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SHORT COMMUNICATIONS

Preparation of Polymer Blend Colloids Containing Polyaniline or Polypyrrole by Fe(II)-, Fe(III)-, and Cu(II)-H_2O_2 Catalyst System

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In spite of the extensive research efforts devoted to conductive aromatic polymers such as poly-*p*-phenylene, polythiophene, polyaniline, polypyrrole, and their derivatives,[1-4] commercial applications of these polymers have been limited to date. One of the main obstacles in commercial application has been the inherent intractability of conductive polymers which, with the rigid π-conjugated backbone structures, decompose without melting when heated, therefore making it impossible to process them by conventional methods such as extrusion or injection molding. Also, few solvents were found for the π-conjugated conductive polymers.

The search for improving processability has been one of the most active areas of conductive polymer research. Polyaniline and polypyrrole, as two of the most "air stable" conductive polymers, have been the focus of much research. Among various methods for enhancing the processability of conductive polymers, an effective one is to combine a conductive π-conjugated polymer with a conventional processable thermoplastic polymer, thus producing a blend (or composite) material with certain processability while retaining (or partially retaining) the material's conductivity. The preparation of this kind of blends or composites could be carried out through several ways, such as by exposing the oxidant containing polymer to pyrrole vapor, or by immersing the pyrrole incorporated thermoplastic polymer into an oxidant solution. Several thermoplastic polymers including polyacrylonitrile, poly(methyl methacrylate), polystyrene, poly(vinyl chloride), and poly(ethylene terephthalate) were employed as the matrix polymer for conductive blends or composites.[5-11] Recently, work related to the conductive polymer blends in latex form is also reported,[12,13] in which polypyrrole or polyaniline is coated onto the surface of the inert sub-micron thermoplastic polymer latex particles *via in situ* polymerization. The particle size of the blend latex is very much dependent on the parent inert latex used.

An alternative route to producing conductive blends is to make colloidal systems in which, contrary to the conductive blend latex systems mentioned above, an inert polymeric surfactant (stabilizer) is coated on the outside of the sub-micron π-conjugated polymer particles through physical absorption. Unlike the conductive blends in latex form, these colloidal systems have the advantage that minimum particle size is adjustable, since no inert parent polymer latex is used in these colloidal systems. For polypyrrole, various colloidal systems were prepared using a commercial water soluble polymer such as methyl cellulose, poly(vinyl alcohol), poly(vinylpyrrolidone), or poly(ethylene oxide).[14] However, attempts to make stable polyaniline colloids by analogous method had been unsuccessful, probably due to the relatively large amount of strong oxidant or catalyst used. Modifications were made using special tailor-made polymeric stabilizers containing *p*-aminostyrene moiety, which could stabilize the polyaniline colloids to different degrees *via* "chemical absorption" introduced by the copolymerization between aniline and the *p*-aminostyrene moiety.[14,15]

In this communication, we report a new method to prepare stable polyaniline or polypyrrole colloids using a Fe(II)-, Fe(III), or Cu(II)-H_2O_2 catalyst system, which was developed recently by Yamamoto and his coworkers.[4] This catalyst system enables us to carry out *in situ* oxidative polymerization with only a very small amount of metal ion catalyst, thus creating minimum interactions between metal ions and polymeric stabilizers.

The polymeric surfactants (stabilizers) used in this work are commercially available water soluble polymers, poly(vinylpyrrolidone) (PVP, $M_w = 360,000$, Tokyo Kasei Co.) and poly(vinyl alcohol) (PVA, $M_n = 73,000$, Yoneyama Chemical Co.).

Preparation of the colloidal blends were carried out by dissolving the polymer(s) (PVP and/or PVA) into deionized water, followed by the dropwise additions of monomer (aniline or pyrrole), acid [HBr (47 wt%) or H_2SO_4 (27 wt%)], catalyst ($FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, or $CuSO_4 \cdot 5H_2O$) and finally, the oxidant H_2O_2 (15 wt%). The color of the solution turned from transparent to dark green immediately after H_2O_2 was added when $FeSO_4$, which is known as the most effective catalyst for Fenton type oxidation using H_2O_2, was used as the catalyst. A similar color change took a few minutes when Fe(III) was used as the catalyst. The polymerizations were allowed to proceed at room temperature for 24 h. No precipitation was observed during or after the polymerization reaction. At the end of the reaction, thin free standing and tough films (thickness: 43—72 μm) of blends were directly cast from the solution, and dried for 24 h under vacuum before use for conductivity measurements by a four-probe tester (Loresta-AP, Mitsubishi Petrochemical Co.). Microscopic studies of the colloidal blends were performed on a scanning electronic microscope (SEM, JEOL JSM-T220) and a transmission electronic microscope (TEM, JEOL JEM-100CX), respectively.

