

Introduction

Extensive research has been done over the last 30 years concerning conducting polymers. Among these, polypyrrole (PPY), polyaniline and polythiophene have been studied most widely (Aldissi, 1993; Nalwa, 1997; Skotheim et.al. 1998). These polymers have various potential applications, such as composite materials (Rodriguez et.al. 1997; Gangopadhyay, 2000) biomedical tests (Miksa & Slomkowski, 1995; Pope et.al 1996; Chehimi et.al.) and corrosion control of metal (Tallman et.al. 2000; Ferreira et.al. 2001). PPY, a heterocyclic polymer is one of the most promising conducting polymers because under certain circumstances it may have high electrical conductivity (Katihir, 1999) and good environmental stability (Omastova et.al. 1996) and is easily synthesized. However some factors currently limiting the applications of PPY including its poor mechanical strength and thus low processability, on the one hand, and high casts, on the other hand. Improvement of these material properties can be achieved, for example, by forming hybrid organic/inorganic PPY (nano) composites (Meda & Armes, 1993; Perruchot et.al. 2000). PPY blends with some commercially available insulating polymers such as poly (alkyl methacrylates) (Armes & Vincent, 1987), PPY-coated polymer latex particles ((Chehimi et.al.; Yassar et.al. 1987; Wiersma et.al. 1995; Khan & Armes, 2000) or polymer powder . All of these approaches are well documented and the results from several laboratories indicate improvement of

processability and conductivity. In order to improve the processability of polypyrrole, efforts have been made to obtain soluble conducting polymers or composites which contain both polypyrrole and non-conducting polymers. The preparation of a conducting polymer as latex dispersion seemed to be an excellent approach towards process ability. Armes et al. indicated that polypyrrole colloids can be obtained through sterically stabilizing polypyrrole particles by physical adsorption of water soluble polymers, such as methyl cellulose , poly (vinyl alcohol-co-vinyl acetate) (Armes et.al. 1987; Zunli Mo et.al. 2007; Sun Hee Cho et. al. 2005; Sihem & Smain, 2005; Smain et. al. 2004; Radhakrishnan & Santosh, 2007; Kun Ae Noh & Dong Wonkim, 2003) or polyvinyl pyrrolidone (Armes & Vincent, 1987). Mechanical blending is an old method for preparing composites. However the percolation thresholds of conductivity for the composites were higher. There are also chemical methods or in-situ polymerization methods to obtain PPY composites. One method includes formation of a substrate film mixed with oxidant first, followed by adding the monomer to the film. The second method is to polymerize pyrrole by means of an oxidant in the presence of a polymer with an emulsifier or a steric stabilizer, followed by precipitation, drying and molding into various shapes . This paper deals with two kinds of conductive PPY composites, prepared through polymerization pyrrole in the presence of urea-formaldehyde resin iso-butylated (70%) latex, along with either span-80(

sorbitan-monooleat) or poly (N-vinylpyrrolidone) as emulsifiers, and ammonium persulfate ((NH₄)₂S₂O₈) as oxidant. The preparation conditions, characterization, properties, and morphology of the composites were studied.

Experimental

Materials:

Pyrrole (from Aldrich) was purified by distillation under reduced pressure nitrogen atmosphere and kept in a refrigerator before use. Ammonium persulfate as oxidant, hydrochloric acid, p-toluene sulfonic acid (pTSA), and Span-80 (sorbitan monooleat), (supplied by Merck) were employed without further purification. Urea-formaldehyde Iso-butylated resin (Co. Jahan Chemie, Iran), 70% butylated), poly (N-vinylpyrrolidone) (PVP) (molecular weight 360000, Merck) and surfactant sodium dodecyl benzene sulfonate (NaDBS) (Co. petroleum chemistry, Iran) were used as received. Methanol and toluene were distilled prior using. FT-IR spectroscopy studies were carried out on the sample dispersed in KBr discs by using a Shimadzu 8101M spectrometer. Scanning electron microscopy (SEM) was performed with LEO 440 i microscope.

