Journal of Fiber Bioengineering and Informatics 6:1 (2013) 33–40
doi:10.3993/jfbi03201303

Structural Features and Microwave Absorbing Properties of Polyaniline-Montmorillonite Composites Prepared by In-Situ

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Abstract

Polyaniline (PANI)/montmorillonite (MMT) composites were prepared by in-situ polymerization of aniline in the presence of MMT with ammonium persulfate (APS) and hydrochloric acid (HCl) as oxidant and acid dopant, respectively. PANI/MMT composites on structural properties were analyzed by FT-IR, XRD and SEM. The result of FT-IR analysis signified an interaction between PANI backbones and MMT layer surfaces. X-ray diffraction showed an increase in the interlayer spacing of MMT, signifying PANI was intercalated into the MMT galleries. PANI prepared in the presence of MMT exhibited flake-like morphology rather than granular particle form of PANI without MMT. PANI/MMT10% showed higher electrical conductivity than pristine PANI. PANI and PANI/MMT were separately used as the fillers to prepare paraffin composites and PANI/MMT10% had a better microwave absorbing performance than PANI. The minimum reflection loss of PANI/MMT10%/paraffin composites with thickness of 8.0 mm were -37 dB at 14.8 GHz and the effective absorption band under -10 dB was from 13 to 16 GHz.

Keywords: Polyaniline; MMT; Composites; Intercalation; Microwave Properties

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1 Introduction

Microwave absorbing materials have shown great potential in the fields of electromagnetic shielding and stealth technology. Polyaniline (PANI) is a promising absorbing material due to its easy synthesis, low density, controllable conductivity and multi-morphologies [1]. Due to its properties, the study on higher wave absorbing performance of polyaniline and its composite materials are now one of the main research directions in the study of polyaniline. Saini prepared polyaniline–graphite composites and found that the highest total electromagnetic interference shielding effectiveness of the composites in the X band (8.2-12.4 GHz) is -33.6 dB [2]. Wu prepared the core-shell PANI/carbon black (CB) nanocomposite and found that PANI/CB can possess a wide range of absorption frequency by adding different contents of CB in PANI [3]. Among the composites of polyaniline, polyaniline/montmorillorite (PANI/MMT) composites, one kind of conductive composite, have received great attention because of its superior properties and potential applications

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March 2013

[4]. The MMT clay, whose lamella is constructed from an octahedral alumina sheet sandwiched between two tetrahedral silica sheets, exhibits a net negative charge on the surface of layers. The monomer (aniline) can be introduced into the galleries easily by ion exchange, in a way so that it is rather inseparable from the galleries [5]. Yoshimoto observed the change in the basal spacing of MMT interlayer before and after polymerization of the aniline when PANI was produced in the presence of MMT [6]. The differences of the MMT interlayer after polymerization is probably a result of the intercalation of PANI chains in the clay nano-interlayers. It has been reported that the incorporation of clay layers in PANI brought about changes in the chemical, physical and mechanical properties of the composite in comparison to the pristine PANI [7-9]. The changes of these properties may alter the microwave absorbing property, but few papers have been reported in the microwave absorption field.

In this paper, the microwave absorbing properties of paraffin composites were investigated. The composites of conducting PANI and insulating Na^+-MMT clay were first synthesized and characterized, and then the PANI and PANI/MMT that was obtained were separately used as a microwave absorbing filler to mix with paraffin.

2 Experimental

2.1 Materials

Montorillonite (MMT) was obtained from Na^+-montmorillonite (Zhejiang Fenghong Clay Chemicals Co., Ltd, China) with its cation-exchange capacity (CEC) of 90 meq/100 g clay. Aniline (Sinopharm Chemical Reagent Co., Ltd, China) was purified by distillation under reduced pressure and stored in a refrigerator before use; ammonium persulfate (APS) (Fluka, 98.0%) and hydrochloric acid (HCl) (Sinopharm Chemical Reagent Co., Ltd, China) were functioned as an oxidant and surfactant (acid dopant), respectively.

