Preparation of Conductive Polypyrrole/Polyurethane Composite Foams by In situ Polymerization of Pyrrole

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Conductive composite foams were prepared by exposing iodine-loaded polyurethane (PU) foams to pyrrole vapor. The kinetics, equilibrium, and mechanism of the in situ polymerization of pyrrole by iodine within a PU foam was investigated. The dopant for the polypyrrole (PPy) was primarily I_3^-, which formed a charge-transfer complex (PPy-I_2) with the amine group of the PPy. The conductivity of the composite foams increased with increasing concentration of the PPy-I_2 complex and depended on the distribution of the PPy-I_2 complex in the PU matrix and the concentration ratio of PPy and iodine. The chemical structure, morphology, mechanical properties, and thermal stability of the composite foams were also characterized.

1. Introduction

Intrinsically, conductive polymers (ICPs) have been the focus of considerable research over the past several decades with foreseeable applications in products such as rechargeable batteries, bio- and chemical-sensors, transducers, antistatic coatings, and EMI shielding.[1,2] Polypyrrole (PPy) is one of the most stable conductive polymers due to its heterocyclic structure,[3] though neat PPy is an intractable, brittle solid, which restricts its direct application. One approach for exploiting the intrinsic electrical conductivity of PPy and overcoming its poor mechanical properties is to blend it with an insulating host polymer with better mechanical properties. Conductive blends may be prepared by impregnating the host polymer first with pyrrole and then with an oxidant, or by treating an oxidant-doped polymer with a pyrrole solution or vapor, which results in the in situ polymerization of pyrrole in the host polymer.[2,4] This process develops heterogeneous conductive composites in which the conductive PPy is dispersed in the host polymer. The rigid PPy molecules may also reinforce the host polymer. For example, Qian et al.[5] reported that the in situ polymerization of pyrrole in a polymer matrix increased the tensile modulus and strength of the host polymer.

Many conductive composites have been prepared by in situ polymerization.[4,6–8] A variation on the composite theme is to use polymer foams as the polymer matrix to prepare porous conductive materials. The mechanical properties of foams depend on the mechanical properties of the strut material that comprises the foam, as well as the geometry and topology of the foam cells. The porous structure of an open-cell foam may improve the efficiency of in situ polymerization of pyrrole by facilitating the diffusion of monomer and oxidant into polymer matrix due to the greater surface area of the polymer phase in the foam.

Conductive foams may have mechanical advantages over conductive bulk polymers. ICPs are usually stiff and brittle and incorporating them into another polymer matrix often embrittles the host polymer. In a conductive foam, the ICP will stiffen the struts of the foam, but the composite foam itself will still be pliable, and the modulus of the composite can be controlled to some extent by varying the foam density. In addition, a foam allows for flow-through sampling, which is advantageous for applications as chemical sensors in that a more representative sample of a vapor or liquid can be analyzed. And sensors prepared from flow-through foams will generally have more surface area in contact with the sample stream than a solid sensor, which should improve sensitivity. The application of the foams described herein as sensors for volatile organic compounds (VOCs) will be discussed in a future publication.

We previously reported the synthesis of conductive polyurethane (PU) foams by diffusing a methanol solution of $FeCl_3$ into the PU foam and then exposing the PU/oxidant composite to pyrrole vapor.[9] The electrical conductivity of

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the PPy/PU composite foams ranged from 1×10^{-1} to 1×10^{-7} S/cm, depending on the amount of oxidant used. A deficiency of that process, however, was that rather large quantities of methanol, a "volatile organic compound" (VOC), were used to introduce the oxidant into the PU foam and remove unreacted oxidant and redox byproduct. In more recent work, we showed that organic solvents could be eliminated by replacing methanol with supercritical carbon dioxide[10] ($scCO_2$) or a mixture of $scCO_2$ and ethanol.[11] That approach, however, necessitated the synthesis of CO_2-phillic, fluorinated metal carboxylate and sulfonate oxidants, and solubility of those compounds was generally low.[11] Electron acceptors such as halogens can be used to replace organometallic oxidants for in situ polymerization of pyrrole in PU foams. Electron acceptors have long been used as dopants for polyacetylene.[12] Kang[13] et al. used halogens in an organic solvent to polymerize and dope PPy. The PPy−halogen complexes were relatively stable in air and exhibited conductivities ranging from 1×10^{-5} to 5 S/cm. Most recently, we described a solvent-free process to prepare conductive PU foams.[14] Iodine readily sublimes, thus allowing for the impregnation of PU foams with iodine vapor, and the iodine vapor condenses within the foam and diffuses into the PU matrix, which can then be exposed to pyrrole vapor to initiate polymerization.

In the current study, a PU open-cell foam of lower density than those we have previously reported was used as the host polymer. Pyrrole and iodine were used as monomer and oxidant, respectively. Both iodine sublimation and iodine solution processes were used to impregnate PU foams with iodine. The iodine impregnation process depends upon the formation of a charge-transfer complex between iodine and PU, which is described elsewhere.[15] In this paper, conductive composite foams were prepared by exposing iodine-loaded PU foams to pyrrole vapor. The kinetics, equilibrium, and mechanism of the in situ polymerization of pyrrole by iodine were investigated, and the factors affecting conductivity were analyzed. The chemical structure, morphology, mechanical properties, and thermal stability of the composite foams, and the relationships between these factors were also characterized.

