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Polymer Nanocomposites for Hydrogen Storage

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Abstract. Hydrogen is considered to be a clean, economical and safe renewable energy source that would be ideal to replace fossil fuels, because it is light, highly abundant and its oxidation product (water) is environmentally benign. However, hydrogen is easy to burn (the chemical energy per mass of hydrogen is at least three times larger than that of other chemical fuels), which has the risk of fire and explosion. The problems of transportation and storage restrict the application of hydrogen energy, which has become a key factor in the development and utilization of hydrogen energy. This gas adsorbs at solid surfaces depending on the applied pressure and temperature. For storage purposes in mobile applications, the adsorption of hydrogen has been studied mainly on carbon species, but light and reasonably cheap materials of high surface area should prove to be attractive as well. Porous material is a very promising hydrogen storage material, which stores the gas in the form of molecules at low temperatures and compresses hydrogen into the holes effectively. The purpose of this work was to develop a hybrid porous materials consisting of sulfonated polyetherimide matrix with aluminum nanoparticles and faujasite type zeolite. Dilute solutions were first prepared under stirring at room temperature and the solutions were dried under vacuum. The hybrids were analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), transmission electron microscopy (TEM) and hydrogen sorption measurements. The addition of aluminum decreased the glass transition temperature of the hybrids when compared to the sulfonated polymer and the TEM images showed that simply physically mixture occurred between polymer and metallic nanoparticles. Hydrogen sorption tests showed an increase in the amount of hydrogen in the presence of zeolite.

Keywords: hydrogen storage, nanocomposites, polyetherimide, aluminum, zeolite.

PACS: 81; 82.

INTRODUCTION

In an age of mobile technology energy storage has become an extremely important issue as the energy sources such as fossil fuels and natural gas are not infinitely available and even if they were, their combustion or end products are not environment friendly. Exploring sustainable clean energy sources and environmental technology to satisfy the world's growing demand are emerging as one of the foremost challenges for this century [1-2]. One of the alternatives among renewable energy resources is to use hydrogen gas (H₂) as a new energy carrier, once it is clean, highly abundant and non-toxic. Major attracting property of hydrogen is its natural compatibility with fuel cells. The higher efficiency of hydrogen (60%) compared to gasoline (22%) or diesel (45%) improves the efficiency for future energy use. However, a main obstacle impeding anticipated future hydrogen economy is the lack of safe, efficient and economical on-board hydrogen storage [3].

The popularity of porous polymers as new high surface area materials for applications in gas storage and separation is increasing very rapidly owing to their ease of preparation, low cost, chemical tenability and thermal stability [4]. On the other hand, after more than 20 years of research, no material yet possesses adsorbing properties required for applications. All porous structures that exist today are far from being optimal when considered as hydrogen sorbents for mobile applications [5]. However, in most of the cases reported, the hydrogen storage capability relies mostly on the intrinsic porosity of the polymers in the solid state and only very few examples of polymeric materials which have specific interactions with hydrogen have been reported [6]. It has also been shown that introduction of different chemical functions such as metal cations, imine, sulfonate, π -conjugated moieties and heteroatoms into the structure of porous materials could indeed increase significantly the hydrogen uptake [7].

Metallic particles and hydrides of some metals and non-metals can also form a class of materials for hydrogen storage characterized by their ability to store larger amounts of H₂ through the formation of chemical bonds. The incorporation of these nanoparticles into polymers or nanoporous structures can be an alternative to obtain materials with excellent hydrogen storage properties. The metal hydrides chosen for those applications usually provide low reactivity (high safety), lower pressure storage, reasonable gravimetric storage capacity, short storage time (which

makes them highly efficient as an on-board storage vehicle but still work needs to be done in order to improve its kinetics), energy density, cycle life, operating temperature and long storage time [4]. Moreira et al. [8] developed composites of polyaniline (NaAlH_4) and sodium alanate using titanium dioxide as doping agent. The polyaniline presented hydrogen sorption values around 1.0 wt.% after 13 hours of hydrogen sorption. The addition of sodium alanate increased this value in 40 %. Oliveira et al. [9] studied porous nanocomposites of sulfonated polyetherimide with carbon nanotubes and sodium alanate. Both nanoparticles were poorly dispersed in the polymer matrix and the nanocomposites could store 1.1 wt.% of hydrogen at 120°C.

