-H out-of-plane deformation) and 784.97 cm^{-1} (C-H out-of-plane ring deformation).

Figure 9 shows the ^1H NMR spectra of PVAc/PPy composite in deuterated m-cresol and NMP. As shown in Figure there are peaks at 9.08284 ppm (OH), $7.01187\text{-}6.97550\text{ ppm}$ (pyrrole ring), $6.75555\text{-}6.60448\text{ ppm}$ (N-CH =) and the observed peaks at range of $1.60086\text{-}2.95262\text{ ppm}$ are all pertained to the hydrogen's of the composite polymer chain.

CONCLUSION

Polypyrrole and its composites can be prepared chemically in aqueous and non-aqueous media using various surfactants in the room temperature. The characteristics of products such as conductivity, morphology and structure were studied. As shown in Table and Figures, the type of solution and additive has a considerable effect on the conductivity, morphology and structure of resultant products which is probably due to additive adsorption and probably polarizability of solution. Among the solvents employed in this oxidative polymerization, a more polar character of solvent such as water gave higher conductivities. However, water seems to be the best solvent from the conductivity observed for polypyrrole powders and the range of surfactant concentrations that may be employed.

In general, conductivity decreases using PEG and PVAc as a surfactant. The SEM micrographs show that the surfactant and solution influence the size and homogeneity of particles, because polymeric surfactant and solution affect the rate of polymerization, also surfactant prevents from gross aggregation of particles. Colloid formation took place by increasing concentration of surfactant. The results indicate that the intensity of peaks is dependent on the type of surfactant and solution, presumably due to the interaction of surfactant and polypyrrole. Furthermore, from the NMR result the formation of PVAc/PPy composite was confirmed.

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