Preparation and Characterization of Conductive Latex Based on Polyaniline–Perlite Composite

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Received 16 June 2003; accepted 8 March 2004
DOI 10.1002/app.20720
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The development of polymers with high electrical conductivity has attracted significant research interest because of the possibility of new applications. Electrically conductive latexes have drawn the attention of scientists over the last few years. The present work reports the preparation of composites in which polyaniline was deposited onto perlite particles by oxidative polymerization. Electrically conductive latex was prepared by homogeneously mixing submicron conductive composites with poly(vinylacetate-*co*-butylacrylate-*co*-butylversitate) resin in a desirable ratio. The conductivity of composites and latex was measured by a standard four-point probe. Morphology of composites was studied by scanning electron microscopy. Adhesion and electroactivity of the latex were also investigated. J Appl Polym Sci 93: 2528–2531, 2004

Key words: conducting polymers; composites; perlite; latexes; adhesion

INTRODUCTION

The synthesis and characterization of organic conducting polymers show potential use in batteries,[1,2] sensors,[3,4] anticorrosion coatings,[5] electromagnetic shielding,[6,7] and electrochromic displays.[8,9] However, in many cases the conjugated backbone of conducting polymers leads to a rigid polymer chain structure, thus making conducting polymers intractable. Out of the different modification techniques available, the one most widely studied and applied in this respect is the formation of composites of different origins.[10] Conducting polymer composites, in fact, constitute a suitable composition of a conducting polymer with one or more insulating materials so that their desirable properties are successfully combined. Synthesis of conductive composites by *in situ* deposition of a conducting polymer onto submicron inorganic oxides[11–13] and homogeneous mixing of prepared conductive composites, with synthetic resins or polymers with desirable formulations in the latex form, is an important method for preparation of electrically conductive coatings. One of the insulating materials used as a filler in the paint industries is perlite, characterized by individual properties such as low price, availability, and lightness.

In this article, we report the preparation of conductive polyaniline–perlite composite that was produced by *in situ* oxidative polymerization of aniline onto perlite particles followed by preparation of a conductive latex by homogeneously mixing a polyaniline–perlite composite with poly(vinylacetate-*co*-butylacrylate-*co*-butylversitate) resin in a specified formulation. The conductivity and adhesion of the latex thin films were measured and the electroactivity of latex was investigated by cyclic voltammetry.

EXPERIMENTAL

Materials

Aniline (Fluka Chemie, Buchs, Switzerland) was distilled twice at reduced pressure and stored in the dark at room temperature before use. Poly(vinylacetate-*co*-butylacrylate-*co*-butylversitate) was obtained from Kimidaru Co. (Tehran, Iran). Carboxymethylcellulose (Merck, Darmstadt, Germany), $(NH_4)_2S_2O_8$ (Merck), and perlite (donated by East Azerbaijan Mining and Industrial Organization) were used as received.

Methods

Preparation of polyaniline–perlite composite[14]

Perlite particles (0.5g) were added to a solution of aniline (0.24 mL, 2.68 mmol) in 75 mL 1*M* HCl with constant stirring. Then $(NH_4)_2S_2O_8$ (0.61g, 2.68 mmol) solution, provided in 25 mL 1*M* HCl, was added dropwise for 20 min into the stirred solution. The polymerization was allowed to proceed for 3 h at 0°C. Then the reaction mixture was filtered, washed with methanol

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Contract grant sponsor: Tabriz University, Iran.

until the filtrate became colorless, and dried at reduced pressure to obtain a dark green powder.

Preparation of conductive latex based on polyaniline–perlite composite

Poly(vinylacetate-*co*-butylacrylate-*co*-butylversitate) (0.41 g, equivalent to 0.2 g dry weight of polymer) was diluted with 2 mL distilled water. Then 0.05 g carboxymethylcellulose, as a thickener, and 0.3 g conductive polyaniline–perlite composite (diameter of perlite in the composite = 36 μm) were slowly added to the stirred solution. Stirring of contents of flask continued until a homogeneous latex was formed.