Preparation of bulk powder PPY / NaDBS

PPY was prepared by chemical polymerization in a deionized water solution. The polymerization began with adding 100 ml of a solution containing an oxidant ((NH₄)₂ S₂O₈) into 100 ml of a stirred solution containing a pyrrole monomer and

surfactant (NaDBS). After the prescribed polymerization time, synthesized PPY was filtered from the solution and washed with deionized water until the filtrate was neutral after which it was washed with ethanol several times, and finally dried in vacuum at about 40° C.

Preparation of the PPY-BUFR latex

Method 1

In a typical experiment, 1.07 g BUFR, 1.07 g pyrrole and 0.033 g a dispersant (span 80) were dissolved in 30 ml toluene. This system was placed in a 250 ml three-necked round-bottomed flask equipped with a mechanical stirrer. Water (30 ml) was introduced into the flask as the dispersing phase and through vigorous stirring (about 700 rpm) an inverted emulsion was generated.

Furthermore, an aqueous solution of 1.5 g ammonium persulfate (APS) and 3.07 g p-TSA in 15 ml water was added dropwise at room temperature into the inverted emulsion and stirred, and, consequently the emulsion solution gradually turned black. The polymerization lasted 1.5 h. Then, 200-250 ml methanol was introduced into the mixture to precipitate the latex. The precipitated latex was filtered, washed three times with methanol and then dried in vacuum.

Method 2

In a typical experiment, 1.07 g BUFR, 0.033 g of a dispersant (PVP) was dissolved in 30 ml toluene. This solution was placed in a 250 ml three-necked round-bottomed flask equipped with mechanical

stirring. An aqueous solution of 1.5 g ammonium persulfate and 3.07 g p-TSA in 30 ml water was introduced into the flask as the dispersing phase and through vigorous stirring (about 700 rpm) an inverted emulsion was generated.

Furthermore, a solution of 1.5g pyrrole in 30 ml toluene was introduced drop wise at room temperature and stirred into the inverted emulsion with the reaction system gradually turning black. The polymerization reaction was allowed to proceed for 1.5 h, and then, the blend was precipitated, washed and dried as in method 1.

Characterization and testing

The conductivity of the composite films was determined by a standard four – point probe method applied directly to the surface of the composite films. Water absorbency was measured by immersing a weighed film sample in water at 20° C for 24h, followed by weighing the sample; the surface water was removed with filter paper. The water absorbency is given by $\%H_2O = (w_a - w_b) \times 100/w_b$ where (w_b) is the sample weight before absorption and (w_a) is the sample weight after water absorption. The morphology of the composite latex was observed with LEO 440 I scanning electron microscope. FT-IR spectra of the composites were recorded on a SHIMADZU 8400 S spectrophotometer.

Results and Discussion

Tables 1 and 2 show the experimental conditions and some results in the preparation of electrically conductive polypyrrole-BUFR composites. Most of the conductive polypyrrole_composites were prepared by the polymerization of pyrrole dissolved in the dispersing phase of an emulsion (method 1). The polypyrrole thus formed deposits on the host polymer chains to form a polypyrrole-host polymer composite. Tables 1 and 2 show the dependence of conductivity on the polypyrrole loading of the composite. The results indicate a percolation threshold, with a reasonably high conductivity even for composites containing relatively low loadings of conductive polymer. The percolation threshold occurs in the range 0.3-1 mol/mol PY/BUFR composites. It is observed that the amount of dispersant affects the conductivity of the composite (Table 1). Since in the first method pyrrole is dissolved in the organic phase and the oxidant (APS) and dopant (p-TSA) are dissolved in the aqueous phase, the polymerization occurs at the interface between the two phases and, therefore, the surface area of contact between the two phases plays an important role in the polymerization process. This surface area is expected to increase with increase in the amount of dispersant. For this reason, pyrrole can be polymerized more rapidly and PPY can be dispersed more uniformly in the blends. As a result, the conductivity of the latex increases.

