

Composite Comprising Sulfonic Acid-Functionalized MCM-41 and Polyaniline and Its Thermal Stability of Conductivity

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A composite of sulfonic acid-functionalized mesoporous silica (MCM-41) with a polyaniline (PANI) conducting polymer was synthesized by *in situ* polymerization method. PANI/MCM-41 conducting polymer composites were characterized by Fourier Transform Infrared (FTIR), UV-Vis, thermogravimetric analysis (TGA), Four-point probe for conductivity measurement and ¹³C CP/MAS NMR. It was revealed that although conductivity of PANI was reduced after addition of MCM-41, its thermal stability of conductivity was significantly enhanced and demonstrated the desirability which efficacy of this polymer-mesoporous silica MCM-41 composite system in relatively high temperature applications.

Introduction

It has been reported by several researchers that a good thermal stability of PANI could be improved by combining PANI with MCM-41 [1,2]. However, the thermal stability of conductivity of these composites has never been investigated. These composites have also been proven to possess a variety of unique properties such as mechanical, electrical and structure properties because of the synergistic effect owing to the intimate mixing between PANI and inorganic or organic components at a molecular level. In this study, MCM-41 was chemically modified by functionalization with 3-mercaptopropyltrimethoxysilane (MPTS) to create sulfonic acid in order to increase the interfacial interaction between PANI and MCM-41. Further, we show that enhancement of the thermal stability of conductivity of PANI/MCM-41 composite was achieved when PANI was combined with sulfonic acid-functionalized MCM-41.

Experimental

The MCM-41 and PANI dodecylsulfate (PANI.DS) were synthesized according to Refs. [3] and [4] respectively. In the synthesis of PANI composite with MCM-41 loaded with sulfonic acid (PANI/MCM-41-SO₃H), MCM-41 was first modified with 3-mercaptopropyltrimethoxysilane (MPTS) based on the procedure reported previously [5]. PANI/MCM-41 conducting polymer composites obtained were char-

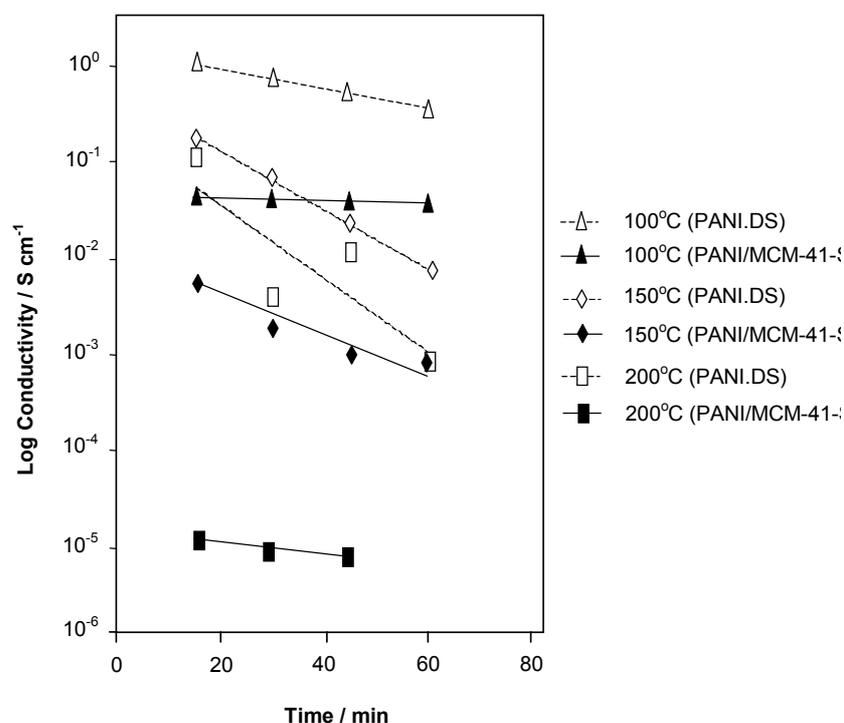


Figure 1: The conductivity of PANI.DS and PANI/MCM-41-SO₃H composites at 100, 150 and 200°C versus time.

acterized by Fourier Transform Infrared (FTIR), UV-Vis, thermogravimetric analysis (TGA), Four-point probe for conductivity measurement and ^{13}C CP/MAS NMR.