2. Experimental Section

2.1. Materials. Polyurethane (PU) foams with a density of 0.045 g/cm^3 were obtained from McMaster-Carr Supply Company. The PU foams were lightly cross-linked elastomers made from 2,6-toluene diisocyanate (TDI) and polyether polyols. The foams were white, skin-free, and had open-cell structures. The foam sample was cut to a size of $2.54 \times 2.54 \times 1.27$ cm^3 and extracted with acetone before use. The extraction was done to remove any additives to the foam that may be subsequently extracted during the procedures used for preparing the conductive foams. That removed any ambiguity from the mass balances used to determine iodine absorption and the amount of conductive polymer produced. Acetone extracted less than 10 wt % of the foam and subsequent extractions with methanol did not remove any additional mass. Pyrrole (99%) and iodine (p.a.) from ACROS and silver nitrate (p.a.) from Aldrich were used as received. Reagent grade acetone, methanol, chloroform, toluene, hexane, and dimethylformamide (DMF) were used as received.

2.2. Iodine Impregnation. Foam samples were impregnated with iodine by using either an iodine sublimation process or iodine/methanol solutions. For the iodine sublimation process, foam samples were placed in a desiccator containing iodine at 70 °C, taking care not to allow contact between the foams and the iodine crystals. After a specified sorption time, the foams were removed from the desiccator and weighed. For iodine/methanol solution process, each foam sample was immersed in a 50 mL iodine/methanol solution of fixed concentration for ca. 2 h to swell the foam and allow iodine to diffuse into the foam. The sample was then removed from the solution and squeezed to remove solvent. The sample was then dried for ca. 1 h to evaporate any remaining solvent and weighed. The iodine solution process was carried out at room temperature and atmospheric pressure. The iodine concentration in the foam was calculated as weight percent (wt %) on the basis of the mass of the original neat foam. The foams described below were prepared using iodine sublimation process, unless otherwise stated.

2.3. In situ Oxidative Polymerization. An iodine-loaded PU foam sample was placed in a jar with a small beaker containing pyrrole liquid or pyrrole solution at the center. The polymerization temperature was controlled by placing the jar in a convection oven. Three reaction conditions were investigated using (1) pyrrole liquid at 40 °C, (2) pyrrole liquid at 60 °C, and (3) a pyrrole/methanol (v/v = 2/1) solution at 60 °C. These conditions are hereafter referred to as Py-40, Py-60, and Py-MeOH-60, respectively. The default polymerization condition was Py-40 if not otherwise stated. The jar was saturated with pyrrole vapor at each condition, and the in situ polymerization of pyrrole by iodine occurred when the iodine-loaded PU foam was exposed to pyrrole vapor. After a specified polymerization time, the resultant PPy/PU composite foam was transferred to a fume hood to allow any unreacted pyrrole to desorb and evaporate from the foam until a constant mass was achieved.

Solvent Extraction of the Composite Foams. The composite foams were extracted with methanol, chloroform, toluene, and hexanes at room temperature. Some dark colored material was extracted from the foams. For each solvent, the extraction was repeated until no additional material dissolved, which was determined when the extract solution remained colorless. A black solid residue was obtained after evaporating the solvent from the extract. The dry mass of the composite foam was determined after thorough drying of the extracted foam.

Materials Characterization. DC conductivity of the composite foams was measured at ambient conditions by a conventional four-point probe method. The morphology of the composite foams was characterized with a JEOL JSM-6335F field-emission scanning electron microscope (SEM) on samples fractured after immersion in liquid nitrogen. A Micrometrics ASAP 2010 accelerated surface area system was used for nitrogen sorption measurements. The experiments were done at 77 K after initially degassing the sample at 100 °C for 2 h. The specific surface area of the samples was determined by the Brunauer–Emmett–Teller (BET) method.

Thermal stability of the composite foams was measured with a TA Instruments thermogravimetric analyzer, TGA-2950, using a

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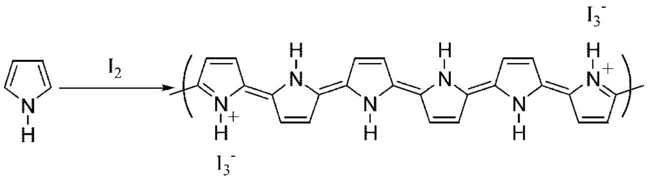

Figure 1. Chemical oxidative polymerization of pyrrole by iodine.

nitrogen atmosphere and a heating rate of 20 °C/min. Compression tests were performed with an Instron model 1011 Universal Testing Machine using a 4.5, 9.1, 22.7, or 45.4 kg load cell and a crosshead speed of 0.635 cm/min.

A Perkin-Elmer Lambda 900 UV spectrometer was used for UV/vis measurements. Fourier transform infrared (FTIR) spectra were obtained with a Nicolet Magna-IR 560 FTIR spectrometer by signal averaging a total of 128 scans. Thin films samples were prepared by casting a solution onto a KBr disk. Powder samples were mixed with KBr powder and the “mull” was pressed into a film.

Results and Discussion

Oxidative Polymerization of Pyrrole by Iodine. As depicted in Figure 1, iodine was the oxidant for the pyrrole polymerization, and after polymerization it provided the charge compensating dopant ions for the conductive PPy, which were principally triiodide.[16–18] The black solid mass extracted from the product contained no free iodine, because it did not react with wet starch/iodide paper. Therefore, it is reasonable to assume that all the iodine used remained in the product foam and complexed with the PPy. The PPy-dopant complex[19,20] is denoted as PPy-I_2, and its mass was taken as the difference between the masses of the composite foam and the original neat PU foam, and the complex concentration was based on the original mass of the PU foam

$$\text{wt \% PPy-I}_2 = (\text{mass of PPy-I}_2\text{ complex/mass of neat PU foam}) \times 100\% \quad (1)$$

The polymerization kinetics were studied for different polymerization conditions, iodine impregnation processes and initial iodine concentrations. The vapor pressures of pyrrole at 40 and 60 °C were 2.69 and 7.55 kPa, respectively, and the vapor pressure of methanol at 60 °C was 84.0 kPa. The partial pressure of pyrrole for the Py-MeOH-60 reaction condition was calculated to be 4.07 kPa using Raoult’s law, so the vapor pressures of pyrrole for the Py-40, Py-MeOH-60, and Py-60 conditions were 2.69 kPa, 4.07 kPa, and 7.55 kPa, respectively. Higher pyrrole vapor pressure produced higher pyrrole concentration in the PU matrix.