2.2 Preparation of PANI/MMT and Paraffin - PANI/MMT Composites

Composites of HCl-doped PANI and Na^+-MMT clay were synthesized through in-situ polymerization. The steps to prepare the HCl-doped PANI/MMT are given as follows. First, the Na^+-MMT clay was introduced into distilled water under constant magnetically stirring for 2hrs at room temperature; then the aniline monomer was added into the previously prepared clay solution. It is then followed by a HCl aqueous solution to reduce the pH value to 1-2 under constant magnetically stirring for 2hrs at room temperature; finally, the solution was cooled to 0° and $(NH_4)_2S_2O_8$ was slowly added dropwise to the solution(the molar ratio of aniline monomer to the ammonium persulfate was 1:1). After stirring at 0° for 14hrs, in order to remove any excess amount of ammonium ions, the composites were isolated by filtration and thoroughly rinsed with distilled water. Different weight ratios of Na^+-MMT composites (0%, 10%, 30%, 50%, 70%) were used. For the secondary doping, the prepared composites were soaked in 1 mol/L HCl under constant magnetically stirring for the whole night. After separation, the final product was dried in a vacuo at 60° for 24hrs. PANI and PANI/MMT were separately used as fillers to mix with the paraffin, then the mixture was heated to 60° to mold, obtaining the cylindrical specimen (with dimensions of 7.0, 3.0 and 5.0 mm for outer diameter, inner diameter, and thickness, respectively) for reflectivity measurements. The mixing ratio of PANI or PANI/MMT powders to paraffin was 1:9 by weight.

2.3 Characterization

By using KBr disc technique, the infrared absorption spectra of PANI/MMT were carried out on a NEXUS-670 spectrophotometer (Nicolet Company). The changes in the gallery structure of PANI/MMT composites were determined by XRD using a Rigaku Corporation Japan/max-2550 PC. The morphology of PANI/MMT composite was characterized by Scanning Electron Microscopy (SEM) with a JEOL JSM-5600LV microscope. Electrical conductivities of PANI/MMT samples were carried out on rectangular shape samples by a two-probe method using Keithley 236 source as the measure unit. Measurements of the microwave radiation attenuation were performed by reflectivity measurements using a HP8722E Vector network analyzer (US Agilent company), both adjusted for the frequency range of 2–18 GHz.

3 Results and Discussion

3.1 FT-IR Analysis of PANI/MMT

The FT-IR spectra of PANI/MMT and pristine PANI are shown in Fig. 1. The peak at 1562 cm^{-1} and 1478 cm^{-1} is assigned to N=Q=N stretching vibrations of quinoid rings and N-B-N stretching vibrations of benzenoid rings, respectively. The peaks at 1295 and 1238 cm^{-1} are attributed to C-N stretching vibrations. The absorption peak at 1104 cm^{-1} is assigned to the doping-mode N=Q=N. These peaks are ascribed to the formation of PANI. The peak at 1030 cm^{-1} and the 461 cm^{-1} are the characteristic vibrations of MMT clay. With increasing MMT content in the composites, the peaks of C-N stretching vibrations bands shifted from 1295 cm^{-1}, 1238 cm^{-1} for pristine PANI to 1304 cm^{-1}, 1248 cm^{-1} for PANI/MMT70%, respectively. On the other hand, the

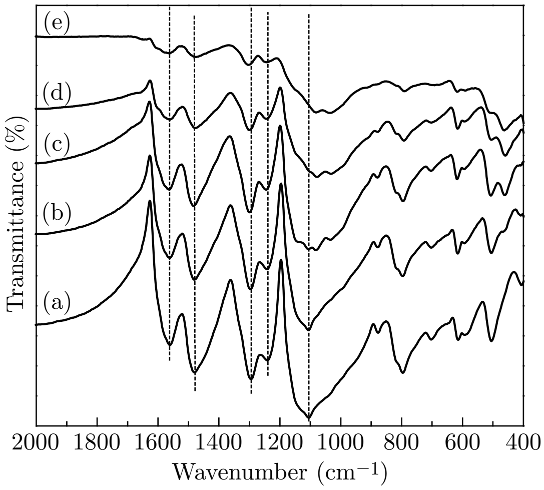
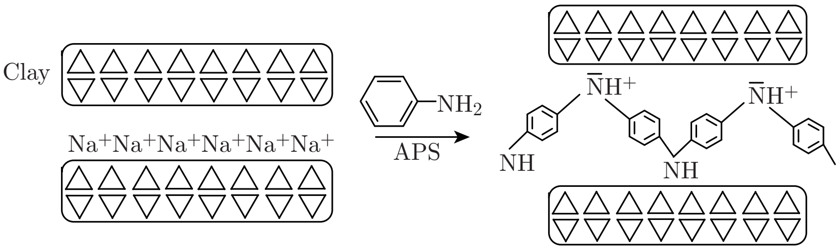