Table 1: Experimental conditions and some results in preparation electrically conductive latexs using method 1

Sample No.	Pyrrrole g(mol)	Dispersant g	Dopant/Pyrrrole	APS/Pyrrrole	Yield of Latex (g)	Polypyrrole in Latex (g)	Conductivity S/cm
1	0.67 (0.01)	Spane 80 0.33	1	0.65	-	-	3.48E-3
2	0.67 (0.01)	Spane 80 0.33	1.5	0.65	-	-	9.4E-3
4	0.67 (0.01)	Spane 80 0.33	1.6	0.65	-	-	8.8E-3
5	0.67 (0.01)	Spane 80 0.4	1.6	0.6	2.71	2.31	0.03044
6	0.67 (0.01)	Spane 80 0.6	1.6	0.6	-	-	7.8E-2
7	0.67 (0.01)	Spane 80 0.33	1.6	0.4	4.11	3.71	2E-3
8	820.67 (0.01)	Spane 80 0.33	1.6	0.8	2.1	1.7	1.72E-3
9	0.67 (0.01)	Spane 80 0.33	1.6	1.23	3.83	3.43	2.43E-2
10	1.4 (0.3)	Spane 80 0.33	1.6	0.65	3.1	2.7	9.5E-4
11	0.67 (0.01)	Spane 80 0.33	1.6	0.65	-	-	3.56E-3
12	0.33 (0.005)	Spane 80 0.33	1.6	0.65	-	-	1.83E-3

Table 2: Experimental conditions and some results in preparation electrically conductive latexs using method 2

Sample No.	Pyrrrole g(mol)	Dispersant g	Dopant/Pyrrrole	APS/Pyrrrole	Yield of Latex (g)	Polypyrrole in Latex (g)	ConductivityS/cm
13	0.67 (0.01)	PVP 0.016	1.6	0.4	1.79	1.39	4.7E-3
14	0.67 (0.01)	PVP 0.016	1.6	0.8	1.96	1.56	6.29E-3
15	0.67(0.01)	PVP 0.016	1.6	1.23	2.39	1.99	3.48E-3

The conductivity of the latex decreases somewhat at higher concentrations of Span 80

using method 1, perhaps because the increase in the viscosity of the inverted emulsion in the

continuous phase decreases the surface area to some extent.

The amount of dopant also affects the conductivities of the latex (Table 1). When, the mol ratio of p-TSA/PY increases from 1.0 to 2.0, under the same conditions using method 1, the conductivity of the latex increases from 3.8×10^{-3} E to 0.0286 E S/cm. The reason is that with an increasing the amount of p-TSA, the acidity of the polymerization medium increases and, hence, polaron and bipolaron doped forms on the PPY chains increase.

The conductivity of the latex corresponds to the nature of the dopant. The p-TSA and the camphorsulfonic acid are more suitable dopants for the latex preparation, since the latex doped with the two acids have good conductivities. The proposed acids not only act as dopants, but also supply the acidity required by the oxidative polymerization reaction. In addition, PPY has a highly conjugated aromatic structure and for this reason is very rigid and incompatible with iso butylated urea-formaldehyde. When PPY is doped with an acid possessing a suitable lipophilic organic group, its compatibility with some organic solvents is enhanced. Since its compatibility with resin also increases, it can be dispersed more uniformly in resin, thus increasing the conductivity of the composite. Generally, the larger organic group shows the higher the lipophilicity of the acid.

The amount of oxidant has an important effect on the conductivities of the composite. When, the

mol ratio of APS/PY is increased from 0.4 to 0.8, using both methods, the conductivity of the latex also increases. However, if the above mol ratio increases further to 1.23, the conductivity of the latex decreases (Table 1 and 2 and Figure 1).

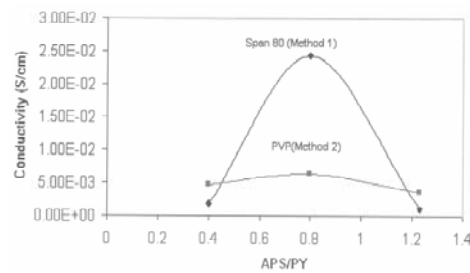


Figure 1: Influence of the oxidant amount on conductivity of latexes.

