

Synthesis, Characterization, and Properties of Polypyrrole/expanded Vermiculite Intercalated Nanocomposite

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ABSTRACT: The conductive polypyrrole (PPy) is intercalated into the interlayers of expanded vermiculite (EVMT) to produce the nanocomposite with high conductivity by a synchronous polymerization of pyrrole and intercalation of PPy reaction in aqueous solution. The structures and properties are characterized by the nanocomposite using powder X-ray diffraction, Fourier transform infrared spectroscopy, conductivity measurements, and stability measurements. The nanocomposite exhibited a typical per-

colation phenomena and the percolation threshold is around mass ratio for pyrrole to EVMT 0.22. Under optimized conditions, a PPy/EVMT intercalated nanocomposite with conductivity of 67 S cm^{-1} is obtained. The intercalated nanocomposite has a good environmental stability. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2862–2866, 2008

Key words: clay; conducting polymer; nanocomposite; polypyrroles

INTRODUCTION

During the last decade, considerable attentions have been paid in the synthesis and evaluation of the clay/polymer nanocomposites^{1–3} via intercalation polymerization of special monomers like aniline, pyrrole, thiophene, or *N*-vinylcarbazole. The most common inorganic host used to prepare polypyrrole (PPy) nanocomposites is clay,^{4–7} because of its capacity to swell and exchange cations.

PPy is a promising conducting polymer for various electronic applications such as light emitting diode, organic field-effect transistor, electromagnetic interference shielding, and the secondary battery, because of its good environmental stability to oxygen and water, high conductivity, and ease of synthesis. If PPy can be intercalated into the interlayers of layered materials to form, it is possible to obtain a nanocomposite consisting of layered compound and PPy with ordered chain structure and better properties than for bulk ones.

In this article, we select PPy as the conducting component and expanded vermiculite (EVMT) as

the host because of its important advantages as follows: (i) EVMT is a natural mineral and has layered structure, stacking of the layers of $\sim 1 \text{ nm}$ thickness by weak dipolar force leads to interlayers or galleries between the layers. The hydrated cations normally occupy galleries to balance the charge deficiency generated by the isomorphous substitution in the tetrahedral sheets. The pyrrole monomer can be introduced into the galleries by ion exchange and are hardly separated from the galleries any more; (ii) EVMT is an inactive inorganic host without redox character, so the *in situ* polymerization can be controlled; (iii) it is a well-ordered host in two dimensions after the intercalation of pyrrole monomer, extrinsic initiator potassium persulfate can enter and initiate the polymerization in the interlayers.⁸

Aiming at the synthesis, characterization, and conductivity research of a novel PPy/EVMT intercalated nanocomposite, the structures of the nanocomposite are determined by X-ray diffraction spectroscopy (XRD) and Fourier transform infrared spectroscopy (FTIR). The conducting properties and stability are investigated in detail, and the preparation conditions are also optimized to obtain high conductivity.

EXPERIMENTAL

Materials

Pyrrole monomer purchased from Shanghai Chemical Reagent (Shanghai, China) was distilled twice under reduced pressure before use. EVMT [(Mg,Ca)_{0.7}(Mg,Fe,Al)_{6.0}[(Al,Si_{8.0})](OH_{4.8}H₂O)] consisting of SiO₂

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38.41%, Fe₂O₃ 23.42%, Al₂O₃ 14.57%, MgO 11.15%, CaO 0.89% was purchased from Hebei Mineral (Hebei, China) and prepared from natural vermiculite heated at 500°C. Iron chloride (FeCl₃) as a oxidant for the synthesis of PPy was purified by recrystallization from 66 wt % ethanol/water solution. Sodium dodecylbenzene sulfate (SDBS) as dopant and surfactant was used as received. The aforementioned materials were all purchased from Shanghai Chemical Reagent.

