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Tannin based foams modified to be semi-conductive: Synthesis and characterization

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ABSTRACT

The objective of this study was to modify highly insulative and lightweight biorenewable foam thermosets to be semi-conductive for primarily building material applications. The foams were formed and then post-treated with in-situ polymerization of polyaniline, both doped and undoped, adsorbing and possibly absorbing (observed by SEM-EDX) to the foam structure at levels of 100–120 wt%.

The modified tannin foams were shown to be semi-conductive in comparison to the highly insulative structure prior to polyaniline modification. While the 50% protonated polyaniline modified foams, or doped foams, had a higher conductivity than the undoped polyaniline modified foams, the acid used in fabrication of the foams provided some degree of conductivity to the undoped PANI modified foams. Moreover, the modified foams had an increased volume of 15% after modification, were more sensitive to moisture, and the polyaniline did not affect the degradation temperature of the foams.

1. Introduction

Formulating materials based on renewable resources instead of fossil fuels is of increasing importance for industry and consumers alike. Most foams used today in building materials are based on composed of plastics such as polyurethane based on petroleum sources. Biorenewable foams have been developed in an effort to provide a biobased alternative. Foam formulations based on furfuryl alcohol, currently derived from hydrolyzed sugars from agricultural crops, and tannin extract, derived from bark, have been combined to make rigid insulative foams that have been targeted for use in metal absorption and building materials. These tannin-based foams have been found to have low thermal conductivity, be resistant to chemicals, and have similar compression strengths to commercially available phenolic foams [1–6].

Interest in intrinsically conducting polymers (ICP) has been prolific in the past few decades [7,8]. Polyaniline is an insulator unless it is oxidized, with protic acids allowing for tuning the degree of conductivity of the material to levels as high as 10^{-2} to 100 S cm^{-1} [9,10]. This tunability of the characteristics makes polyaniline of interest in many different applications including in electronic devices, batteries, solar cells, anti-static building materials, electric heaters, and even filtration of heavy metals [11,12].

The foams are an insulating material in the range of 10^{-16}–10^{-12} S cm^{-1}. Anti-static and static-dissipating materials are those with conductivities in the range of 10^{-11}–10^{-6} S cm^{-1} which allow movement of electrons from higher to lower charge densities, inhibiting the delivery of a spark or shock. In addition to this anti-static activity, ICPs are useful in protecting against electromagnetic radiation. The materials used for this application are currently petroleum based matrices with high levels of ICP particles in them for use in panels and thick coatings. The goal with producing foams modified to be semi-conducting would be to replace these dense petroleum based materials with a lighter renewable based material that has similar or better protection abilities.

Other types of conductively functional foams being developed include those containing graphite and carbon nanotubes, however these conductive fillers are often added to petroleum derived

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polymer matrices and sufficient dispersion of the particles within the matrix is a common problem [13–15].

Adsorption of polyaniline (PANI) particles throughout the structure of the foam may be possible if the aqueous monomer solution is able to swell the foams since the reaction proceeds slowly at low temperatures, with the polyaniline particles precipitating out of solution, filling in pores of the material [16–20]. If not, an interior coating may suitable to cause bulk semi-conducting properties. The structure of the foams provides a three dimensional template that is lightweight yet has mechanical strength even in the presence of water.

The aim of this research is to determine if furan based foams can be made to be semi-conductive with this method of in-situ polymerization of polyaniline. Further, the modification of furan based foams with polyaniline is evaluated.

2. Materials and methods

2.1. Materials

The aniline (≥99.5% purity), phosphoric acid (85 wt% in H_2O, 99.9% trace metal basis), and peroxydisulfate (≥98.0%) were all used as received from Sigma Aldrich. Mimosa (Acacia Mearnsii) tannin extracts were received from Silva Chimica (Italy), while formaldehyde, diethyl ether, furfuryl alcohol, and para-toluene sulfonic acid were used as received from Sigma Aldrich.

2.2. Preparation of the foams

The preparation of the foams was as follows: 15 g tannin, 5.2 g furfuryl alcohol, 3.2 g formaldehyde, 3 g H_2O, 1.5 g diethyl ether, 5.5 g 65 wt% aqueous solution of pTSA. The furfuryl alcohol, formaldehyde, and water were mixed in a 200 ml beaker. The tannin was quickly added to the liquid mixture and stirred until homogeneous. Next the diethyl ether was added to the tannin mix, and stirred until homogeneous. Lastly, the 65 wt% aqueous pTSA solution was added and mixed to catalyze the reaction with acidity. The foam was then removed from the mold directly after it had hardened.