In this work composites of sulfonated polyetherimide with aluminum nanoparticles and different amounts of faujasite-type zeolite (used as catalyst) were produced. The influence of both nanoparticles on thermal, structural and hydrogen sorption behavior of these materials was evaluated.

EXPERIMENTAL

Materials

A polyetherimide (PEI), grade Ultem™ 1000, was supplied by Sabic Innovative Plastics. It has a density of 1.28 g/cm³ and MFI of 9.0 g/10 min (6,6 kg/337 °C). The chemical modification of the polymer, in order to produce the sulfonated polyetherimide (PEIS), was done using an acetyl sulfate made of N-Methyl-2-pyrrolidinone (NMP), acetic anhydrid and sulfuric acid (volume ratio of 20:2:1). Aluminum nanoparticles (Al) were purchased from Nanostructured and Amorphous Materials Inc., with 99% of purity, density of 2.699 g/cm³ (20 °C) and average particle size of 80 nm. A faujasite-type zeolite (ZEO), grade CBV780 was supplied by Zeolyst International and has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 80, surface area of 780 m²/g and average particle size of 2 µm.

Sulfonation of Polyetherimide

A small round bottom flask equipped with a magnetic stirrer was charged with 6 g of PEI dissolved in 40 ml of NMP at 80 °C. The acetyl sulfate was added to this solution gradually within 1 h and after that the reaction continued for another hour. At the end, the reaction product was precipitated with ethanol, washed three times with the same solvent, filtered and dried under vacuum at 80 °C.

Preparation of PEIS/ZEO/Al Nanocomposites

The nanocomposites had to be prepared in two steps because the aluminum powder is highly reactive with the chemical modification environment of the PEI: (1) *in-situ* nanocomposites of PEIS and ZEO were prepared and then (2) dissolved in NMP and mixed with aluminum powder. The concentration of the solutions during the preparation of all nanocomposites was 0.7 g / ml. The content of aluminum was fixed at 30 wt.% in all samples and the zeolite contents were 2.5, 5 and 10 wt.%. Samples without aluminum (only with PEIS and ZEO) were also prepared.

Thermal Characterization

Differential scanning calorimetry (DSC) was done on a Q2000 equipment, from TA Instruments and thermograms were obtained from room temperature up to 250 °C under nitrogen flow and heating rate of 10 °C/min. Thermogravimetric analysis (TGA) were carried on a Q50 equipment, also from TA Instruments, under nitrogen atmosphere and heating rate of 20 °C/min from room temperature up to 800 °C.

Structural Characterization

Morphological analysis was carried out on a transmission electron microscope (TEM), Magelan, model 400L, with an operating voltage of 25kV.

Hydrogen Sorption Measurement

Kinetic measurements of hydrogen absorption (PCT) were collected in a volumetric device (Sievert's apparatus) built and designed in the Laboratory of Hydrogen in Metallic Materials (LHM) of the Federal University of São

Carlos, Brazil. Sorption measurements were performed at fixed temperature of 120 °C and hydrogen pressure of 32 bar for the following samples: PEIS/Al (70/30 wt.%) and PEIS/ZEO/Al (60/10/30 and 65/5/30 wt.%), using 100 mg of each one. Temperature and pressure used in hydrogen sorption was based on literature review [1-2,8].

RESULTS AND DISCUSSION

Figure 1 shows the DSC curves for polyetherimide before and after sulfonating procedure and for the nanocomposites with aluminum and zeolite.

