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Research paper

High electrical anisotropy in hydrochloric acid doped polyaniline/phyllosilicate nanocomposites: Effect of phyllosilicate matrix, synthesis pathway and pressure

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ABSTRACT

Pressed tablets from polyaniline/phyllosilicate nanocomposites have been prepared under various conditions in order to optimize anisotropic conductivity of composite by ordering of flat phyllosilicate particles intercalated with polyaniline (PANI). Powder samples of PANI/phyllosilicate nanocomposites have been prepared using two phyllosilicates, montmorillonite and vermiculite, with a different layer charge. Two precursors were used, anilinium hydrochloride and anilinium sulfate. Prepared PANI/phyllosilicate composites were subsequently doped by hydrochloric acid via rinsing after polymerization process and for the DC conductivity measurements pressed into tablets. Applied pressure was 28 MPa and 128 MPa. Highly anisotropic conductivity has been achieved in pressed tablets. The in-plane conductivity for PANI/montmorillonite was 0.084 S/cm, i.e., 1000× higher than in the direction perpendicular to the tablet plane. Increase of pressure up to 128 MPa led to dramatic decrease of conductivity.

1. Introduction

Various preparation methods of polyaniline/clay composites were used by many authors (Bae et al., 2004; Ballav and Biswas, 2004; Do Nascimento et al., 2002; Kim et al., 2001; Lu and Zhao, 2002; Sohn et al., 2002; Sun et al., 2010; Yeh et al., 2001; Yoshimoto et al., 2005) in order to achieve a combination of superior electrical and mechanical properties (Do Nascimento et al., 2006; Zaarei et al., 2008) for the applications in electrorheology (Cho et al., 2004; Lu and Zhao, 2002; Sung et al., 2003) and in the corrosion protection of metals (Yeh et al., 2001). It has been proved, that nanostructure of polyaniline (PANI) affects the conductivity (Gregory et al., 1989; Laslau et al., 2012; MacDiarmid, 1997; Sapurina et al., 2001; Stejskal et al., 2010) and phyllosilicate flat particles offer a good chance to order polymer chains and in addition to improve the thermal and mechanical properties of nanocomposite functional units (Semakov et al., 2010). Prokeš and his co-workers (Prokeš et al., 2011) showed the dependence of conductivity of PANI pressed tablets on compression pressure. In design of organo/inorganic nanocomposites based on phyllosilicates the key question is the effect of silicate layer charge, which affects significantly first of all the intercalation behavior and consequently the structure and properties of intercalated surface-modified phyllosilicates (Čapková et al., 2004; Klika et al., 2009, 2011; Simha Martynková, 2008). That is why we have chosen two phyllosilicate matrices with a different silicate layer charge: montmorillonite and vermiculite.

Various synthesis pathways and precursors for pure PANI preparation have been described in literature (Sapurina and Stejskal, 2008; Stejskal and Sapurina, 2005) and there are also several articles on preparation of PANI/MMT composite (Bekri-Abbes and Srasra, 2010; Bober et al., 2010; Kazim et al., 2012; Wu et al., 2000). Their effect on conductivity of resulting product has not been studied systematically. In present work we tested two different polymerization pathways: (1) one-step process with polymerization in the presence of phyllosilicate and (2) two-step process with intercalation of anilinium and subsequent polymerization in the intercalated phyllosilicate structure. Two different aniline precursors have been used in both polymerization pathways: anilinium sulfate and anilinium hydrochloride.

The main problem in design of PANI/clay nanocomposites is to create the functional units with thermal and mechanical stability by keeping and/or improving all the desirable properties. Pressed tablets have been shown as suitable form guaranteeing good reproducibility

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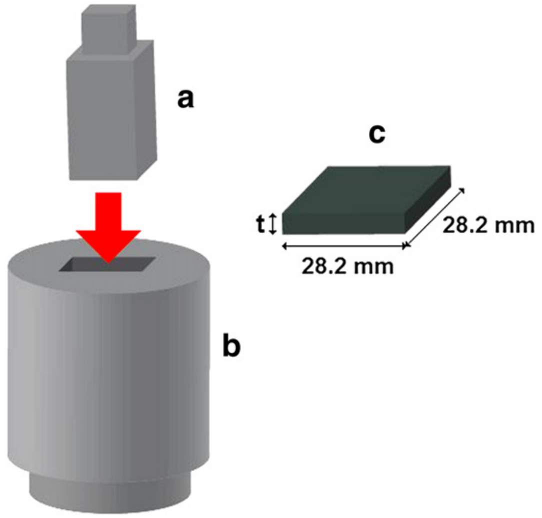

Fig. 1. a) Piston, b) matrix and c) pressed tablet. Thickness *t* varies in dependence on type and amount of composite.

of conductivity measurements and easy handling. Among various solid layered particles phyllosilicates offer several advantages: (1) first of all good thermal and mechanical stability; (2) expandable layered structure of 2:1 phyllosilicates can be intercalated with PANI and ordering of PANI chains results in the strong anisotropy of electrical conductivity; (3) variable layer charge in different types of phyllosilicates enables to modify the interlayer concentration and nanostructure of PANI guest species; and (4) in addition the layer charge of phyllosilicates can be tuned (reduced) by the cointercalation of lithium (Klika et al., 2009). Anisotropic electroconducting PANI/phyllosilicate composite has been prepared by Semakov et al. (2010), using aniline intercalation into montmorillonite and subsequent polymerization. In spite of the low conductivity values achieved in their work, Semakov et al. (2010) showed the possibility to prepare strongly anisotropic electroconducting PANI/phyllosilicate composites as pressed tablets with in-plane conductivity 115× higher than in orthogonal direction.