Fig. 1: FT-IR spectra of (a) PANI, (b) PANI/MMT10% , (c) PANI/MMT30%, (d) PANI/MMT50%, (e) PANI/MMT70%

peak of the doping-mode N=Q=N stretching vibration band shifted from 1104 cm^{-1} for pristine PANI to 1081 cm^{-1} for PANI/MMT70%, moreover, double peaks around doping-mode N=Q=N vibration appeared. These peak shifts may be due to the interaction between PANI chains and clay layers which could be attributed to the static action between the MMT layers with a negative charge, and PANI backbones with positive charge, or the formation of hydrogen bonding between the N-H of the PANI and the surface oxygen atoms of the clay as shown in Scheme 1.



Scheme 1 Schematic structure of the synthesis of PANI/MMT composite

3.2 XRD Analysis of PANI/MMT

WAXS patterns for the MMT and PANI/MMT composite are given in Fig. 2. The variation of the d-spacing (001) of the clay interlayer in MMT could be calculated from the observed peaks using the Bragg equation: $\lambda = 2d\sin\theta$. The MMT shows a peak at 2θ=7.0°, which corresponds to 1.26 nm of the interlayer spacing. After polymerization, the corresponding diffraction peak shifted to a lower angle. The d-spacing of clay interlayer in PANI/MMT10%, PANI/MMT30%, PANI/MMT50%, PANI/MMT70% rose up to 1.429 nm, 1.404 nm, 1.404 nm, 1.390 nm, respectively. The spacing of completely anhydrous clay galleries is 0.96 nm [10]. The expansion of the basal spacing of clay in PANI/MMT indicates PANI intercalation in MMT. With the content of MMT increasing, no sufficient PANI intercalated into the interlayer plane of MMT, so the data of d-spacing of clay interlayer in PANI/MMT10% is the highest. The extended value of interlayer is about 0.4-0.5 mm, which is about the dimension of an aromatic ring, suggesting that the aromatic rings of PANI are regarded as to have a planar (parallel) orientation to the layers [6]. This means that the intercalation of PANI chains has an extended chain conformation rather than a coiled conformation of polyaniline in the galleries of the host MMT. Fig. 3 shows the WAXS results for the pristine PANI, MMT, PANI/MMT30% and PANI/MMT30% etched with hydrofluoric acid. The diffraction peak of the d-spacing (001) of etched PANI/MMT30% disappeared, indicating that the MMT in composites were totally removed.

3.3 Morphology of PANI and PANI/MMT

The morphology of PANI in the presence of MMT may change. Fig. 4 shows SEM micrographs of PANI/MMT composites with different MMT content. It could be seen that the morphologies of PANI/MMT composites are strongly affected by MMT content in the composites. Pristine PANI (Fig. 4 (a)) shows granular particles, while an obvious flake-like morphology is observed in the PANI/MMT composite. Compared to pristine MMT (Fig. 4 (f)), the flake sheets of composite are much looser. When the content of MMT reaches to 70%, the flake sheets are closely stacked together and it's in accord with the results of XRD, i.e. the d-spacing becomes small when MMT content is high in PANI/MMT. Fig. 4 (g) shows that the etched composite without MMT still exhibits morphology of flake sheet, which explains why PANI is formed between the interlayers of MMT, and could be kept stably in flake-like sheet even when MMT is removed.

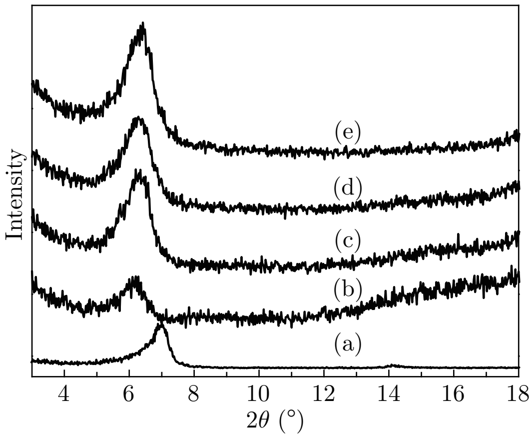


Fig. 2: XRD spectra of (a) MMT, (b) PANI/MMT10%, (c) PANI/MMT30%, (d) PANI/MMT50%, (e) PANI/MMT70%