Both the iodine sublimation and iodine/methanol solution processes were evaluated as the iodine impregnation step. Figure 2 shows an example where both processes produced similar iodine concentrations and similar polymerization kinetics were observed when the Py-40 condition was used to produce PPy. Pyrrole readily swelled the PU foams. At room temperature, the swelling of a PU foam in liquid pyrrole achieved equilibrium very rapidly, but pyrrole vapor took about 5 h to achieve an equilibrium swelling as judged by visual observation of the foam during the polymerization. The pyrrole polymerization kinetics was relatively slow and completion of the reaction equilibrium took about 40 h.

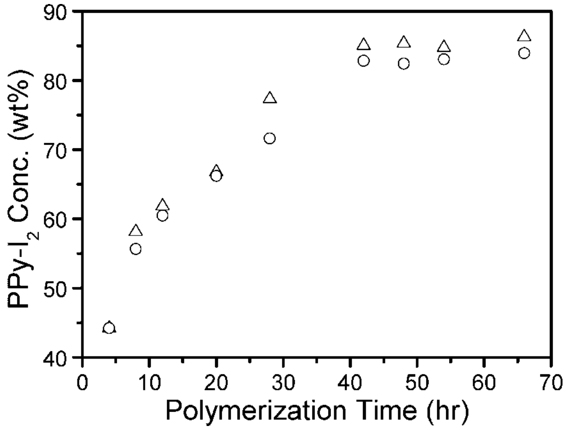

Figure 2. PPy-I_2 complex concentration as a function of polymerization time in Py-40 condition: (*o*) PU foams impregnated with 36.2 ± 1.5 wt % iodine by iodine sublimation, (Δ) PU foams impregnated with 37.1 ± 1.5 wt % iodine by iodine/methanol solutions. Each data point represents an individual polymerization.

To calculate the polymerization kinetics, it was necessary to assume that no iodine evaporated from the foam during the polymerization, or when the product was obtained before completion of the reaction, and that all unreacted pyrrole evaporated from the product. If the assumption concerning the iodine is correct, any excess iodine remaining in the foam could be used latter to polymerize more pyrrole. The assumptions for the residual iodine and pyrrole allow one to calculate the amount of PPy formed from a mass balance on the PPy-I_2 complex. The initial iodine concentration varied from ca. 16 wt % to ca. 60 wt % in these studies. The ratio of the PPy concentration [PPy] and the initial iodine concentration $[I_2]_0$ is plotted against polymerization time in Figure 3 for the Py-40 condition. The data for different initial iodine concentrations superposed and increased exponentially with polymerization time. This implies first-order kinetics with respect to $[I_2]$ as shown in eq 2, where k is the rate constant and x is the order of reaction with respect to [pyrrole]. Because [pyrrole] was kept relatively constant and in excess by the large reservoir of pyrrole used in the polymerization vessel, $k[\text{pyrrole}]^x$ was defined as a new constant k'. Integrating eq 2 gives eq 3. The ratio between the amount of PPy formed and the amount of iodine consumed in polymerization is a constant, c, which provides eq 4. Combining eqs 3 and 4 leads to eq 5.

$$\frac{d[I_2]}{dt} = -k[\text{pyrrole}]^x[I_2] \quad (2)$$

$$[I_2]_t = [I_2]_0 e^{-k't} \quad (3)$$

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$$[\mathrm{PPy}] = c([\mathrm{I}_2]_0 - [\mathrm{I}_2]_t) \qquad (4)$$

$$\frac{[\mathrm{PPy}]}{[\mathrm{I}_2]_0} = c(1 - e^{-k't}) \qquad (5)$$

The solid curve in Figure 3 represents the least-squares fit of eq 5 to the experimental data in Figure 3.

The validity of the assumption concerning the retention of unreacted iodine in the foam, even after drying the sample and storing it at ambient conditions, was confirmed by exposing some of the samples used to prepare Figure 3 to fresh pyrrole. Those experiments are denoted by the four composite foams represented by the symbol Δ. These four samples were first exposed to pyrrole vapor for 6, 14, 24, and 36 h, respectively, and then transferred to a fume hood to allow for the unreacted pyrrole to evaporate until a constant mass was achieved. After that, the four composite foams were exposed to pyrrole vapor again to achieve a total overall polymerization time of 60 h for each. Additional polymerization did occur, and the final amount of PPy formed in each case was close to the value that would be expected if the initial pyrrole polymerization had been run for 60 h. This result supports the assumption that excess iodine remained in the foam during drying and storage at ambient conditions, and it is capable of polymerizing more pyrrole at a later time.

The $[\mathrm{PPy}]/[\mathrm{I}_2]_0$ ratio is plotted against polymerization time in Figure 4 for all three polymerization conditions. The reaction rate increased with increasing pyrrole vapor pressure (see Table 1), in the order of Py-40 < Py-MeOH-60 < Py-60. The values of the constants, *c* and *k*′, for each reaction condition were determined from the least-squares fit of eq 5 to the data in Figure 4, and these values are listed in Table 1. The values of the rate constant, *k*′, and the prefactor, *c*, increased as the vapor pressure (or concentration) of pyrrole increased. Equation 5 indicates that the equilibrium concentration of PPy is a linear function of the initial iodine concentration (provided that the pyrrole concentration during the reaction remained constant), and this is confirmed by Figure 5. As shown in Figure 4, the polymerization reaction was essentially complete after 40 h. The data in Figure 5 were collected from polymerization reactions run for a fixed time of 48 h. In this study, a polymerization time of 48 h was employed to achieve equilibrium unless stated otherwise.