Preparation of PPy/EVMT nanocomposites

EVMT was pretreated with HCl according to the Ref. 9. EVMT (50 g) was added into 1000 mL 2M HCl solution and the resulting slurry was kept stirring for 20 h. Then the acid-treated EVMT was filtrated and rinsed for 5 min using a large amount of distilled water until the pH of filtrate at 7.0. The obtained product was dried at 80°C overnight and stored in a desiccator.

The ultrasonic technique was introduced for exfoliating the EVMT, similar to that of exfoliating graphite oxide, as follows:¹⁰ 5 g of the pretreated EVMT was saturated with 300 mL distilled water for 12 h. After a sonication irradiation under a power of 59 kHz for 10 h, the dispersion was centrifuged and dried at 70°C in a vacuum oven. Thus exfoliated EVMT sheets were obtained and kept in a dry desiccator.

PPy/EVMT nanocomposites were prepared according to the following steps: a mixed solution of exfoliated EVMT, SDBS, pyrrole, and distilled water was made in a three-mouth flask by mixing pyrrole (2 mL), distilled water (100 mL), SDBS, and EVMT and stirring at a rotation speed of 450 r min⁻¹ for 1.5 h. Then, FeCl₃ solution was dropped to the flask within 15 min, which resulted in a synchronous polymerization of pyrrole and intercalation of PPy reaction, the reaction was carried out and stirred at 450 r min⁻¹ for required times. The product was washed five times with distilled water and then dried at 80°C for 24 h.

Measurement and characterizations

For the measurement of conductivity, sample was prepared in pellet form (diameter: 13 mm, thickness: 1 mm) at pressure of 14 MPa using a Carver model C Press. The electrical conductivity of sample was measured with a four-probe Conductivity Test Meter (RTS-9, Guangzhou, China) in ambient environment.

Powder X-ray diffraction (XRD) studies were performed using a D8 ADVANCE X-ray diffractometer BRUKER (Ettlingen, Germany), Cu K α with wavelength 0.1541 nm, running at 40 kV and 30 mA, scanning from 2° to 40° at 5° min⁻¹. FTIR spectro-

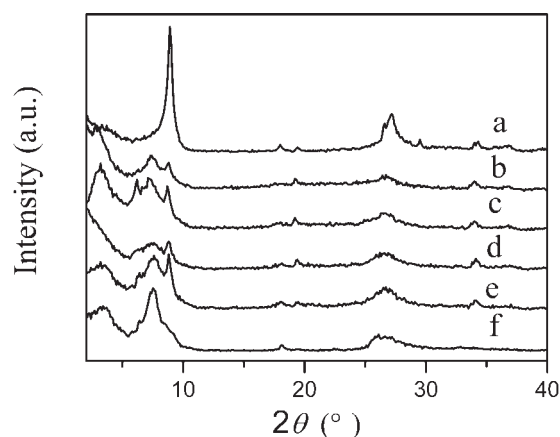


Figure 1 XRD patterns of untreated EVMT (a), PPy/EVMT composite with different EVMT content (b), (c), (d), (e), and HCl and sonication treated EVMT (f) [the mass ratio of EVMT to pyrrole monomer is 2.0, 3.0, 3.5, 4.5, respectively, from (b) to (e)].

scopy measurements were performed in a Nicolet Impact 410 FTIR spectrophotometer in absorption mode. All spectra were acquired in the range of 3600–400 cm⁻¹ with a 2-cm⁻¹ spectral resolution from compressed pellets of KBr and samples.

