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Synthesis, characterization and properties of polyaniline/expanded vermiculite intercalated nanocomposite

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Abstract

The synthesis characterization and conductivities of polyaniline/expanded vermiculite intercalated nanocomposite are presented in this paper. The conductive emeraldine salt form of polyaniline is inserted into the interlayer of expanded vermiculite to produce the nanocomposite with high conductivity. The structures and properties are characterized by transmission electron microscopy x-ray diffraction spectroscopy fourier transform infrared spectroscopy thermogravimetry analysis and by the measurements of conductivity and stability. The results show that an intercalated nanocomposite with high conductivity and stability is obtained. The synthesis conditions are optimized to obtain the highest conductivity which is 6.80 S cm^{-1} .

Keywords: polyaniline, expanded vermiculite, intercalated nanocomposite, conductivity, stability

(Some figures in this article are in colour only in the electronic version)

1. Introduction

During the last decade, considerable attention has been paid to the synthesis and evaluation of clay/polymer nanocomposites [1–3] via the intercalation polymerization of special monomers such as aniline, pyrrole, thiophene or *N*-vinylcarbazole. Among these synthetic materials, polyaniline (PANI) nanocomposites have attracted special attention, because by the intercalation polymerization, it is possible to obtain structure with a more ordered chain and better properties than those of bulk ones [4]. The most common inorganic host used to prepare PANI nanocomposites is clay [5–7], owing to clay's swelling capacity and exchange cations.

In this paper, PANI is chosen as a conducting component and expanded vermiculite (EVMT) as the host on the basis of the following. (i) EVMT is a natural mineral and has a layered structure; the stacking of the layers of about 1 nm thickness by weak dipolar

forces leads to interlayers or galleries between the layers. The galleries normally occupied by hydrated cations that balance the charge deficiency are generated by the isomorphous substitution in the tetrahedral sheets. The aniline monomer can be introduced into the galleries by ion exchange, and consequently, it becomes barely separable from the galleries. (ii) EVMT is an inactive inorganic host without a redox character, so the situ polymerization can be controlled. (iii) It is a well-ordered host in two dimensions after the intercalation of the aniline monomer; the extrinsic initiator, potassium persulfate, can enter and initiate the polymerization in the interlayers [8]. To improve the exfoliation effect of EVMT, an ultrasonic technique is introduced, and a polyaniline/expanded vermiculite intercalated nanocomposite is prepared by aqueous solution polymerization. The structures of the nanocomposite are determined by transmission electron microscopy (TEM), x-ray diffraction analysis (XRD), and Fourier transform infrared spectroscopy (FTIR).

2. Experimental method

2.1. Materials

The aniline monomer purchased from Shanghai Chemical Reagent Co., China was distilled twice under reduced pressure prior to use. Expanded vermiculite {EVMT, [(Mg, Ca)_{0.7}(Mg, Fe, Al)₆[(Al, Si)₈](OH)_{4.8}H₂O]}], consisting of 38.41% SiO₂, 23.42% Fe₂O₃, 14.57% Al₂O₃, 11.15% MgO, and 0.89% CaO was purchased from Hebei Mineral Co., China and prepared from natural vermiculite heated at 500 °C. Potassium persulfate (KPS), a radical initiator for the synthetic reaction of PANI, was purified by recrystallization from 66 wt.% ethanol/water solution. Sodium dodecyl benzene sulfate (SDBS) as dopant and emulsifier were used as received. Both materials were purchased from Shanghai Chemical Reagent Co., China.

2.2. Preparation of PANI/EVMT nanocomposites

EVMT was pretreated with HCl according to the method described in [9]. Fifty grams of EVMT was added to 1000 ml of HCl solution (2 mol l⁻¹) and the resulting slurry was stirred continuously for 20 h. Then, the acid-treated EVMT was filtered and rinsed for 5 min with distilled water until the pH of the filtrate reached approximately 7.0. The obtained EVMT was dried at 80 °C overnight and stored in a desiccator.

The ultrasonic technique was introduced to expand the interlayer of EVMT and intercalate PANI into the interlayer of EVMT in the same manner as that for graphite oxide [10]. The steps are as follows: 5 g of expanded EVMT was mixed with 300 ml of distilled water. The suspension was ultrasonically vibrated under a power of 59 kHz for 10 h, then centrifuged and dried at 70 °C in a vacuum oven. The resultant expanded EVMT sheets were kept in a desiccator prior to test and further use.