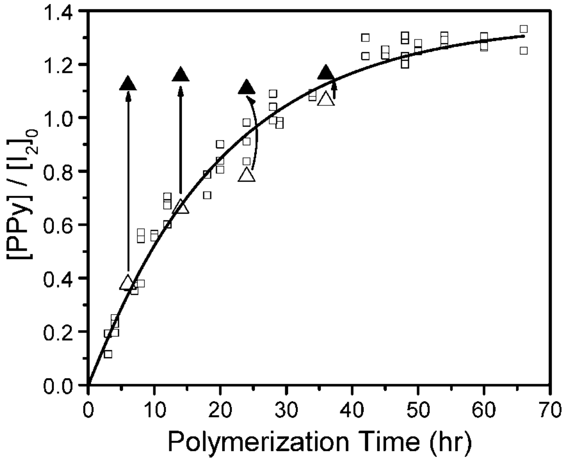

Figure 3. Ratio between PPy concentration and initial iodine concentration as a function of polymerization time for Py-40 condition: (■ and Δ) composite foams prepared after a single pyrrole vapor exposure period, (▲) composite foams prepared by re-exposing the composite foams represented by Δ to pyrrole vapor to achieve a 60 h overall polymerization time. The same composite foam before and after the second polymerization period is related by an arrow. The solid curve is the least-squares fit of eq 5 to the (■ and Δ) data.

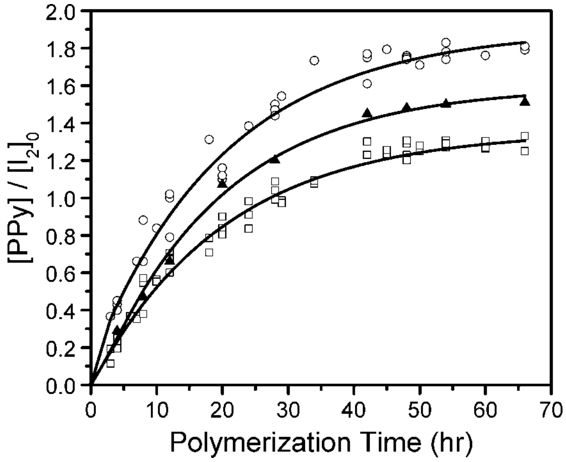

Figure 4. Ratio between PPy concentration and initial iodine concentration as a function of polymerization time for three polymerization conditions: (■) Py-40, (▲) Py-MeOH-60, and (*o*) Py-60. Each data point represents an individual polymerization. The curves are the least-squares fit of eq 5.

Table 1. Estimated Values of *c* and *k*′ from eq 5

polymeriztion condition	Py-40	Py-MeOH-60	Py-60
P^{vap} (kPa)	2.69	4.07	7.55
c	1.37	1.65	1.84
k' (h^{-1})	0.0489	0.0509	0.0610

The mechanism of electrochemical pyrrole polymerization is widely accepted to entail oxidative coupling of monomers.[22,23] A pyrrole molecule is first oxidized to form a radical cation, which then reacts with another radical cation to produce a neutral dimer by eliminating two protons. The dimer participates in the same reactions in a stepwise manner. If the oxidative coupling mechanism also applies to chemical polymerization of pyrrole, more than two moles of oxidant are needed to polymerize one mole of pyrrole. It has been proposed that the majority of chemical polymerizations of pyrrole are additional reactions.[24–26] After initial radical cation generation, rather than radical–radical coupling, the radical cations attack the monomers and generate dimer radical cations. The polymer chains propagate in this fashion until termination. But, there is little experimental evidence for the addition mechanism because of the low solubility of PPy and the intermediate products. In this study, the ratios between pyrrole repeat units and iodine molecules in the PPy-I_2 complex were 4.6 and 6.6 at 40 and 60 °C, respectively,

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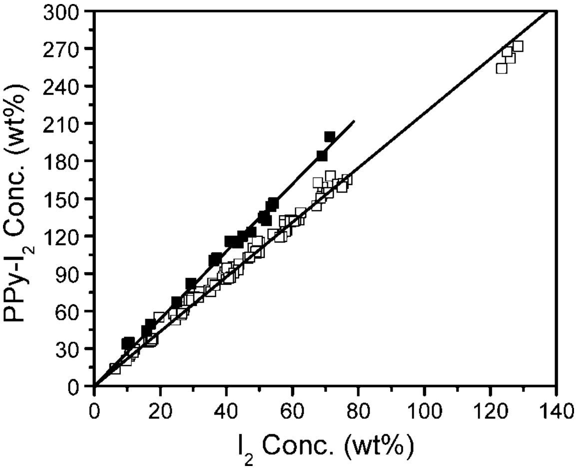

Figure 5. Equilibrium PPy-I_2 complex concentration versus initial iodine concentration in (■) Py-40 and (□) Py-60 conditions.