RESULTS AND DISCUSSION

XRD patterns

Figure 1 shows the XRD patterns of the untreated EVMT, HCl/sonication treated EVMT, and PPy/EVMT nanocomposites. As-received EVMT has diffraction peaks at $2\theta = 8.90^\circ$ (d_{001}) and 27.22° (d_{003}), which belong to periodicity in the direction of (001) of the phlogopite in EVMT and represent the interlayer spacing of EVMT ($d = 1.006$ nm) using Bragg's formula $n\lambda = 2d\sin\theta$. The exfoliation process of EVMT can be observed by a XRD technique. As shown in Figure 1 (curve f), for the EVMT acid-treated longer than 20 h and subsequently sonication irradiated, the peak corresponding to a layer gap of 1.006 nm moves to $2\theta = 7.43^\circ$ with an interlayer distance of 1.193 nm. And the intensity also dramatically decreases, which indicates that the silicate is delaminated and the platelets of EVMT are less than 10 cells or layers of single crystals.⁹ For PPy/EVMT nanocomposites (Fig. 1, Curves b–e), the diffraction peaks at $2\theta = 8.90^\circ$ and 27.22° have all shifted. The shift of diffraction peaks to low angles and decrease of intensities reveal that the interlayer is further delaminated in the process of *in situ* polymerization of pyrrole monomers, especially for the Curve b. The new diffraction peak at around 3.4° is attributed to PPy. The sharp peak indicates a well-ordered and crystallization of PPy in the interlayers of EVMT,⁸

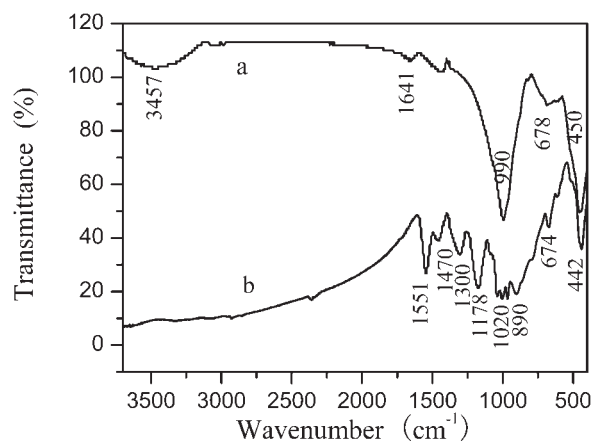


Figure 2 FTIR spectra of (a) EVMT and (b) PPy/EVMT nanocomposite under preparation conditions of molar ratio of FeCl_3 to pyrrole at 2.0, mass ratio of EVMT to pyrrole at 4.0, SDBS 2.5 g, and reaction at 15°C .

which is the reason that we choose EVMT as a two-dimensional host.

FTIR spectra

Figure 2 shows the FTIR of EVMT and PPy/EVMT nanocomposite. In Figure 2, the absorption peak at 3457 cm^{-1} is attributed to the H—O—H stretching, 3715 cm^{-1} is for O—H in Mg_3OH stretching, 1641 cm^{-1} is for H—O—H in absorbed water bending, and 990 and 450 cm^{-1} are for Si—O—Si stretching of EVMT, respectively. PPy ring vibrations are located between 800 and 1600 cm^{-1} .¹¹ The bands due to PPy are clearly indicated in this spectrum. The band at 1551 cm^{-1} is attributed to C=C backbone stretching, 1470 cm^{-1} is attributed to C—C ring stretching, 1300 cm^{-1} corresponding to C—N ring stretching, and 1178 cm^{-1} corresponding to ring breathing stretching.^{12,13} Thereby, the characteristic peaks of PPy in EVMT system shows the intercalation of PPy in the EVMT interlayers. In PPy/EVMT nanocomposite, adsorption bands at similar wave numbers of PPy are observed. This suggests that PPy was formed during the process of *in situ* polymerization of pyrrole monomers. The formation of PPy in PPy/EVMT nanocomposites is expected to offer high conductivity.

Influence of FeCl_3 on conductivity of the PPy/EVMT nanocomposites

The polymerization process of PPy/EVMT nanocomposites dispersed in an aqueous medium. As shown in Figure 3, the conductivity of PPy/EVMT nanocomposite increases with increasing of FeCl_3 dosages in the molar ratio range for FeCl_3 to Py from 2.0 to 2.4, beyond the molar ratio of 2.4, the conductivities of the nanocomposites decrease gradually.