PANI/EVMT nanocomposites were prepared as follows: a mixed solution of predetermined amounts of EVMT, SDBS, aniline monomer (2 ml), hydrochloric acid solution (100 ml, 1.5 mol l⁻¹) and distilled water (250 ml) was made in a three-mouth flask by stirring with a rotation speed of 450 rpm in an 80 °C water bath for 90 min. Then, the flask was cooled to room temperature. KPS acid solution prepared by dissolving KPS in 80 ml of distilled water and 50 ml of hydrochloric acid solution (1.5 mol l⁻¹) was placed in the flask within 15 min under 450 rpm stirring at ambient temperature. The product was washed 5 times with hydrochloric acid solution (1.5 mol l⁻¹) and distilled water, and then dried in an 80 °C oven for 24 h. Thus, a PANI/EVMT nanocomposite was obtained.

2.3. Conductivity measurement

For the conductivity measurement, all the test samples were prepared in pellet form (diameter: 13 mm, thickness: 1 mm) at pressure of 14 MPa using a Carver model C Press. The four-probe method was used to measure the conductivity of the PANI/EVMT nanocomposites.

2.4. Characterizations

For TEM observations, a small amount of powder sample was dispersed in high-purity methanol solution by ultrasonic vibration for 20 min to ensure the complete separation of the particles. A drop of the suspension was pipetted onto a copper grid coated with holey carbon film or gold, and the solvent was allowed to evaporate. The TEM morphologies of the samples were observed with a JEM-2010 at an acceleration voltage of 100 kV.

The powder XRD analysis of the samples was carried out using a D8 ADVANCE x-ray diffractometer of Germany BRUKER Co., CuK α of 0.1540 nm wavelength, running at 40 kV and 30 mA, scanning from 2° to 40° at 5° min⁻¹. The sample surface was observed using a scanning electron microscope (S-3500 N, HITACHI). The FTIR spectroscopy of the samples was carried out with a Nicolet Impact 410 FTIR spectrophotometer using KBr pellets. The thermogravimetric (TG) curves of the samples were measured using an SDT 2960 simultaneous DSC-TGA device (USA TA Instrument).

3. Results and discussion

3.1. TEM observation

The TEM images of untreated EVMT and PANI/EVMT nanocomposite are shown in figure 1. The layered structure of the EVMT is perceptible in figure 1(a). The typical diffraction spots in its selected-area diffraction pattern are shown in the top right corner of figure 1(a). From the figure, it can be seen that the untreated EVMT as received is a single crystal with some impurities that result from the VMT mineral (the mineral was purchased from Hebei Mineral Co., China and not purified before use). The particle size is large before the acid treatment, while in the PANI/EVMT nanocomposite, the size of the EVMT particles decreases to approximately 100 nm and the layered structures of the EVMT are also exfoliated. This is consistent with result of Liu *et al* [9].

3.2. XRD patterns

Figure 2 shows the XRD patterns of the untreated EVMT, ultrasonically treated EVMT, and PANI/EVMT nanocomposites. The as-received EVMT (curve a in figure 2) has diffraction peaks at $2\theta = 8.78^\circ$ (d_{001}) and 27.22° (d_{003}), which belong to phlogopite in the EVMT and represent an interlayer spacing of EVMT ($d = 1.01$ nm). The exfoliation of the EVMT can be determined from the XRD spectra. For the sample acid-treated longer than 20 h and subsequently sonicated (curve b in figure 2), the peak corresponding to a layer gap of 1.01 nm moves to $2\theta = 7.53^\circ$ with an interlayer distance of 1.17 nm. Moreover, the intensity also markedly decreases, which indicates that the EVMT is delaminated and the platelet of the EVMT is less than ten cells or layers of single crystals [9]. For the PANI/EVMT nanocomposite, the diffraction peaks at $2\theta = 8.78^\circ$ and 27.22° shift to $2\theta = 6.33^\circ$, 25.93° (curve c in figure 2) and 7.52° , 26.49° (curve d in figure 2), respectively. The shift of the diffraction peaks to low angles and the diffraction intensity decrease