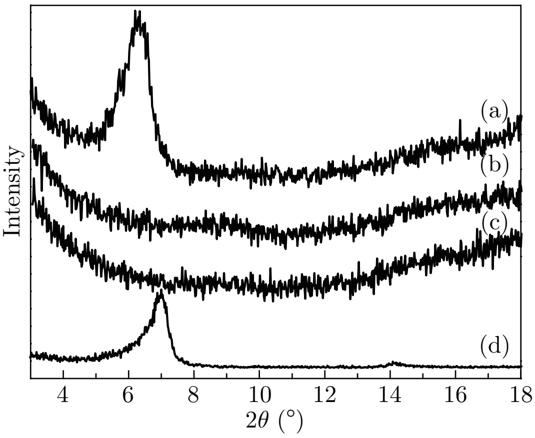
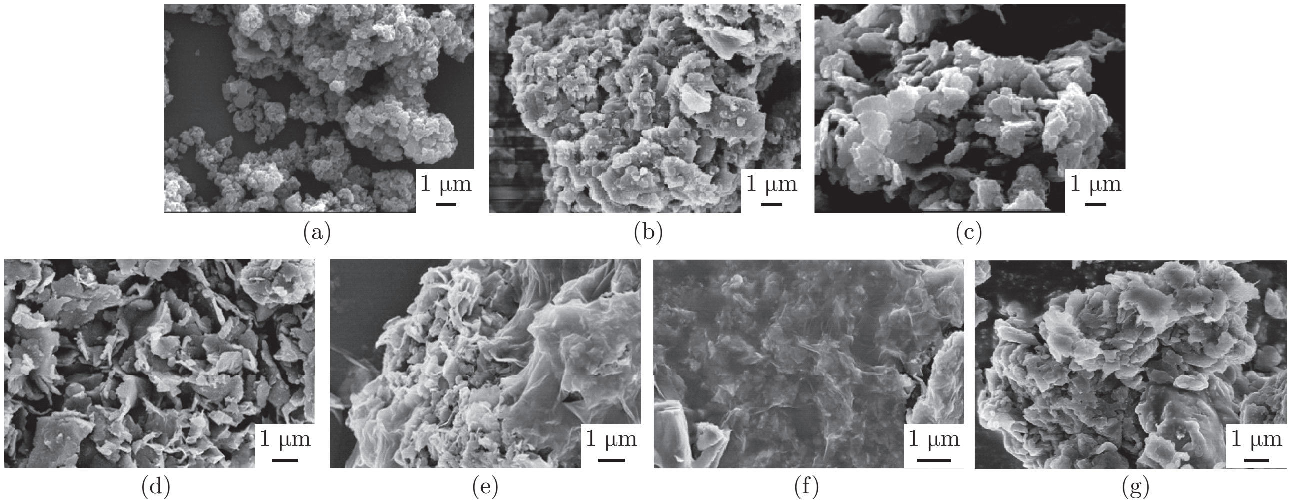


Fig. 3: XRD spectra of (a) PANI/MMT30%, (b) PANI, (c) PANI/MMT30% etched with hydrofluoric acid, (d) MMT



(a) (b) (c)

(d) (e) (f) (g)

Fig. 4: SEM micrographs for (a) pristine PANI, (b) PANI/MMT10%, (c) PANI/MMT30%, (d) PANI/MMT50%, (e) PANI/MMT70%, (f) MMT, (g) etched PANI/MMT30% without MMT

3.4 Conductivity of PANI/MMT Composites

The electrical conductivity data of PANI/MMT composites is listed in Table 1. It is evident that MMT has an important effect on the conductivity of PANI/MMT composites. From examining Table 1, it could be seen that the electrical conductivity of the secondary doped PANI is apparently higher than the once doping PANI because filtering and washing may result to the de-doping and the lowering of the electrical conductivity of PANI. The highest conductivity of the secondary doped composite was 0.501 s/cm when the weight of MMT was 10%, even higher than the conductivity of pristine PANI. Although MMT is a kind of insulation material and exhibits electrical resistance, the conductive PANI chains in the interlayer spaces are assumed to take a more extended and regular conformation than in its bulk form, thus enhancing the conductivity of the composites. Due to the electrical resistance from insulated MMT, when the amount of MMT is greater than 10%, the conductivity of the composites decreases with increasing weight ratio of MMT. The similar result was also found in polypyrrole/MMT composites and the DBSA doped PANI/MMT composites [11, 12].