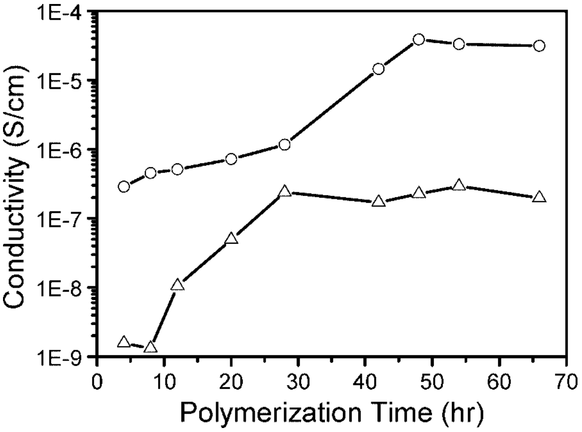

Figure 6. Conductivity of the composite foams as a function of polymerization time for Py-40 condition: (*o*) PU foams impregnated with 36.2 ± 1.5 wt % iodine by iodine sublimation, (Δ) PU foams impregnated with 37.1 ± 1.5 wt % iodine by iodine/methanol solutions.

based on the data in Figure 5. A ratio of 4 was previously reported by Kang et al.[13] Based on XPS studies, Kang et al. concluded that the electron acceptor in the PPy-I_2 complex was primarily I_3^-, which means that only a portion of iodine acts as the oxidant for the pyrrole polymerization. The addition polymerization mechanism is more consistent with the experimental values for the stoichiometry of 4–6.

Conductivity and Morphology of the Composite Foams. Figure 6 shows electrical conductivity of the composite foams as a function of polymerization time for the Py-40 condition. The PU foams were impregnated with 36.2 ± 1.5 wt % iodine by iodine sublimation or with 37.1 ± 1.5 wt % iodine using iodine/methanol solutions. The neat PU foam is a dielectric material, and the conductivity of the composite foams is developed by percolation, i.e., when the PPy-I_2 concentration increases above a critical threshold value.[9] Although the polymerization kinetics data for the two cases were nearly identical, see Figure 2, the conductivity of the composite foam was significantly higher when the iodine was introduced as a vapor (sublimation process) than when introduced by a liquid solution. Our previous study,[15] however, indicated that the iodine sublimation process produced a more heterogeneous iodine distribution in the PU matrix, with higher concentrations of iodine near the surface. The iodine solution process produced a more homogeneous iodine distribution. Because the four-point probe method for conductivity measurement preferentially weights the surface conductivity for heterogeneous materials, the conductivity differences observed after polymerization are probably also due to differences in the iodine distribution that occurred during the two iodine impregnation methods.

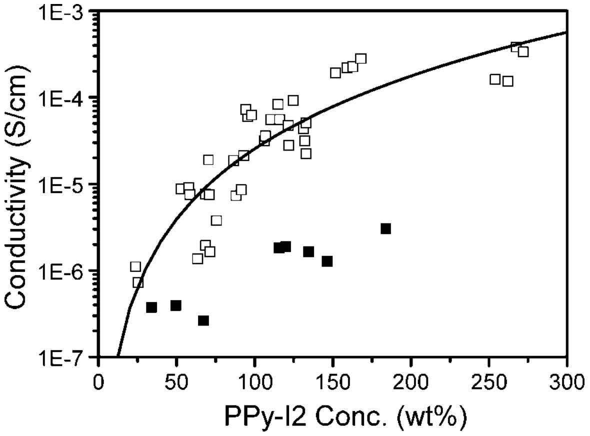

Figure 7. Conductivity of the composite foams versus equilibrium PPy-I_2 complex concentration in (■) Py-40 and (□) Py-60 conditions.

Figure 7 plots the electrical conductivity of the composite foams as a function of the PPy-I_2 complex concentration for the Py-40 and Py-60 polymerization conditions using the iodine sublimation to add the oxidant. For Py-40 condition, conductivity of the composite foams increased from ~1 × 10^{-6} to ~3 × 10^{-4} S/cm as the PPy-I_2 concentration increased from ca. 25 to ca. 270 wt %. Within that concentration range, the conductivity followed a power law relationship,

$$\text{Log}(\sigma) = -6.63 + 0.28c^{0.43} \tag{6}$$

where σ is the conductivity in S/cm and c is the PPy-I_2concentration in wt %. The conductivity achieved with these foams was considerably lower than that achieved with higher density foams used in our previous studies at similar PPy-I_2 concentrations.[9–11,14] This is believed to be related to the effect of foam density on the integrity of percolated network - that is, the higher polymer density provided a less tortuous continuous pathway through the foam. The relatively few experiments run at the Py-60 condition did not provide suitable statistics for determining a power law fit of those data. However, for similar PPy-I_2 concentrations, the conductivity of the composite foams prepared by Py-60 condition was considerably lower than that achieved by Py-40 condition. The ratio between pyrrole repeat units and iodine molecules for Py-60 condition (6.6) was higher than that for Py-40 condition (4.6), which might indicate a lower doping level, which would explain the lower conductivity. Alternatively, the higher polymerization temperature could have also introduced more defects in the conjugation of the PPy formed.