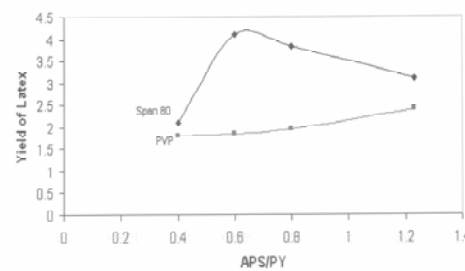


Figure 2: Influence of the oxidant amount on yield of latexes (g) using method 1.

By increasing the molar ratio of APS/PY from 0.4 to 0.8, the yield of composite and PPY in the oxidative polymer increases and, therefore, the conductivity of the latex also increases. However, the reason may be that the PPY loading increases with the increase oxidant/PY ratio, but excess oxidant would over-oxidize PPY with a concomitant decrease in conductivity and yield. Table 1 and 2 list the composites prepared by the procedures described in the previous section. It is clear that the conductivities of the composites prepared by method 2 are much lower than those

obtained with method 1. The concentrated emulsion, which is generated in the first step in method 1, is responsible for this behavior. Indeed, in the first step, a concentrated emulsion composed of a solution of the host polymer and pyrrole in an organic solvent constitutes the dispersing phase and in an aqueous surfactant solution constitutes the continuous phase. The continuous phase is in the form of a network of liquid films that separate the cells of the dispersed phase. The stability of this emulsion is ensured by the surfactant adsorbed upon the interface between the two phases as an oriented interfacial film. Consequently, the dispersed phase possesses a very large surface area of contact with the continuous phase. The aqueous solution of the oxidant which is introduced in the second step can easily contact the dispersed phase and the pyrrole molecules polymerize on the host polymer chains to form a composite.

FT-IR Spectroscopic studies

The FT-IR spectrum of polypyrrole have been extensively reported and studied. The main peaks can be assigned as follows: 3500 and 3400 cm^{-1} (N-H stretching vibration of an aromatic amine) as very weak bonds, and 3050 cm^{-1} (aromatic C-H stretching), 1550, 1320, 1180, 1040 cm^{-1} as strong bonds.

Figure 3 shows the FT-IR spectra of the produced blends using method 1 (sample 4) and method 2 (sample 15). All characteristics of bonds belonging to PPY are observed in the above mentioned blends. The absorption bonds over 1600

cm^{-1} indicate the presence of host polymer (BUFR) and dispersant: 1675 cm^{-1} (C=O stretching vibration bond of resin containing amid groups), and 1715 cm^{-1} (C=O stretching vibration of span 80 containing ester groups) as weak bonds of sample 4 and 1675 cm^{-1} (C=O stretching vibration bond of resin containing amid groups of resin and PVP) of sample 15.

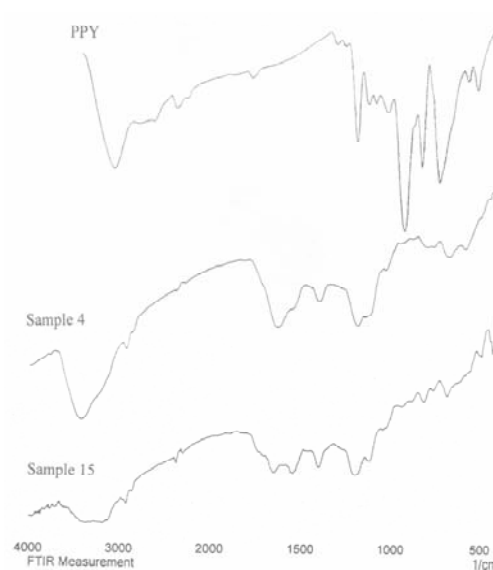
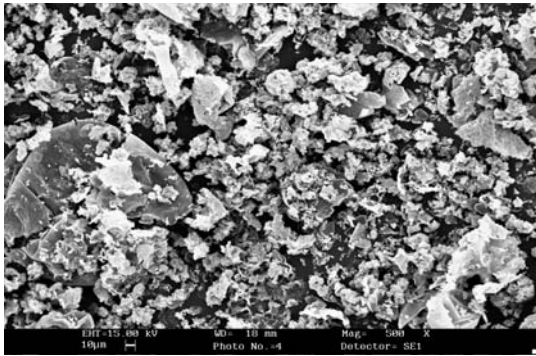