It is believed that the conduction of PPy/EVMT nanocomposites comes from PPy chain.¹⁴ The length of Π conjugated chain, structure order degree, dopant, and microstructure of PPy affect the conductivity of the nanocomposite. In our system, FeCl_3 has two functions, one is a dopant and the other is an oxidant. When the molar ratio for FeCl_3 to Py is less than 2.4, as a *p*-type dopant, the FeCl_3 mainly plays an electron acceptor rule. Fe^{3+} accepts electrons from the valence band of PPy to form movable carriers in PPy, which changes the band gap energy of Π electrons in PPy, decreases the resistance of carrier motion, and increases the conductivity of composite with the increase Fe^{3+} dosage. On the other hand, according to Nernst Equation, as an oxidant, the oxidation potential and oxidation ability of Fe^{3+} increases with the increase FeCl_3 dosage, when the FeCl_3 dosage exceeds the molar ratio of 2.4, higher oxidation potential for Fe^{3+} causes an overoxidation and disjunction of PPy chains, the access of carriers motion is destroyed and the conductivity decreases with the increase FeCl_3 dosage.

Influence of SDBS on conductivity of PPy/EVMT nanocomposite

It was found that the conductivity of PPy/EVMT nanocomposite depend on the dosages of the dopant SDBS, like conducting composites based on polyaniline.^{15–18} Conductivity measurements as a function of increasing amount of SDBS are carried out by keeping a ratio for EVMT to pyrrole, oxidant to pyrrole, reaction temperature, and time constant, and the data are plotted in Figure 4. Because of the distribution of electrons in PPy chains can be optimized by the negative ions in SDBS, a conductivity increasing is induced.¹⁹ Much more dopants make negative

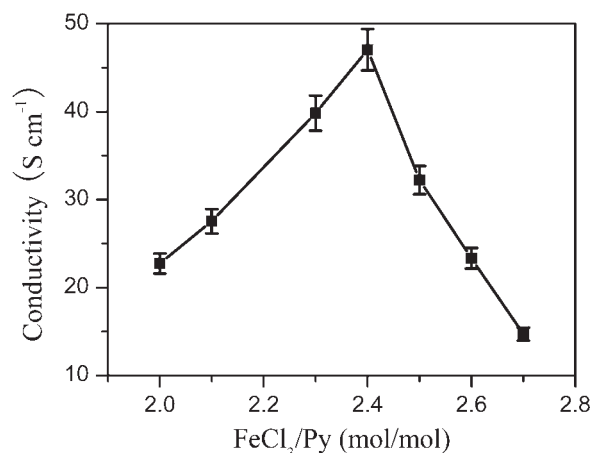


Figure 3 Conductivity of PPy/EVMT nanocomposite as a function of FeCl_3 under preparation conditions of mass ratio of EVMT/pyrrole 2.5, SDBS 2.5 g, and temperature 15°C .

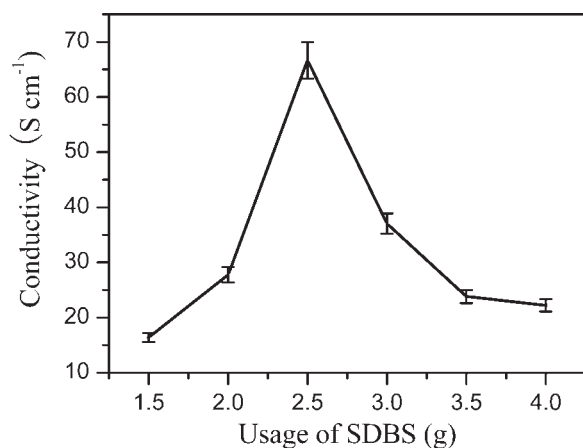


Figure 4 Conductivity of PPy/EVMT nanocomposites as a function of SDBS under preparation conditions of molar ratio of FeCl₃/pyrrole 2.0, mass ratio of EVMT/pyrrole 4.0, and temperature 15°C.

ions enrich in PPy chains, which leads to an instability of conjugated chains for the repulsion force. Thus, conduction of electron is blocked and conductivity declines. Under our conditions, PPy chains are distributed orderly and conducting structures are perfect at the SDBS dosage of 2.5 g.