Table 1: Electrical conductivity date for PANI/MMT composites

System	Electrical conductivity (S/cm) (once doping)	Electrical conductivity (S/cm) (secondary doping)
Pristine PANI	0.079±0.002	0.314±0.003
PANI/MMT10%	0.158±0.004	0.501±0.004
PANI/MMT30%	0.062±0.002	0.258±0.004
PANI/MMT50%	0.051±0.003	0.184±0.001
PANI /MMT70%	0.033±0.001	0.034±0.002

3.5 Microwave Absorbing Properties of PANI/MMT/Paraffin Composites

During the preparation of PANI/MMT/paraffin composites, the addition of pristine PANI or PANI/MMT was controlled at the same level of 10wt% and paraffin at 90wt%. Fig. 5 shows the dependence of the calculated reflection loss of the PANI/MMT/paraffin composites on frequency in the frequency range of 2-18 GHz. It is clearly demonstrated that the reflection loss of composites depends on the content of MMT. The minimum reflection loss occurred almost at the same frequency area with the same thickness. The filler PANI/MMT10% showed the best microwave absorption among three samples with the minimum reflection loss of −37 dB. There is no microwave absorption for MMT, but the PANI/MMT30% showed better microwave absorption than pristine PANI. The main cause is the morphology change of PANI, from the granular particles for pristine PANI to flake sheets for PANI/MMT composites [13]. On the other hand, the PANI that was inserted into the interlayers of MMT increased the path of microwave attenuation. The increasing thickness of PANI/MMT/paraffin shifted the absorbing peak value to the

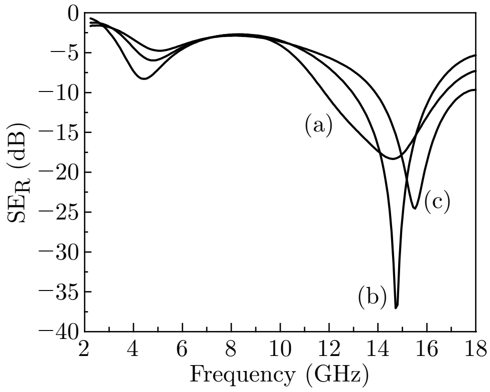


Fig. 5: Microwave reflection loss of PANI/MMT composites at 2-18 GHz (the thickness was 8 mm.) (a) pristine PANI, (b) PANI/MMT10%, (c) PANI /MMT30%

lower frequency band, as shown in Fig. 6. The minimum reflection loss of the sample with 8.0 mm thickness reaches −37 dB at 14.8 GHz and the effective absorption band under −10 dB is from 13 to 16 GHz. Meanwhile, a further increase of thickness to 9 and 10 mm could not enhance the reflection loss.

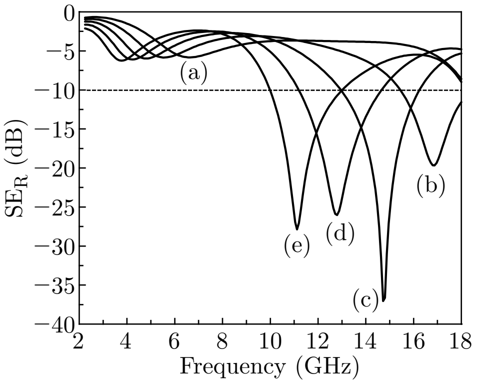


Fig. 6: Reflection loss of PANI /MMT10% with different thickness versus frequency (2-18 GHz) (a) 6 mm, (b) 7 mm, (c) 8 mm, (d) 9 mm, (e) 10 mm

4 Conclusion

PANI/MMT composites were prepared by in-situ polymerization. An interaction between PANI backbones and MMT layer surfaces may be present according to FT-IR analysis. XRD showed that PANI was intercalated into the MMT galleries and expended the interlayer spacing of MMT. Compared to the granular particle form of pristine PANI, PANI/MMT showed flake-like morphology and higher electrical conductivity than pristine PANI as the content of MMT is 10wt%. Both pristine PANI and PANI/MMT were used as fillers to prepare PANI/paraffin and PANI/MMT/paraffin composites. PANI/MMT10% showed better microwave absorbing performance than pristine PANI.

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