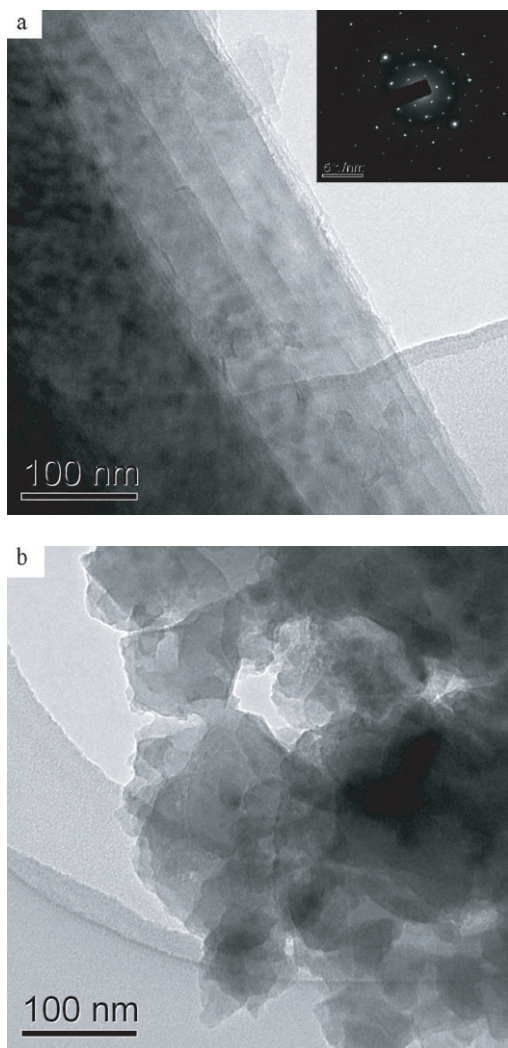


Figure 1. TEM image of untreated EVMT (a) and PANI/EVMT nanocomposite (b).

compared with curve b reveal that the interlayer is further expanded (the interlayer distance is $d = 1.40$ nm) during the situ polymerization of aniline monomers. The new diffraction peak at approximately 3.37° is attributed to PANI. The sharp peak indicates a well-ordered crystallization of PANI in the interlayers of EVMT [8].

3.3. FTIR spectra

In figure 3, 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 the Si–O–Si stretching of EVMT. The absorption peak at 1557 cm^{-1} is attributed to the quinoid ring stretching, 1480 cm^{-1} is for the benzene ring stretching, 1300 and 1243 cm^{-1} are for the N–H stretching in the connecting benzene ring–quinoid ring and benzene ring–benzene ring, respectively, and 1124 and 814 cm^{-1} are asymmetric peak stretchings of SO_3^- . There are two absorption peaks at 1020 and 664 cm^{-1} , which is consistent with the results given in a previous report [11]. Owing to the doping of SDBS into the PANI, a $-\text{CH}_2-$ absorption at

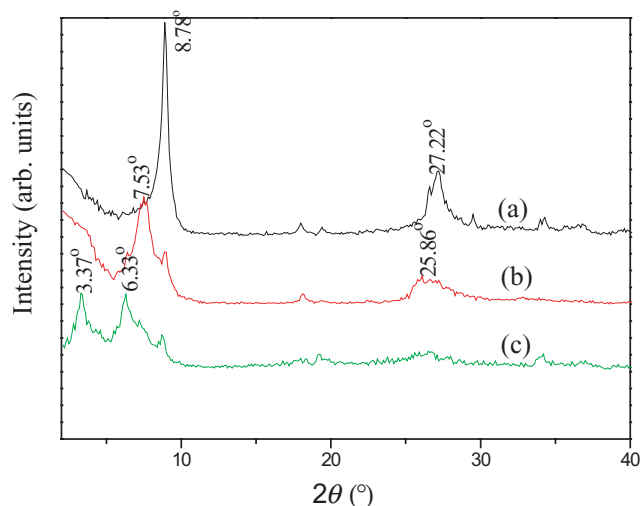


Figure 2. XRD patterns of untreated EVMT (a), ultrasonically treated EVMT (b), PANI/EVMT (c).