Influence of PPy content on conductivity of the PPy/EVMT nanocomposite

The effect of PPy content on the electrical conductivity of the PPy/EVMT nanocomposites is plotted in Figure 5. When the mass ratio for pyrrole monomer to EVMT changes from 0.22 to 0.28, the conductivity of the nanocomposite dramatically increases from 2 to 44 S cm⁻¹. If the mass ratio increases to 0.5, the conductivity can even reach to more than 52 S cm⁻¹.

The nanocomposites prepared by aqueous solution polymerization show a typical percolation phenomenon in terms of electrical conductivity as a function of PPy content. It has been reported that the percolation phenomenon occurs in polymer matrix-conducting composites,^{20–24} and percolation theory was also introduced as shown in eq. (1)

$$\frac{(1 - \phi)(\sigma_1^{1/t} - \sigma_m^{1/t})}{\sigma_1^{1/t} + A\sigma_m^{1/t}} + \frac{\phi(\sigma_k^{1/t} - \sigma_m^{1/t})}{\sigma_k^{1/t} + \sigma_m^{1/t}} = 0, \quad A = \frac{1 - \phi_c}{\phi_c} \quad (1)$$

where σ_m , σ_1 , and σ_h are the conductivities of the medium-, low-, and high-conductivity components, respectively. ϕ is the volume fraction of the high-conductivity component (PPy in this case) and ϕ_c is the critical concentration (i.e., percolation threshold). t is an exponent related both to the percolation threshold and the shapes of the grains making up

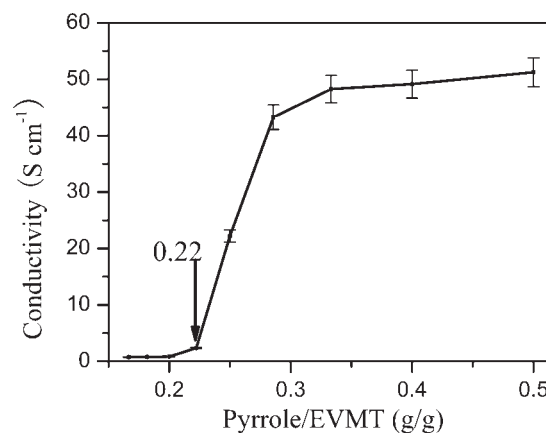


Figure 5 Conductivity of PPy/EVMT nanocomposites as a function of pyrrole monomer content under preparation conditions of molar ratio of FeCl₃/pyrrole 2.0, SDBS 4 g, and temperature 15°C.

the medium. From the trend of the variation of electrical conductivity of the composite with PPy content, the percolation threshold occurs at around 0.22 (mass ratio for pyrrole to EVMT). More than the mass ratio of 0.22, the electrical conductivity of the PPy/EVMT nanocomposites increases dramatically.

Influence of reaction temperature and time on conductivity of the nanocomposite

The reaction temperature and time also affect the structure and conductivity of the composite. From Figure 6 it is obvious to see that the conductivity of the composite increase and then decrease with reaction time prolonging for three temperature curves, and the higher temperature, the shorter reaction time for reaching the highest conductivity. Higher reaction temperature resulting in a shorter reaction