Results and Discussion

The IR spectra of PANI.DS, MCM-41-SO₃H and PANI/MCM-41-SO₃H showed the absorption in the region between 3500 and 2700 cm⁻¹ in which are typical to hydrogen bonded propyl and SO₃H groups in MCM-41-SO₃H. The absence of bands of -SH at 2600 to 2550 cm⁻¹ in the spectrum of MCM-41-SO₃H and PANI/MCM-41-SO₃H confirmed that only SO₃H is present in the structure of MCM-41 after modification. The appearance of peaks around 1560, 1467, 1296, and 1237 cm⁻¹ suggested that all the polyaniline compounds have the emeraldine salt structure. The UV-Vis spectra of PANI.DS and PANI/MCM-41-SO₃H composites showed characteristic absorptions at 300–420 and 740–1000 nm wavelength which are assigned to π - π^* electron transition within benzenoid segments and formation of polaron, respectively. TGA analysis showed that the decomposition rate of the polymer when combined with MCM-41 is found to be very different from the decomposition rate of the bulk polymer. The bulk PANI emeraldine salt (PANI.DS) decomposes between 200 and 700 °C, but the polymer composite decomposes slowly from 300 to 600°C. This result implies that PANI interacted strongly with the surface MCM-41-SO₃H, enhancing the thermal stability of polyaniline. For further confirmation, the interaction between sulfonic acid attached in the structure of the MCM-41 and PANI was demonstrated by using ^{13}C /CP MAS NMR. When MCM-41-SO₃H was combined with PANI to produce PANI/MCM-41-SO₃H composite, a broad peak of PANI at around 120 ppm was appeared, and the signals at 54 ppm, 14 ppm and -2 ppm of -(CH₂)₃SO₃H were shifted towards a higher magnetic field. The high field chemical NMR shift of these signals can be explained by the interaction of the free electron pairs of the nitrogen atoms of the PANI with a charged molecule on the surface of MCM-41-SO₃H with PANI.

Fig. 1 illustrates the effect of curing temperature on the conductivity of PANI.DS and PANI/MCM-41-SO₃H composite at 100, 150 and 200°C. As seen in Fig. 1, the increase in curing temperature reduces the conductivity of PANI.DS. However, at 100°C, the conductivity of the PANI.DS and PANI/MCM-41-SO₃H composites are steadily maintained with the increase of time from 15 minutes to 1 hour. The increase of temperature to 150°C causes a larger reduction rate of conductivity of PANI.DS than PANI/MCM-41-SO₃H composite. This explains why the reduction rate of conductivity is the highest for PANI.DS. In contrast, the reduction rate of conductivity of PANI/MCM-41-SO₃H is low after the temperature was increased to 200°C. However, the conductivity of the PANI/MCM-41-SO₃H became so low that after 45 minutes, it could no longer be measured through the four-point probe method. On the basis of the above results, a model of the interaction of polyaniline with MCM-41-SO₃H in PANI/MCM-41-SO₃H composite is proposed (see Fig. 2).

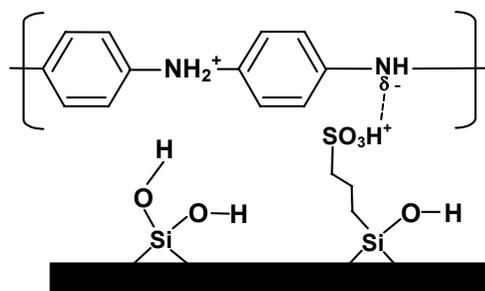


Figure 2: The propose interaction between polyaniline and MCM-41-SO₃H in PANI/MCM-41-SO₃H composite.

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