It was found that both poly(vinyl alcohol) and poly(vinylpyrrolidone) could be used as polymeric surfactants for the preparation of stable polypyrrole colloids, while only poly(vinylpyrrolidone) was effective as a polymeric surfactant for the polyaniline colloids catalyzed by the Fe(II)-, and Fe(III)-H_2O_2 system, and precipitation was observed when poly(vinyl alcohol) only was used as the polymeric surfactant for polyaniline colloids. Since the solubility of poly(vinylpyrrolidone) in water is much better than that of poly(vinyl alcohol), it is possible that stronger interactions between poly(vinylpyrrolidone) and H_2O make poly(vinylpyrrolidone) a more effective polymeric surfactant for the polyaniline colloids. Also for polyaniline colloids, a minimum 0.02 g cm^{-3} poly(vinylpyrrolidone) concentration was required to achieve stability of the polyaniline colloids. However, the film quality of the polyaniline colloid was not good enough for conductivity measurement when only poly(vinylpyrrolidone) was used. Therefore, poly(vinyl alcohol) was added to improve film quality (Run 1—6 in Table I).

Detailed polymerization conditions and conductivity of the blends are listed in Table I. No deterioration of conductivity was observed after exposing the blend films to air

Table I. Polymerization conditions and conductivity

Run	Monomer[a] mol dm^{-3}	PVP g cm^{-3}	PVA g cm^{-3}	Catalyst[b] mol dm^{-3}	Acid[c] mol dm^{-3}	H_2O_2 mol cm^{-3}	σ[d] S cm^{-1}
1.	A, 0.215	0.019	0.018	C, 0.001	F, 0.21	0.28	0.54×10^{-3}
2.	A, 0.215	0.019	0.009	C, 0.001	F, 0.21	0.28	0.35×10^{-3}
3.	A, 0.215	0.019	0.018	C, 0.001	G, 0.27	0.28	0.30×10^{-4}
4.	A, 0.215	0.019	0.018	D, 0.001	H, 0.27	0.28	0.31×10^{-2}
5.	A, 0.215	0.019	0.018	D, 0.001	F, 0.21	0.28	0.45×10^{-2}
6.	A, 0.215	0.019	0.018	D, 0.001	G, 0.27	0.28	0.38×10^{-3}
7.	B, 0.298	—	0.018	D, 0.001	H, 0.14	0.28	0.34×10^{-3}
8.	B, 0.596	—	0.018	D, 0.001	H, 0.27	0.52	0.76×10^{-2}
9.	B, 0.298	0.019	—	C, 0.001	F, 0.11	0.28	0.18×10^{-2}
10.	B, 0.596	0.019	—	C, 0.001	F, 0.21	0.52	0.47×10^{-1}
11.	B, 0.596	0.019	0.018	E, 0.001	H, 0.27	0.52	0.27×10^{-5}
12.	B, 0.164	—	0.018	C, 0.001	F, 0.21	0.14	0.12×10^{-3}
13.	B, 0.373	—	0.018	C, 0.001	F, 0.21	0.28	0.97×10^{-2}

[a] A, aniline; B, pyrrole.

[b] C, $FeCl_3$; D, $FeSO_4$; E, $CuSO_4$.

[c] F, HBr; G, HCl, H, H_2SO_4.

[d] Measured with cast film.

for a prolonged period of time (two months); the initial conductivity of the film obtained in Run 1 in Table I ($\sigma=0.54\times10^{-3}\,\mathrm{S\,cm^{-1}}$) showed only a minor change after two months to give the σ value of $0.52\times10^{-3}\,\mathrm{S\,cm^{-1}}$. This was probably due to the fact that the Fe(II)-, Fe(III)-, and Cu(II)-H_2O_2 catalyst system contained only a very small amount of metal ion, consequently little metal ion residue was left in the films of polymer colloids. Figures 1 and 2 show the results of morphology studies of polyaniline colloids (Run 1 in Table I) by TEM and SEM, respectively. The colloidal particles appear to be in a "rice-grain" shape with an approximately average length of 400—600 nm. The surfaces of these particles are not smooth, and under high magnifications [×50,000, ×100,000, Figure 1(b) and Figure 1(c), TEM] it could be observed that these "rice-grain" shape colloids were composed of even smaller particles of 20—30 nm size.

The forming process of the "rice-grain" shape colloids was probably dependent upon several factors, such as reaction conditions, type and molecular weight of the polymeric surfactant, and catalyst system. Since poly(vinylpyrrolidone) was completely dissolved in water, it is reasonable to assume that the poly(vinyl pyrrolidone) macromolecular chains were fully extended as macromolecular "clouds", and uniformly distributed in the solution before the polymerization reaction started. The size of these poly(vinylpyrrolidone) macromolecular "clouds" is probably approximately 20—30 nm, as estimated from the $r_0/M^{1/2}$ value of poly(vinylpyrrolidone).[16]

With the presence of these "cloud-shape" polymeric surfactant, the aniline oligomers or polymer (or the cation radicals of aniline oligomers or polymer), once generated during the oxidative polymerization, should become insoluble in water and aggregate to the macromolecular clouds of poly(vinylpyrrolidone). As a result, small 20—30 nm size globules of polyaniline/poly(vinylpyrrolidone) blend were formed. The further aggregation of these 20—30 nm globules resulted in 400—600 nm long "rice-grain" shape polyaniline colloids (Figures 1 and 2). The absorption of polyaniline onto poly(vinylpyrrolidone) seems