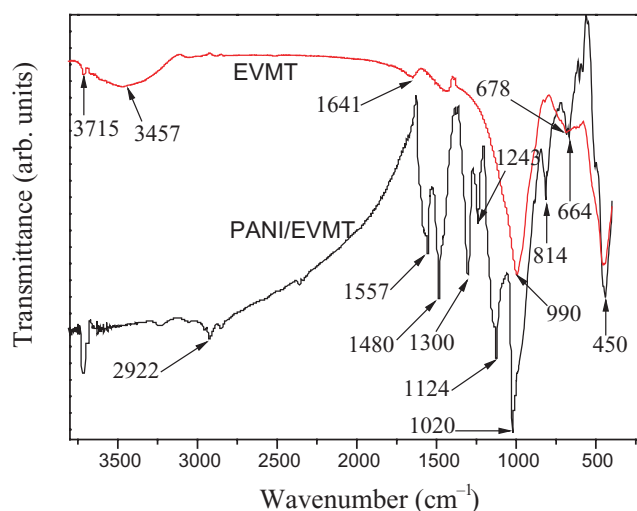


Figure 3. FTIR spectra of EVMT and PANI/EVMT nanocomposite. Preparation conditions: molar ratio of SDBS to aniline of 0.5 (3.83 g of SDBS), KPS to aniline of 0.8 and mass ratio of EVMT to aniline of 3.0.

2992 cm^{-1} is observed. In the PANI/EVMT nanocomposite, adsorption bands at wave numbers similar to those of PANI are observed. This suggests that PANI was in the form of emeraldine salt during the situ polymerization of aniline monomers. The formation of emeraldine salt in PANI/EVMT nanocomposites is expected to lead to high conductivity.

3.4. TG curves

The TG curves of pure PANI and PANI/EVMT were determined and shown in figure 4. It can be seen that pure PANI almost burned up at 600°C , while the PANI/EVMT composite still maintained 72 wt.% of the original weight at this temperature, which is approximately equal to the weight of EVMT in the composite. The TG experimental results imply that 25 wt.% of PANI is intercalated into the interlayer of EVMT or deposited on the EVMT surface to form a

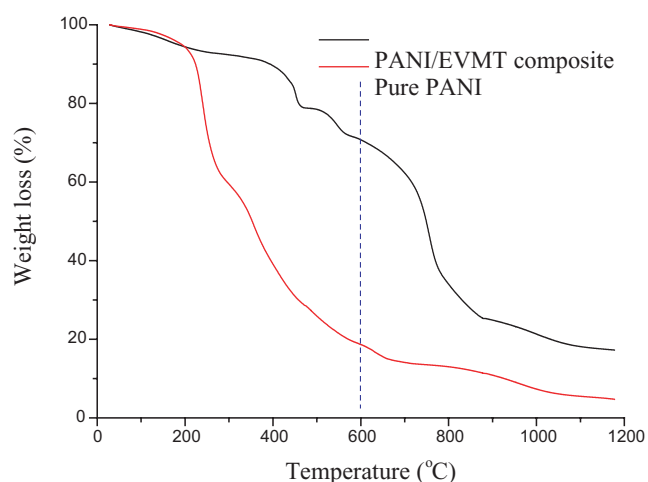


Figure 4. TG curves of pure PANI and PANI/EVMT nanocomposite. Preparation conditions: molar ratio of SDBS to aniline of 0.5, KPS to aniline of 0.8 and mass ratio of EVMT to aniline of 3.0.

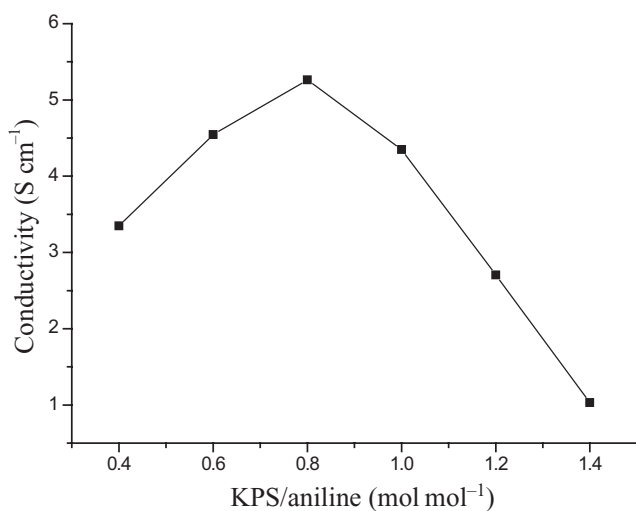


Figure 5. Conductivity of PANI/EVMT nanocomposites as a function of KPS under preparation conditions of molar ratio of SDBS to aniline of 0.5 (3.83 g of SDBS), mass ratio of EVMT to aniline of 5.0, reaction temperature of 15 °C and reaction time of 8 h.