The polymer rich skin was then sawn off along with any large porous defects to form cubes. These cubes had varying dimension due to the inhomogeneity of the production method. These were dried for 16 h at 60 °C, with weights and dimensions taken before and after. The next day these were vacuum impregnated with a mixture of polyaniline. Dimensions were measured the next day after removing the foams from the polyaniline solution and compared to the dimensions measured before impregnation. The foams were then dried overnight at 60 °C. As a reference, three foam specimens were placed in water at pH 2, adjusted with phosphoric acid, for comparison to determine the weight loss.

2.3. In-situ polyaniline synthesis

The in-situ polyaniline formation required the preparation of an aqueous aniline monomer solution with 4.66 g aniline (0.2 M solution in 200 ml of water), 5.77 g of a phosphoric acid solution (85 wt%), and 14.26 g of ammonium peroxydisulphate. The aniline in water was at a concentration of 0.20 M phosphoric acid in 200 ml of water, with a (dopant)/aniline molar ratio of 1 and peroxydisulphate/aniline ratio of 1.25. These reactant ratios have been found to result in the emeraldine salt form of polyaniline with 50% of the emeraldine base protonated or oxidized [21] (Fig. 1).

The phosphoric acid was added to 225 ml of water, using a stir bar to mix the solution, next the aniline was added dropwise, mixing until the salt has dissolved. The solution was then chilled with an ice bath down to 0 °C. In a separate beaker, ammonium peroxydisulfate was added to 25 ml of water and mixed until dissolved. This solution was then also chilled in an ice bath. The dried foam samples were added to the desiccator in an ice bath, and weighed down. The two reactant solutions were then added together, and then added to the foam samples. A vacuum was pulled for around 3 min, when the aniline solution began to change from transparent to cloudy. The first hour, the solutions were kept at 0 °C and then room temperature for the remaining time. The solutions were then left to sit for 16 h. The samples were then taken out of the treatment solution, the dimensions and weight taken in order to determine the degree of swelling of the foams, and dried at 60 °C for 16 h.

2.3.1. Polymer weight percent gain (WPG), bulking of the foam structure, equilibrium water content, moisture content, and leaching evaluation

The uptake of polyaniline was calculated by taking the weight of the dry samples and then gravimetrically calculating the weight gained in the samples removed from the oven after treatment. The volume change of the foams with the addition of PANI was calculated by comparing the dimensions of the samples, measured with a slide-calliper at midpoints of each sample, in the dried state, both before and after modification. The equilibrium water content and volume change of the specimens after being in the impregnation solutions was calculated by comparing the measured values before and after impregnation. Once modified, the foams were conditioned at three different relative humidities (RH). Each micro-environment was created inside a desiccator, where a solution of deionized water and salts was placed together with a control moisture meter (hygrometer). Silica gel was used to create a 0% RH environment; sodium nitrite ($NaNO_2$) for 66% RH; and copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) for 98% RH.

The density was measured for each RH condition. To calculate the moisture content (MC), formula (1) was used.

$$(\%)\mathrm{MC} - \left(\frac{W_w - W_d}{W_d}\right) \times 100 \quad (1)$$

The initial weight is that of the conditioned state, (wet weight, W_w) at each RH. The final weight being the dry weight (W_d) of the sample dried in an oven at 105 °C until reaching a constant mass.

Once conditioned, the moisture content (MC) of the foams was calculated.

Leaching of modified foam samples was performed in water for 4 h with initial vacuum evacuation. All measurements are reported as the average of five sample measurements.

2.4. Dynamic scanning calorimetry (DSC)

Experiments were performed on a DSC 820 equipped with a sample robot and a cryocooler (Mettler-Toledo). The DSC runs were carried out in closed sample pans sealed in air using the following temperature program: heating from 25 °C to 250 °C (50 °C min^{-1}), cooling from 100 °C to −30 °C (10 °C min^{-1}) and then heating up to 250 °C (10 °C min^{-1}). Isothermal segments of 5 min were performed at the close of each dynamic segment.

2.4.1. Thermal gravimetric analysis (TGA)

TGA measurements were performed to determine degradation temperatures and weight losses due to volatilization and degradation of the foams. The experiments were conducted on a TGA/SDTA 851e (Mettler-Toledo) with a sample robot. The TGA runs were carried out in nitrogen atmosphere (20 ml min^{-1}) heating the sample from 30 °C up to 600 °C (10 °C min^{-1}).

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