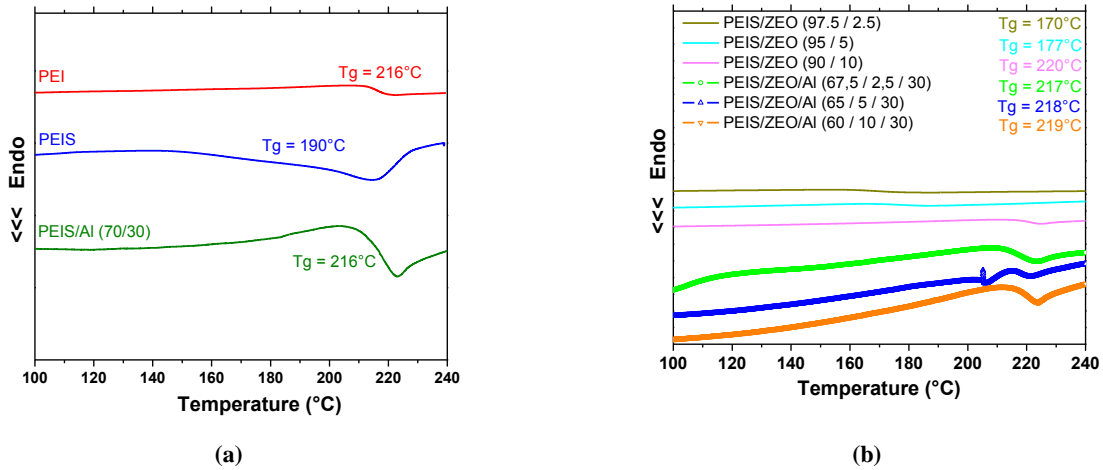


FIGURE 1. DSC curves for: (a) PEI, PEIS and PEIS/Al and (b) PEIS/ZEO nanocomposites.

From the results above, it is observed that the PEI has a glass transition temperature (T_g) of approximately 216 °C and the sulfonating reaction promoted a decrease to 190 °C, probably due to the introduction of sulfonic groups which increased the free volume between polymeric chains. In the presence of aluminum (PEIS/Al), this transition temperature returned to its initial value prior to the sulfonating procedure. Thus, it can be concluded that the presence of aluminum nanoparticles reduced the mobility of macromolecules [10]. On the other hand, the presence of 2.5 and 5 wt.% of zeolite had an opposite effect; there was a decrease in the glass transition temperature of the polymer. Thus, small amounts of zeolite (less than 10 wt.%) can increase the mobility of the sulfonated polymeric chains, but 10 wt.% had the same effect of aluminum nanoparticles. In all samples with aluminum and zeolite (PEIS/ZEO/Al), only a slightly increase in glass transition temperature of the sulfonated polymer was observed. However, since this variation in T_g is not significant in those cases, it can be stated that the addition of a small amount of zeolite (up to 10 wt.%t), with 30 wt.% of aluminum, does not change the thermal behavior of PEIS.

