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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

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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[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