The temperature dependence of the electrical resistance between −15 and 100 °C for the composite foams is shown in Figure 8. Log(R) exhibits a linear relationship with $T^{-1/4}$ for both samples, which agrees with the three-dimensional

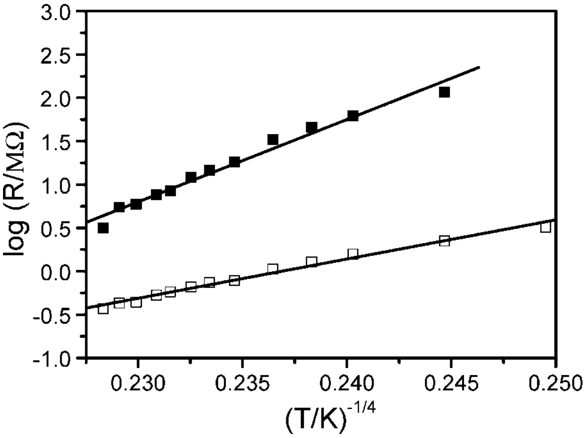

Figure 8. Temperature dependence of electrical resistance for composite foam samples with (■) 52.8 and (□) 35.9 wt % PPy-I_2.

variable range hopping (3D-VRH) model proposed by Mott[27] for conventional disordered semiconductors such as α-Ge. This model also works well for moderate temperatures and doping levels for intrinsically conductive polymers.[28–30]

The composite foams were black due to the PPy. Based on SEM studies, the in situ polymerization process did not affect the open-cell structure of the PU foams. The polymer strut surface in the PPy/PU foam was only slightly rougher than that in the neat PU foam and no PPy particles were observed, which indicates that the PPy resides within the struts and not on the surface. That observation is consistent with the nonmarking characteristics of the composite foams; that is, no black marks were observed when the foams were rubbed onto white paper. The specific surface area for the foams, measured by BET analysis, increased after the in situ pyrrole polymerization, e.g., about 20% for a composite foam containing 86% PPy-I_2.

Thermal and Mechanical Properties of the Composite Foams. In general, increasing the PPy-I_2 concentration changed the properties of the composite foams from elastomeric to ductile plasticlike and finally to brittle. At very high PPy-I_2 concentration (>180 wt %), the composite foam was so brittle that the foam crumbs broke off even with careful handling.

Figure 9 shows the compressive stress–strain curves for a neat PU foam and composite foams prepared from similar initial iodine concentration, but for different polymerization times. As the polymerization time increased, the concentration of PPy-I_2 increased, as indicated by the number associated with each curve. The curves are typical for polymer foams,[35–38] showing linear elastic behavior at low strains, followed by a plateau region characteristic of cell collapse, and a high strain regime of densification over which the stress rises steeply. In the initial linear region, the strain is mainly due to the elastic bending of the polymer struts, and the modulus of foam is determined by the modulus of the polymer phase. At higher strains, air cells collapse as the air is squeezed out of the open-cell structure to such an extent that struts interfere with one another. The resistance to further compression is mainly due to the polymer phase. Prior to total collapse of the air cells, the compression of foam is due to a combination of the bending of polymer struts and the compression of air cells. For the composite foams, as the PPy-I_2concentration increased, the yield point became more apparent and the yield strength increased. Above ~107 wt % PPy-I_2, the stress–strain curves exhibited a shoulder prior to the yield point, which may be due to local yielding.[38] That might be expected if the material was not homogeneous. The strain at which the densification started decreased with increasing PPy-I_2 concentration, which may be due to the swelling of the PU struts by PPy-I_2, which decreased the volume fraction of the air cells in the foam.[36]

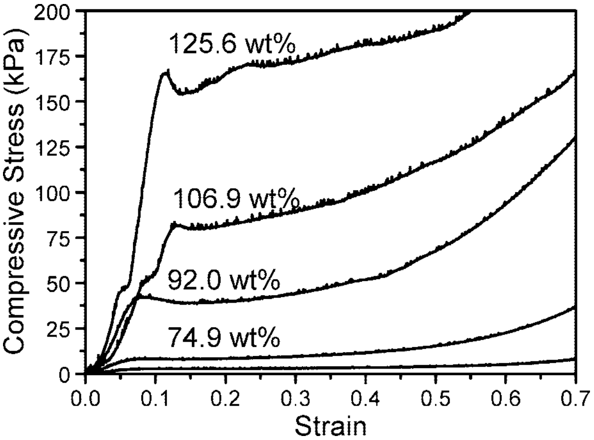

Figure 9. Compressive stress–strain curves of a neat PU foam (bottom one) and composite foams prepared in Py-40 condition with different polymerization times (7.5, 15, 30, and 48 h from bottom to top). The composite foams contained 53.8 ± 1.9 wt % iodine before polymerization. The number on each curve is the PPy-I_2 concentration.

TGA results for a neat PU foam and composite foams prepared from similar initial iodine concentrations but for different polymerization times are shown in Figure 10. The composite foams were less thermally stable than the neat PU foam at lower temperatures, but more stable at higher temperatures, see insets in Figure 10. The neat PU foam lost less than 1% mass at 200 °C and had less than 1% mass remaining at 600 °C. If we assume that the thermal stability of the PU was not affected by the pyrrole polymerization, the mass lost at 200 °C and the mass remaining at 600 °C for the composite foams must be due to the PPy and iodine. The higher thermal stability of composite foams at higher temperature was similar to the results from our previous

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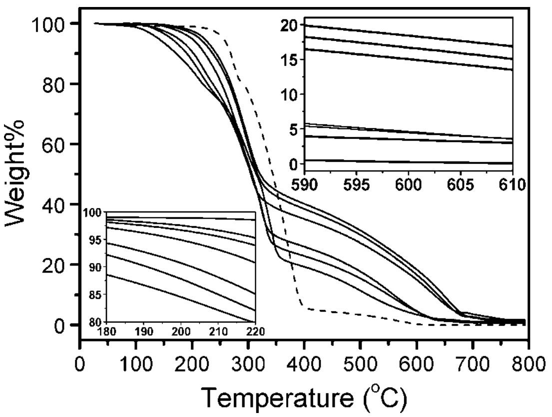