Preparation of the latex thin film for electrical conductivity measurement

For the preparation of a homogeneous thin film, it is necessary that applied surfaces be cleaned and polished. For this reason, surfaces of glassy plates (2.5 $\times$ 7.5 cm^2) were washed with distilled water, ethanol, and acetone, sequentially, and placed on a level surface. Then the latex was slowly poured onto the glassy plate until it spread evenly onto the surface.

After being dried at room temperature for 24 h, the thin film was placed in distilled water for 2 h to facilitate easy separation from the glass surface. After the film was allowed to dry, its conductivity was measured (stage 1).

Also, the conductivity of a free-standing thin film was measured after dipping in 1*M* HCl for 2 h and then drying again for 24 h at room temperature (stage 2).

Preparation of the latex thin film on iron plate

To measure adhesion of the latex, a thin film was prepared on an iron plate (2.5 $\times$ 7.5 cm^2) in the same way represented above (see previous section).

Characterization

Conductivity of polyaniline–perlite composite and the latex was measured by a standard four-probe method. Scanning electron microscopy (SEM) studies were carried out using a LEO 440i SEM instrument (LEO Electron Microscopy, now The Nano Technology Division of Carl Zeiss NTS GmbH, Oberkochen, Germany). Adhesion measurements were done by using the ASTM D3359-83 method.

A standard three-electrode system (Pt: working and supporting electrode, SCE: reference electrode made in Azarelectrode Co., Tehran, Iran) was used for cyclic voltammetry studies. For recording of cyclic voltammograms, a Potentiostat Digital DP8 instrument was applied.

RESULTS AND DISCUSSION

Characterization of the composites

Electrical conductivity measurement of these composites shows that use of smaller perlite particles causes an increase in electrical conductivity. As presented in Table I conductivity is completely dependent on the size of perlite particles, which is explained by the following: with decreasing size of perlite particles, the percentage of polyaniline deposited onto perlite particles increases, resulting in a greater degree of adhesion of polyaniline onto perlite surfaces and an increase in conductivity.

The SEM images (Fig. 1) confirm that the amount of deposition of polyaniline onto small perlite particles is greater than that onto large particles.

TABLE I
Effect of Perlite Particle Size on the Conductivity of Composites[a]

Sample	Perlite particle size (μm)	Polyaniline content (wt %)	Conductivity (S cm^{-1})
1	36	19.35	4.25×10^{-2}
2	45	18.03	4.08×10^{-2}
3	100	18.03	2.15×10^{-2}

[a] All reactions were carried out using 0.24 mL aniline, $(NH_4)_2S_2O_8$/aniline molar ratio of 1:1, 1*M* HC1 as a dopant, 0°C, 0.5 g dry weight of perlite, total volume: 10 mL.

Electrical conductivity of the latex thin films

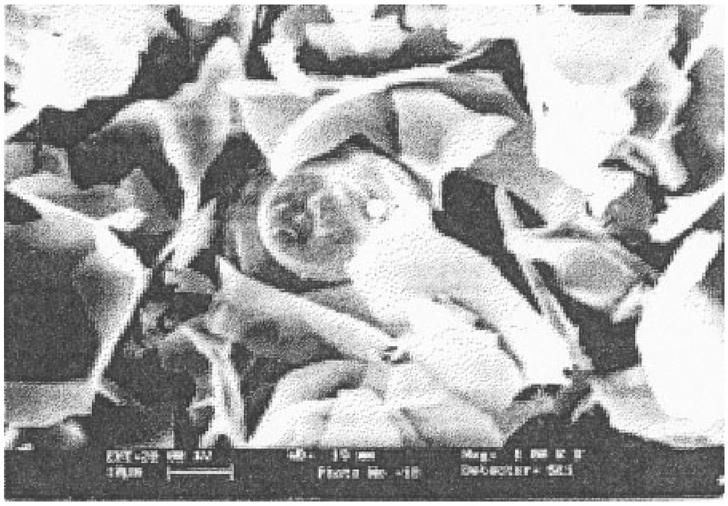
Table II shows that with increasing percentage of polyaniline–perlite composite in the latex composition, the electrical conductivity becomes greater. This suggests that greater polyaniline content is presented in the prepared thin film.