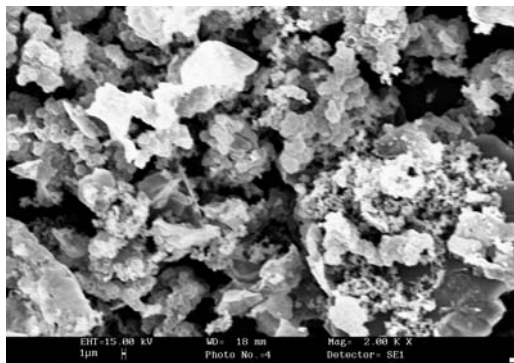
Figure 3: The FT-IR spectra of Selected prepared blends.

Scanning electron microscopy (SEM) studies

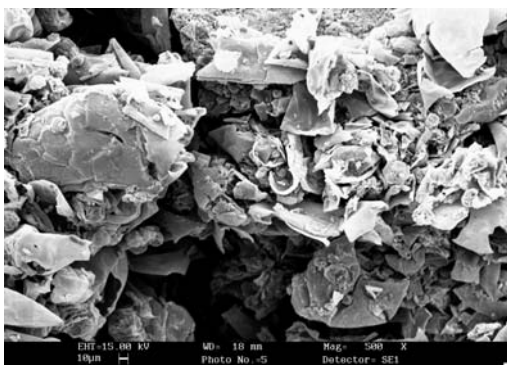
Scanning electron microscopy (SEM) pictures of six samples are shown in figures 4. PPY shows sponge-like morphology in contrast to prepared blends for which no morphological characteristics could be observed. But with SEM studies of reference PPY and prepared blends, it is seen that polypyrrole has been deposited onto BUFR particles non-uniformly. These pictures indicate that, as expected, the amount of deposition of polypyrrole onto small BUFR particles is more than that large on to ones.



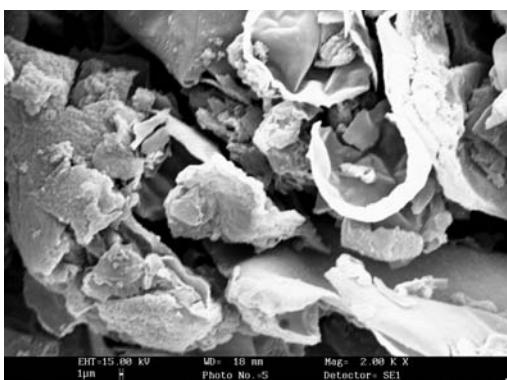
Fig(4-a)



Fig(4-b)



Fig(4-c)



Fig(4-d)

Figure 4: SEM images of some prepared latexes and PPY as reference to compare

Figure (4-a): sample No. 5 Mag = 500 X

Figure (4-b): sample No. 5 Mag = 2.00 K X

Figure (4-c): sample No.15 Mag = 500 X

Figure (4-d): sample No.15 Mag = 2.00 K X

Conclusion

Electrically conductive polypyrrole-BUFR composites have been prepared via inverted emulsions by two methods. In the first method, aqueous solution of an oxidant and a dopant introduced into an inverted emulsion containing a host polymer (isobutylatd urea formaldehyde resin), pyrrole and dispersant. In the second method, the polymerization proceeds by introducing an organic solution of PY into an inverted emulsion containing a host polymer (isobutylatd urea formaldehyde resin).

Method 1 was more successful since the PPY-BUFR so prepared had higher conductivities. The oxidant, dispersant, and solvent in the inverted emulsion are important factors that affect the conductivity of the latexes. The amount of water absorbed by polymer latex PPY-BUFR in the presence of span-80 and in presence PVP were 2.6% and 1.2% respectively.

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