PANI/EVMT composite, which correlates with the feed ratio for this sample.

3.5. Effect of initiator on conductivity of PANI/EVMT nanocomposites

The polymerization of PANI/EVMT nanocomposites dispersed in an aqueous medium proceeds with a typical color change from blue to dark green, indicating the formation of PANI emeraldine salt. As shown in figure 5, the conductivity of the PANI/EVMT nanocomposite increases with increasing KPS dosage in the range of 0.4–0.8; beyond a molar ratio for 0.8, the conductivities of the nanocomposites decrease gradually.

The conductivity of the nanocomposite depends on the PANI chain, and the formation of the PANI chain is initiated by KPS; thus, the amount of initiator KPS affects the

conductivity of the composite. Clearly, a lower amount of KPS does not produce sufficient crosslink points to construct a PANI chain and a conducting channel, which results in the decline of the conductivity of the nanocomposites. On the other hand, KPS is not only an initiator, but also an oxidizer; excessive KPS causes a side reaction for oxidizing PANI, which results in the disruption of the PANI chain to some extent. A conducting channel cannot run through the material effectively; therefore, the conductivity of the nanocomposite decreases. According to figure 5, the mass ratio of KPS to aniline monomer of 0.8 is the better for a high conductivity.

3.6. Effect of SDBS on conductivity of PANI/EVMT nanocomposite

The conductivity of the PANI/EVMT nanocomposite also depends on the amount of the SDBS dopant [12–15]. Figure 6 shows the dependence of conductivity of the PANI/EVMT nanocomposite on the amount of SDBS under the same preparation conditions. It can be seen that with the increase in the SDBS amount, the conductivity of PANI/EVMT increases and then decreases. The classical protonation (doping) concept assumes that the acid reacts with the imine nitrogens in the emeraldine PANI base; as a result, PANI salt is produced. The two electrons from the electron pairs located at the imine nitrogen are injected into an adjacent quinoid ring, and the latter is converted to a benzenoid ring. The remaining unpaired electron present in the imine nitrogen and cation radicals act as carriers in the electric conduction. The increase in the amount of SDBS dopant causes an increase in the degree of protonation and leads to an increase in the conductivity when the molar ratio of SDBS to aniline is lower than 1.5. However, much SDBS may protect against H⁺ doping of the chains of PANI, which leads to the decrease in the doping degree of PANI when the molar ratio of SDBS to aniline is higher than 1.5. Moreover, the electrostatic repulsion forces of the dopant make it unstable for conducting chains and restrict electron conduction. Under our conditions, the molar ratio of SDBS to aniline of 1.5 is the better for high conductivity.

3.7. Effect of EVMT on conductivity of PANI/EVMT nanocomposite

The effect of EVMT content on the electrical conductivity of the PANI/EVMT nanocomposites is shown in figure 7. When the mass ratio of aniline monomer to EVMT changes from 0.14 to 0.25, the conductivity of the nanocomposite markedly increases from 0.33 to 6.10 S cm⁻¹. When the mass ratio of aniline monomer to EVMT increases to 1, the conductivity reaches 6.80 S cm⁻¹.