Because the homogeneous latex is not available with more than 0.3 g (10.9 wt %) of conductive composite in the latex composition, the maximum amount of polyaniline–perlite composite in the latex is 0.3 g.

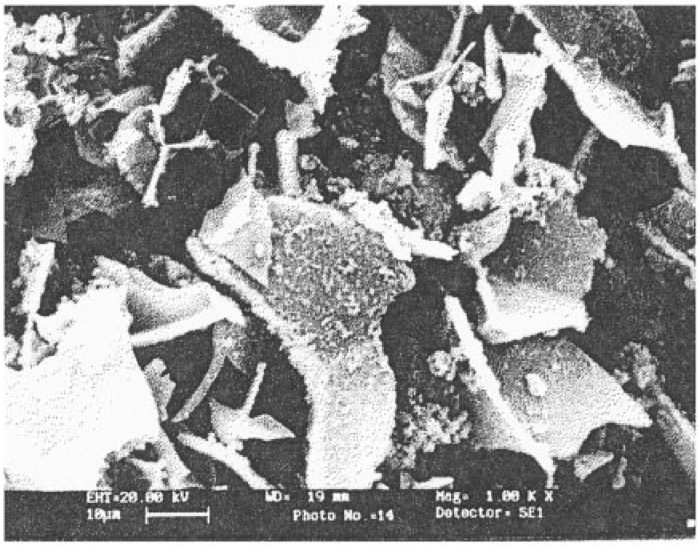
TABLE II
Electrical Conductivity of Latex Thin Films

Sample	Polyaniline–perlite composite content in the latex[a] g (wt %)	Conductivity (S cm^{-1})	
		Stage 1	Stage 2
1	0.1 (3.9)	1.53×10^{-5}	2.16×10^{-4}
2	0.2 (7.5)	2.27×10^{-5}	2.38×10^{-4}
3	0.3 (10.9)	9.30×10^{-5}	1.78×10^{-3}

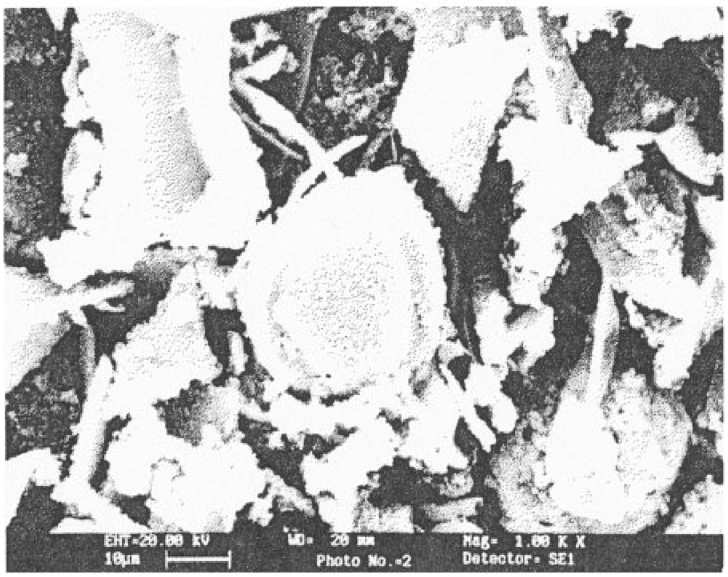
[a] Diameter of perlite in the composite = 36 μm.