Figure 10. TGA of a neat PU foam (dashed line) and composite foams prepared in Py-40 condition with different polymerization times (solid lines). The composite foams contained 34.0 ± 1.3 wt % iodine before polymerization. The insets show the magnification of TGA curves around 200 and 600 °C. In the 200 °C inset, TGA curves from bottom to top are for the composite foams with 4, 8, 12, 28, 42, and 48 h polymerization time and the neat PU foam. In the 600 °C inset, TGA curves from bottom to top are for the neat PU foam and the composite foams with 4, 8, 12, 28, 42, and 48 h polymerization time.

study,[9,10] where pyrrole was polymerized by ferric chloride or ferric triflate in higher density PU foams, and can be attributed to the thermal stability of the PPy. The higher mass loss of the composite foams at lower temperature was probably due to unreacted iodine in the foams, which complexed with iodide from the redox reactions to serve as dopants for the PPy. Although the complexation was stable at room temperature (see earlier discussion), the iodine can be removed at relatively high temperatures,[39] in this case ~100 °C, according to Figure 10. As the polymerization time increased, the PPy production increased and less unreacted iodine remained. As a result, the mass loss between 100 and 300 °C decreased, see Figure 10.

Solvent Extraction of the Composite Foams. The extraction of material from the composite foams depended on the solvent used. The composite foams with 154.9 wt % PPy-I$_2$ were used for the extraction experiments. Methanol substantially swelled the composite foam and dissolved some dark-colored material, whereas hexanes barely swelled the composite foam and extracted no material. Chloroform swelled the foam and extracted material, but not as much as methanol did, and toluene swelled the foam slightly, but extracted very little material. The amount of PPy-I$_2$ remaining after extraction and the conductivity of the composite foams before and after extraction are summarized in Table 2, which also includes the dielectric constants, ϵ, of the solvents. Solvents with higher values of ϵ extracted more material, which was mainly PPy oligomers, evidence for which is discussed below. The decrease of conductivity of the composite foams as material was extracted is also consistent with the conclusion that PPy oligomers were dissolved by methanol and chloroform. In all cases, however, the conductivity before and after extraction were of the same order of magnitude, which implies that the extracted material did not contribute significantly to conductivity.

Table 2. Remaining PPy-I$_2$ Concentration and Conductivity Comparison of the Composite Foams (154.9 wt % equilibrium PPy-I$_2$ concentration) Extracted with Different Solvents

solvent	ϵ^a	remaining PPy-I$_2$ conc. (wt %)	conductivity (S/cm) before extraction	conductivity (S/cm) after extraction
methanol	33.0^{20}	92.8	7.19×10^{-4}	1.49×10^{-4}
chloroform	4.81^{20}	132.4	8.61×10^{-4}	1.94×10^{-4}
toluene	2.38^{23}	150.1	2.76×10^{-4}	2.85×10^{-4}
hexanes	1.89^{20}	154.9	NA	

[a] The superscript is the temperature at which ϵ was reported.

FTIR, UV/vis, TGA, and conductivity measurements were used to characterize the material extracted by each solvent. IR spectra of PPy reported in the literature are inconsistent because the structure of PPy depends on the polymerization conditions. The interpretations of the IR spectra are also sometimes contradictory.[40–47] The very small amount of material extracted by toluene did not produce a sufficiently high quality IR spectrum for making an identification. IR spectra of the materials extracted by methanol and chloroform are compared to that of pyrrole monomer in Figure 11. The two spectra of the extracted materials are similar, and most of the characteristic peaks of pyrrole were observed, confirming that the extract was, indeed, PPy. The peaks at 1378, 1424, 1469, and 1562 cm^{-1} are characteristic of the in-plane vibration of pyrrole ring, which indicates the ring structure was not affected by polymerization.[45] The strong peak between 700 and 800 cm^{-1}, characteristic of a five-membered aromatic ring,[43] was present for both pyrrole monomer and the extracted PPy, which again indicates the ring structure remained in PPy. One concern is that the N-H stretching peak between 3400 and 3450 cm^{-1}, which was present in the monomer spectrum and most PPy spectra reported in the literature, was not observed in the extracted materials. However, two strong peaks at 3288 and 2930 cm^{-1}, not present in pyrrole monomer, were observed. These were thought to be due to the N−H group, specifically one complexed with iodine. The complexation of iodine with a polyurethane causes a similar shift of the N−H stretching peak to a lower frequency.[48,49] To confirm this assignment, the PPy oligomers extracted by chloroform were dissolved in DMF and a silver nitrate aqueous solution was then added to the DMF solution until no more precipitate (silver iodide) was produced. This process removed most iodine from the PPy-I$_2$ complex, because of the low solubility of silver iodide in water (8.3×10^{-17} at 25 °C). The PPy

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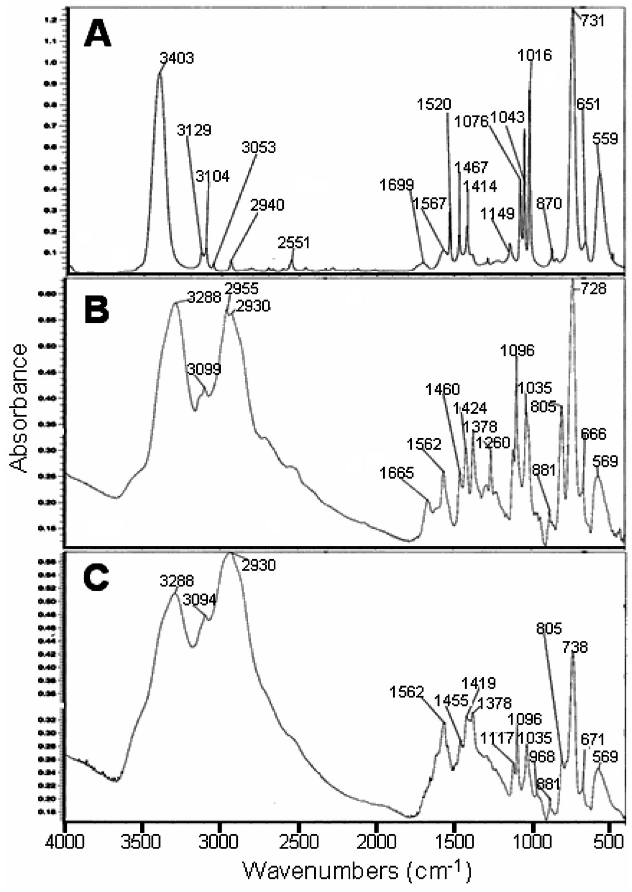

Figure 11. FTIR spectra of (A) pyrrole monomer and PPy oligomers extracted from composite foams by (B) chloroform and (C) methanol.