The nanocomposites prepared by aqueous solution polymerization show a typical percolation phenomenon in terms of electrical conductivity as a function of PANI content. It has been reported that the percolation phenomenon occurs in polymer-matrix-conducting composites [16–20], and the

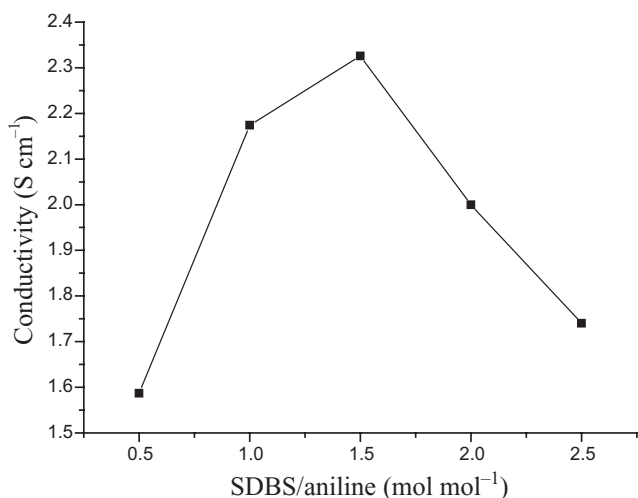


Figure 6. Conductivity of PANI/EVMT nanocomposites as a function of SDBS under preparation conditions of mass ratio of EVMT to aniline of 3.0, molar ratio of KPS to aniline of 1.0, reaction temperature of 15 °C, and reaction time of 8 h.

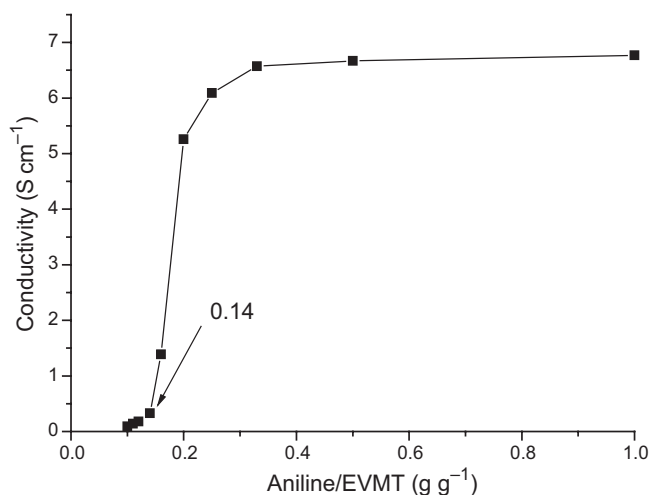


Figure 7. Conductivity of PANI/EVMT nanocomposites as a function of EVMT content under preparation conditions of molar ratio of SDBS to aniline of 0.5 (3.83 g of SDBS), KPS to aniline of 0.8, reaction temperature of 15 °C and reaction time of 8 h.

percolation theory is introduced in equation (1):

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

Here, σ_m , σ_1 and σ_h are the conductivities of the medium and the low- and high-conductivity components, respectively. ϕ is the volume fraction of the high-conductivity component (PANI in this case) and ϕ_c is the critical concentration (i.e. percolation threshold). t is an exponent related to both the percolation threshold and the shapes of the grains making up the medium. From the variation of the electrical conductivity of the composite with PANI content, the percolation threshold seems to occur at 0.14 (mass ratio of aniline monomer to EVMT). If the mass ratio is higher than 0.14, the electrical conductivity of the PANI/EVMT nanocomposites increases markedly.

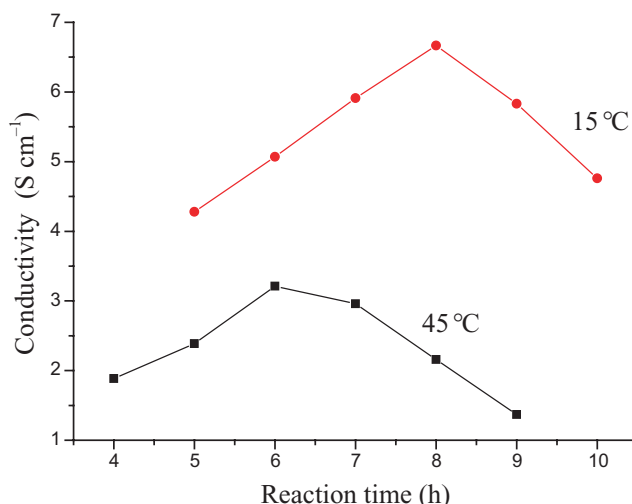
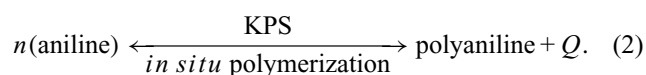


Figure 8. Conductivity of PANI/EVMT nanocomposites as a function of reaction temperature and time under preparation conditions of molar ratio of SDBS to aniline of 0.5 (3.83 g of SDBS), KPS to aniline of 0.8, and mass ratio of EVMT to aniline of 3.0.