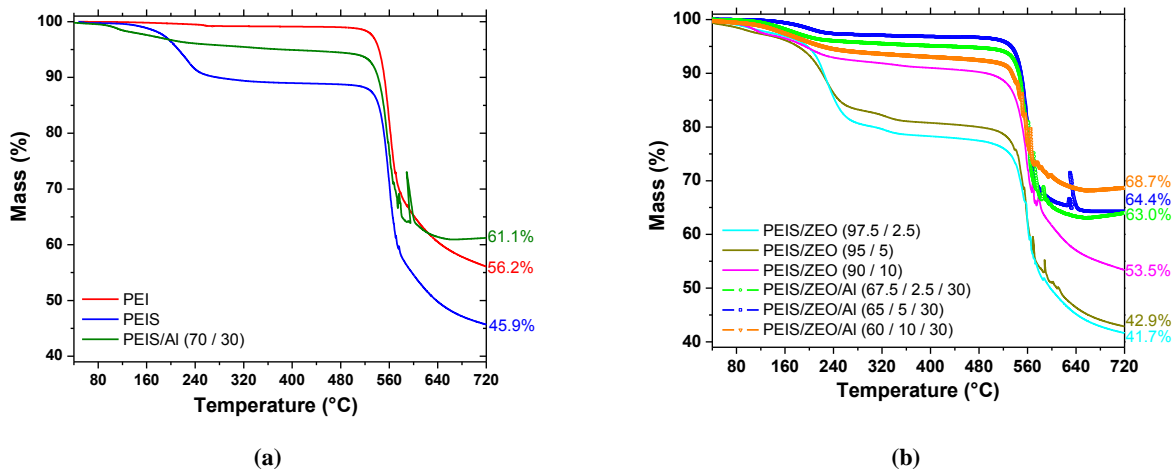


FIGURE 2. TGA curves for: (a) PEI, PEIS and PEIS/Al and (b) PEIS/ZEO nanocomposites.

In Figure 2 the thermal stability of the polymer matrix and the nanocomposites with aluminum and zeolite can be observed. The degradation of all materials occurred in two stages: (1) the degradation of the sulfonic chains and (2) around 440 °C, the degradation of the PEI main chains. The first stage also contains a small loss of weight due to the presence of zeolite, which contains moisture within its pores and channels. Therefore, decomposition and release of gas molecules begins after the 100 °C [10]. It can be also observed in Figure 2 that the residues at the end of analysis increases with the zeolite content, since its structure is thermally stable up to higher temperatures. The presence of aluminum made the thermal behavior of the nanocomposites more stable at high temperatures, but did not change significantly their initial temperatures of decomposition.

Figure 3 shows the morphology of the PEIS/ZEO/Al nanocomposites obtained by TEM analysis. The aluminum nanoparticles are spheres with large size distribution and average diameter between 30 and 500 nm. The presence of zeolite was difficult to observe due to its wide distribution of particle size and small amount added to the mixtures. It is also possible to observe that the aluminum may be interacting with the zeolite, but it tends to form many small and medium-sized agglomerates within the polymer matrix [10]. The nanocomposite with 10 wt.% of zeolite has a larger number of agglomerates, but with smaller size, when compared to the sample with 5 wt.%. These agglomerates may be contributing negatively to hydrogen sorption of the samples, due to a smaller contact area with the gas during sorption conditions. Thus, the average size, the dispersion and the amount of agglomerates in each sample are important parameters to be determined once they will contribute to the behavior of hydrogen sorption.

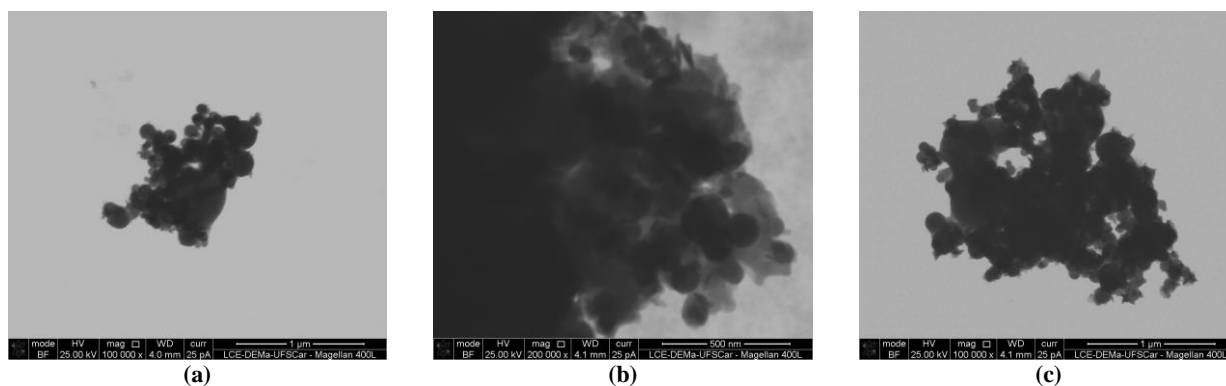


FIGURE 3. TEM analysis for PEIS/ZEO/Al nanocomposites with: (a) 2.5, (b) 5 and (b) 10 wt.% of zeolite.