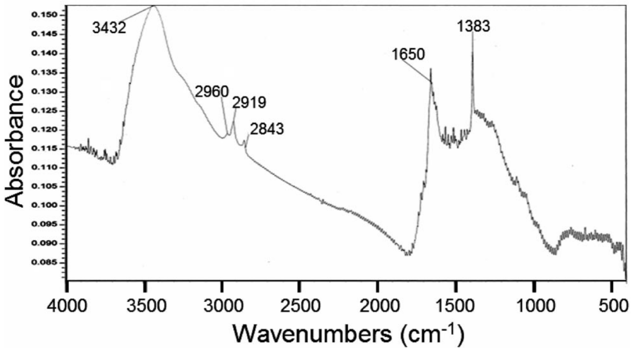

Figure 12. FTIR spectrum of the PPy oligomers without iodine dopants.

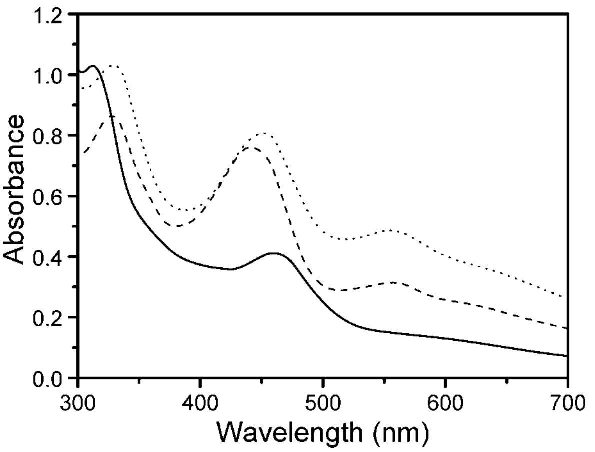

Figure 13. UV/vis spectra of PPy oligomers extracted from the composite foam by (—) toluene, (- -) chloroform, and (• • •) methanol.

oligomers remained dissolved in the DMF after filtering off the silver iodide, but precipitated as a black powder when the DMF solution was diluted with chloroform. IR spectrum of the PPy oligomers after removing the iodine dopant is shown in Figure 12. In this case, N−H stretching peak occurred at 3432 cm^{-1}, which is consistent with uncomplexed pyrrole. This result also confirms that iodine dopants complex with PPy through the amine groups.

UV/vis spectra of the PPy oligomers extracted by methanol, chloroform, and toluene are shown in Figure 13. The spectra in methanol and chloroform are very similar, and the three peaks at 330, 440 (chloroform) or 450 (methanol), and 560 nm correspond to PPy oligomers, PPy of higher molecular weight, and radical cations, respectively.[32,50–53] The spectra in toluene shows no peak at 560 nm, which was expected considering the low polarity of toluene. The two peaks at lower wavelength also appear at different positions compared with those in methanol and chloroform. An absorption at 800 nm, characteristic of dications,[51] was not observed for any of the three samples, probably because of the low molecular weight of the oligomers. Oligomers extracted by methanol had higher thermal stability, as measured by TGA, than those removed from chloroform and toluene, which most likely reflects their relative molecular weight (lower molecular weight being less stable). The electrical conductivity of the PPy oligomers was low, $<1 \times 10^{-8}$ S/cm.

Conclusions

PPy/PU composite foams can be prepared by first impregnating PU foams with iodine, followed by an in situ polymerization of pyrrole by iodine in PU matrix. The dopant for PPy is triiodide, which forms a charge-transfer complex (PPy-I_2) with the amine groups of PPy. The polymerization is a slow process. Completion of the polymerization takes about 40 h. The polymerization reaction is first-order with respect to iodine concentration. The initial iodine concentration in the impregnated foam, regardless of how the iodine is introduced, determines the equilibrium PPy-I_2 complex concentration. The stoichiometry of the PPy-I_2 complex indicates that the chemical PPy polymerization is an addition polymerization process.

The conductivity of composite foams increases with PPy-I_2 complex concentration, but also depends on the heterogeneity of distribution of the PPy-I_2 complex in the PU matrix and the ratio between PPy and iodine dopant. The composite foams remain open-cell structure after the

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in situ polymerization and the PPy is contained within the polymer phase of the PU foam. As a result, the foams are nonmarking.

The compression strength of the composite foams increases with PPy-I_2 complex concentration, due to reinforcement of the foam by PPy. The composite foams change from elastomeric to brittle as the PPy-I_2 complex concentration increases. The composite foams exhibit lower thermal stability at low temperature and higher thermal stability at high temperature with respect to the neat PU foam, which was due to loss of unreacted iodine at the low temperatures (>100 °C) and stability of PPy at the high temperatures (>300 °C), respectively. The composite foam contains a small amount of low molecular weight PPy that can be extracted with polar solvents, such as methanol and chloroform.

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