3.8. Effect of reaction temperature and time on conductivity of nanocomposite

The reaction temperature and time also affect the structure and conductivity of the composite. From figure 8, it is clear that the conductivity of the composite increases and then decreases with reaction time for two temperature curves, and the higher the temperature, the shorter is the reaction time for reaching the highest conductivity. Higher reaction temperature resulting in a shorter reaction time is in accordance with the general rule of chemical reactions shown in the equation (2):



However, KPS is a stronger oxidant for initiating aniline monomer to form PANI. A longer reaction time leads to a side reaction for oxidizing PANI, which results in the breakage of the PANI conducting chain to some extent and a decrease in the conductivity of the composite. Because of an exothermic polymerization reaction, the higher temperature would produce PANI with more short chains and decrease the conductivity. To obtain a high conductivity composite, the reaction temperature should be reduced, as has been implemented in PANI systems by other groups [21, 22].

3.9. Stability of nanocomposites

In our work, the conducting PANI was prepared by directly doping PANI with SDBS. Because of the hydrophilic nature of the doped PANI, it is soluble or dispersible in water. Moreover, the hydrophilicity increases with increasing length of the hydrophilic chain in the dopant, and this also leads to increased solubility in water [23].

To investigate the environmental stability of the PANI/EVMT conducting nanocomposites, the samples

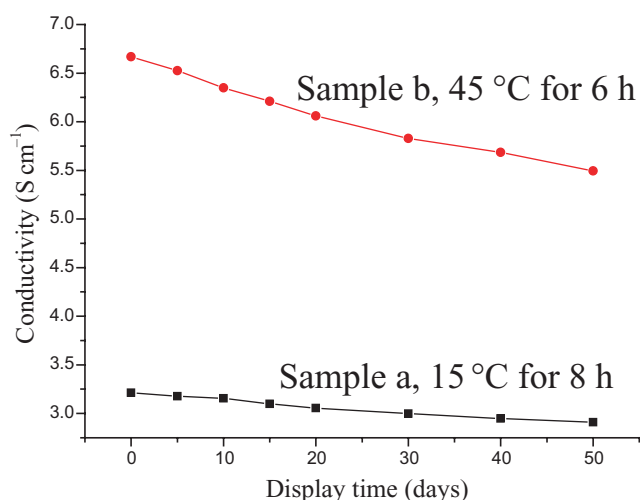


Figure 9. Effects of display time on conductivity of PANI/EVMT nanocomposites at 25 °C under preparation conditions of molar ratio of SDBS to aniline of 0.5 (3.83 g of SDBS), KPS to aniline of 0.8, and mass ratio of EVMT to aniline of 3.0.

prepared under different conditions (reacted at 15 °C for 8 h (sample a) and at 45 °C for 6 h (sample b)) were displayed at room temperature and 35% humidity for days, and their conductivities were then determined. From figure 9, it can be seen that the composites have good stability, and the stability depends on the reaction temperature. The conductivities of samples (a) and (b) after 50 days of display were maintained at 90.6 and 82.4%, respectively. The nanocomposite synthesized at low temperature shows a better stability.

4. Conclusions

A PANI/EVMT intercalated conducting nanocomposite was prepared by aqueous solution polymerization with aniline monomer and exfoliated EVMT powder in the presence of SDBS as dopant and KPS as initiator. When the preparation conditions were optimized at a molar ratio of SDBS to aniline of 0.5, KPS to aniline of 0.8, mass ratio of EVMT to aniline of 3.0, and polymerization at 15 °C for 8 h, the PANI/EVMT nanocomposite possessed a conductivity of 6.667 S cm⁻¹. The nanocomposite exhibited a typical percolation phenomena and the percolation threshold was approximately 0.14 in

terms of the mass ratio of aniline monomer to EVMT. Moreover, the PANI/EVMT conducting nanocomposites have good environmental stability.

Acknowledgments

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