The aim of the present work is to optimize the technology PANI/phyllosilicate nanocomposites in order to achieve a high electrical anisotropy, where the ratio of in-plane and orthogonal conductivity $\sigma\|/\sigma\perp$ will be at least ~10^3, striving to design the functional unit with nearly two-dimensional conductivity. The second aim was to simplify the preparation method, i.e., to reduce the number of technological steps by keeping reasonable mechanical properties allowing easy handling.

2. Experiment

2.1. Materials

Two phyllosilicates with various layer charges have been used in the present study: (1) commercially available Na-montmorillonite Portaclay® (The mineral company Ankerpoort NV, Netherland) with basal spacing of 1.245 nm, structural formula (Si_8) $(Al_{2.85}Mg_{0.71}$ $Ti_{0.02}$ $Fe^{3+}{}_{0.42})$ O_{20} $(OH)_4$ with layer charge ~0.7 el. per unit cell and (2) natural Mg-vermiculite from Letovice (Czech Republic) with basal spacing of 1.445 nm, structural formula $(Si_{6.26}$ $Al_{1.72}$ $Ti_{0.04})$ $(Mg_{4.66}$ $Fe^{3+}{}_{0.90}$ $Al_{0.02})$ O_{20} $(OH)_4$ with layer charge ~0.8 el. per unit cell. Aniline, sulfuric acid, aniline hydrochloride and ammonium peroxodisulfate were purchased from Lach-Ner, Czech Republic, and used as received.

2.2. Powder sample preparation

Two different pathways have been used for polymerization: (1) one-step process with the polymerization in the presence of phyllosilicate matrix and (2) two-step process, starting with intercalation of anilinium into phyllosilicate matrix and subsequent polymerization in the intercalated phyllosilicate structure. For both pathways we used two different precursors: anilinium hydrochloride and anilinium sulfate.

2.2.1. One-step process

The anilinium sulfate and ammonium peroxodisulfate were added into aqueous suspension of montmorillonite (MMT) or vermiculite (VER) at room temperature. Although the polymerization of aniline was completed within 40 min (blue color of suspension turned into dark emeraldine green — conductive form of PANI), the suspension was stirred for 6 h. The green solid was collected on a filter and doped by rinsing with 0.2 M hydrochloric acid in order to exchange the sulfate counter-ions for chloride ions. Resulting samples were dried at 40 °C in a kiln and denoted as PANI/MMT-I-AnS and PANI/VER-I-AnS.

The anilinium hydrochloride and ammonium peroxodisulfate (according to the procedure described by Bober et al. (2010)) were

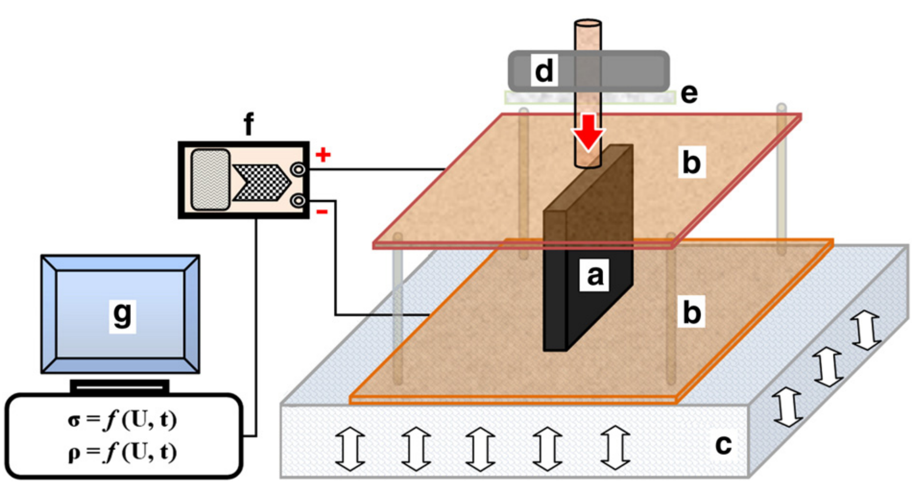

Fig. 2. The apparatus for direct measurement of resistivity and conductivity of pressed pellets. a: pressed tablet sample (oriented for measuring in direction perpendicular to the direction of pressing), b: polished Cu electrodes, c: flexible insulator, d: weights to ensure a constant pressure on the sample in the direction of the red arrow, e: felt muffler, f: DC source and measuring card, g: computer with software.