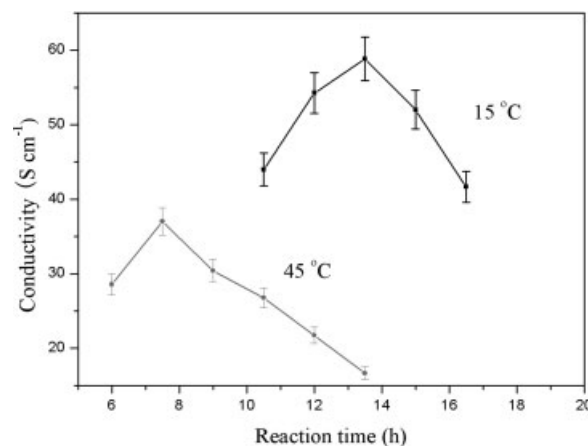


Figure 6 Conductivity of variation of reaction temperature and time in PPy/EVMT composite under preparation conditions of molar ratio of FeCl₃/pyrrole 2.4, mass ratio of EVMT/pyrrole 2.5, and SDBS 2.5 g.

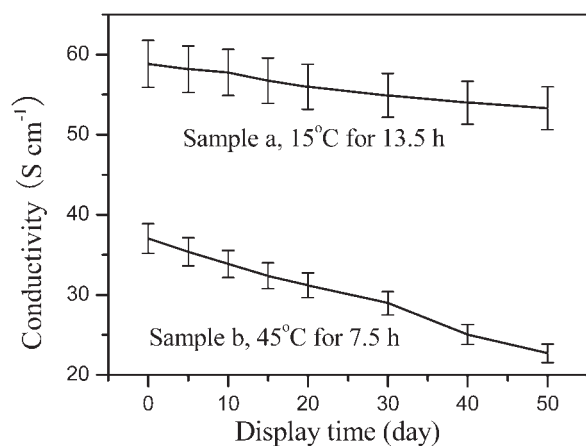


Figure 7 Influences of display time on conductivity of the PPy/EVMT nanocomposites at 25°C under preparation conditions of molar ratio of FeCl_3 /pyrrole 2.4, mass ratio of EVMT/pyrrole 2.5, and SDBS 2.5 g.

time is accorded with the general rule of chemical reactions in the eq. (2).



But FeCl_3 is an oxidant for pyrrole monomer or PPy. A longer reaction time brings about a side reaction for oxidizing PPy, which results in the breakage of the PPy conducting chain to some extent and decline of conductivity of the composite. Because of an exothermic reaction of polymerization, higher temperature will produce more short chains PPy and decrease the conductivity. To obtain high-conductivity composites, the reaction temperature should be reduced, as has been approved in polyaniline systems by other groups.^{25,26}

Stability of the nanocomposites

In our work, the conducting PPy was prepared by directly doping SDBS with PPy. Because of the hydrophilic nature of the doped PPy, it is soluble or dispersible in water. And the hydrophilicity increases with increasing length of hydrophilic chain in the dopant, also leads to increase in its solubility in water.

To investigate environmental stability of the PPy/EVMT conducting nanocomposites, the samples with different preparation conditions [reacted at 15°C for 13.5 h (Sample a) and at 45°C for 7.5 h (Sample b)] were displayed at room temperature and humidity of 35%. The conductivities of samples were measured and are shown in Figure 7. It can be seen that the composites have good stability and the stability is influenced by reaction temperature. Their conductivities are kept at 91% for Sample (a) and

61.3% for Sample (b), respectively, after displaying for 50 days. The nanocomposite synthesized at low temperature exhibits better stability.

CONCLUSIONS

A conducting PPy/EVMT intercalated nanocomposite was prepared by aqueous solution polymerization using pyrrole monomer and exfoliated EVMT powder in the presence of SDBS and FeCl_3 . When the preparation conditions were optimized as molar ratio for FeCl_3 to pyrrole 2.4, mass ratio for pyrrole to EVMT 0.4, SDBS 2.5 g polymerization at 15°C for 13.5 h, the PPy/EVMT nanocomposite possessed a conductivity of 67 S cm^{-1} . The nanocomposite exhibited a typical percolation phenomena and the percolation threshold is around mass ratio for pyrrole to EVMT 0.22. The conducting PPy/EVMT intercalated nanocomposite has a good environmental stability.

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