(a)



(b)



(c)

Figure 1 SEM images of (a) perlite, (b) polyaniline–perlite composite (diameter of perlite > 250 μm), and (c) polyaniline–perlite composite (diameter of perlite = 36 μm).

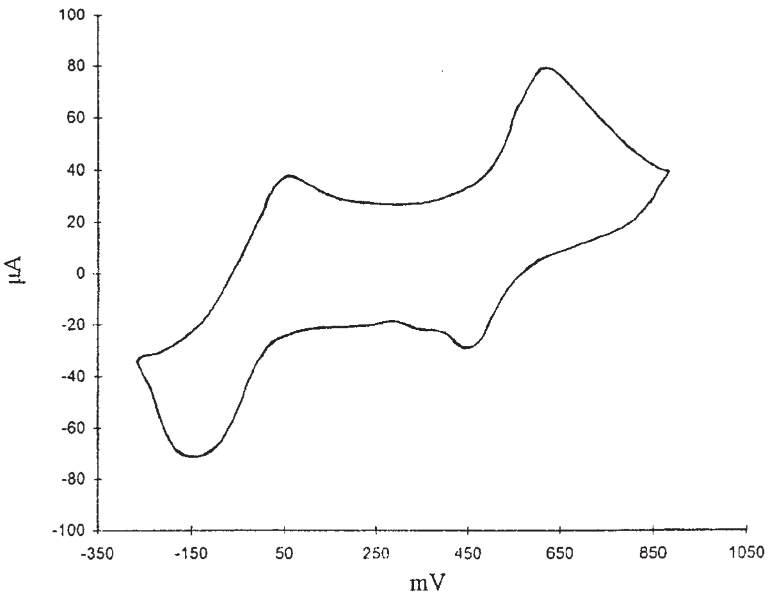


Figure 2 Cyclic voltammogram of the conductive latex coated on Pt electrode in 1*M* HCl solution at 50 mV/s. (Pt: working and supporting electrode, SCE: reference electrode).

Adhesion of conductive latex onto iron plate

After the preparation of a homogeneous thin film on an iron plate, the adhesion characteristic of the film was investigated. Table III presents the results of adhesion of conductive latex on iron plate. With increasing composite content in the latex, adhesion decreases.

TABLE III
Adhesion of Latex Thin Films on Iron Plate

Conductive composite content in the latex[a] (wt %)	Adhesion
0	5B
3.9	4B
7.5	3B
10.9	2B

[a] Diameter of perlite in the composite = 36 μm.

Electroactivity of the latex

To investigate the electrochemical behavior of the latex, a thin film of the latex was cast onto a Pt electrode. After the film was dried, its electroactivity was investigated in a standard three-electrode system by cyclic voltammetry.

Figure 2 shows that the cyclic voltammogram of the conductive latex is similar to that of pure polyaniline.[15] The redox activity of the latex is pH-dependent in aqueous medium. It has been established that the electroactivity ceases in aqueous media of pH > 4[16]; for example, no electrochemical behavior for a prepared conductive latex is seen in a buffer solution of acetate (pH 5.5).

CONCLUSIONS

Polyaniline–perlite composite was prepared by *in situ* deposition of a thin film of polyaniline onto perlite particles. With increasing particle size of perlite, electrical conductivity of composites decreased. A conductive latex was obtained by mechanical mixing of a submicron polyaniline–perlite composite with poly-(vinylacetate-*co*-butylacrylate-*co*-butylversitate) in a specified ratio. The results showed that for preparation of an acceptable conductive latex with reasonable adhesion and conductivity, the optimum ratio of polyaniline–perlite composite in the latex should be used. The electroactivity of latex thin films was confirmed by cyclic voltammetry.

The authors thank Prof. A. A. Entezami and Prof. M. H. Pournaghi Azar at Tabriz University for helpful discussion, and Tabriz University for the financial support for this research.

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