Figure 4 shows the PCT curves for the samples analysed after 12 hours measurements.

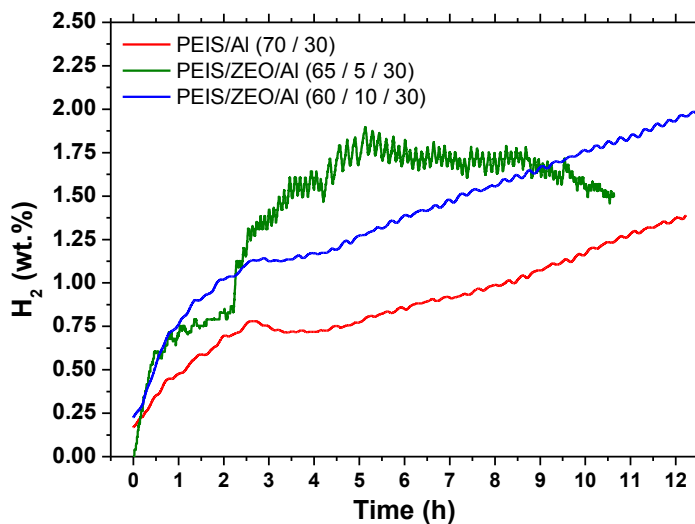


FIGURE 4. PCT curves for PEIS/Al nanocomposites.

For two of the nanocomposites analyzed (the one with 10 wt.% of zeolite and the one only with aluminum) it can be observed that hydrogen sorption quickly increased in the first three hours until reach a maximum value. In the next few minutes the absorption slightly decreased and then, after 4 hours of experiment, it started to increase again with a slower rate. After 12 hours, the sample with 10 wt.% of zeolite could absorb 2 wt.% of hydrogen; near 50 % more than the sample without this porous silicate [10]. On the other hand, it can be observed that the presence of a smaller amount of zeolite (5 wt.%) made the hydrogen sorption much more instable. After 5 hours of measurement this sample absorbed almost 2 wt.% of hydrogen and then the amount of gas started to decrease and reached 1.5 wt.% at the end of the analysis. The presence of larger agglomerates of aluminum and zeolite in this sample, compared to the nanocomposite with 10 wt.% of zeolite, had probably caused this unexpected behavior. These results have evidenced that those hybrid materials can be used for hydrogen storage, but the dispersion of the metallic and inorganic particles is still a problem to be solved in the future development.

CONCLUSION

Polymer nanocomposites were prepared from the mixture of sulfonated polyetherimide with aluminum and zeolite nanoparticles. These hybrid materials were obtained in order to produce new materials to reach greater hydrogen storage capacity for mobile applications.

Zeolite and aluminum added during the preparation of the nanocomposites had few influence on the sulfonated polymer structure. However, they did not change its thermal properties, such as glass transition temperature and the onset temperature of degradation. By TEM analysis it was observed that the zeolite and aluminum nanoparticles were located inside the sulfonated polyetherimide and also on its porous surface, but they were not well dispersed and distributed. The amount of zeolite modified the average size and size distribution of the agglomerates.

Hydrogen sorption tests were carried out and it was observed a significant increase in the amount of hydrogen in the nanocomposite with 10 wt.% of zeolite relative to the one without zeolite. The larger agglomerates in the sample with aluminum and 5 wt.% of zeolite made the hydrogen sorption much more instable. Dehydrogenation tests of these materials will be performed in the future, as soon as better dispersion of the nanoparticles will be reached.

Obtaining polymeric materials for hydrogen storage is important for the scientific and technological development and the polymer matrix and the nanofillers chosen in this work have a great potential to obtain new hybrid materials with ability to store larger amounts of hydrogen.

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