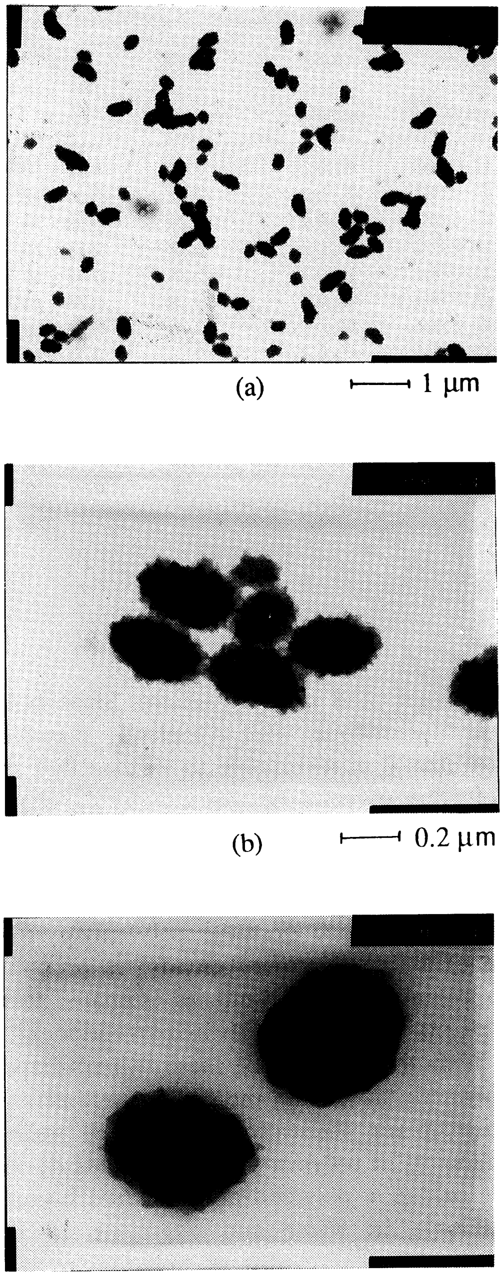

Figure 1. Transmission electronic microscopy (TEM) of polyaniline colloidal blends (sample of Run 1). (a) × 10,000; (b) × 50,000; (c) × 100,000.

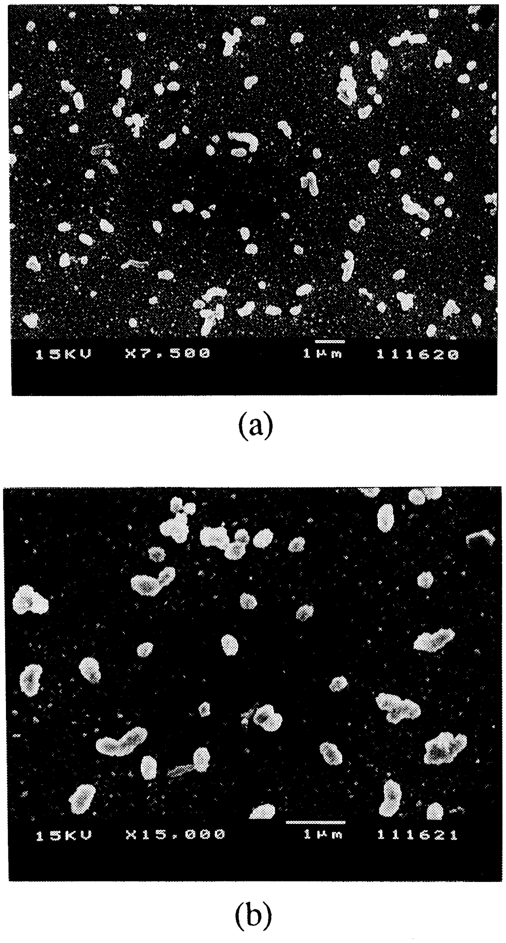

Figure 2. Scanning electronic microscopy (SEM) of polyaniline colloidal blends (sample of Run 1). (a) × 7,500; (b) × 10,000.

to be a physical process driven by physical interactions between two polymers. In competition with this physical absorption, polyaniline macromolecules aggregate with each other. Since no precipitation of polyaniline was observed, the absorption between poly(vinylpyrrolidone) and polyaniline was obviously the dominating one.

Thus, it has been concluded that stable colloidal blends containing polyaniline or polypyrrole can be prepared using Fe(II)-, Fe(III)-, and Cu(II)-H_2O_2 catalyst system, which has the advantage of creating minimum interactions between the metal ion catalyst and stabilizers. The stability of the colloids seems to be achieved *via* "physical absorption" between the π-conjugated conductive polymer and polymeric surfactant. These stable polymer blend colloids have applications such as conductive coating. Virgin paper (filter paper, Toyo Roshi Kaisha, Ltd.) coated with the polymer blend colloids prepared by dipping the paper into the dispersion system (Run 10) and drying under vacuum, showed a conductivity of $0.24 \times 10^{-3}\,\mathrm{Scm}^{-1}$.

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