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SIMPLE METHOD FOR MASS PRODUCTION OF POLYPYRROLE/CARBON NANOTUBES HYBRID ARTIFICIAL MUSCLE

Marcelo R. dos Santos and Helinando P. de Oliveira*
Instituto de Pesquisa em Ciência dos Materiais, Universidade Federal do Vale do São Francisco, 48902-300 Juazeiro – BA, Brasil

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Large scale preparation of hybrid electrical actuators represents an important step for the production of low cost devices. Interfacial polymerization of polypyrrole in the presence of multi-walled carbon nanotubes represents a simple technique in which strong interaction between components is established, providing composite materials with potential applications as actuators due to the synergistic interaction between the individual components, i.e., fast response of carbon nanotubes, high strain of polypyrrole, and diversity in the available geometry of resulting samples.

Keywords: artificial muscles; polypyrrole; carbon nanotubes; composites.

INTRODUCTION

Electroactive actuators (or artificial muscles) are devices used in the conversion of electrical energy into mechanical work.[1,2] The principle of actuation is based on electrochemical reactions (doping/undoping process) induced by external electrical field, which results in a flux of ions from electrolyte to actuator (swelling) and from actuator to electrolyte (contraction).[2,3] The resulting strain depends on density of charge transferred to/from actuator, which corresponds to the variation in solvation sphere volume of the actuator.[4]

Soft materials (such as conducting polymers) and carbon nanotubes are prime candidates when considering high-strain properties and high-speed response, respectively, as necessary attributes of a composite.

Polypyrrole (PPy) is a prominent conducting polymer characterized by superior environmental stability, simple synthesis, low cost, high conductivity level, and high strain.[5] As a consequence, PPy has been used in the development of mechanical actuators such as microscopic valves, pumps, robots, membranes, and prototypes of artificial muscles.[2,4,6-9] The use of PPy in such processes is favored due to the strong dependence of oxidation state of PPy on external voltage, which results in conformational changes (bond length and bond angle) of polymeric chains.[7] As a consequence, ions from neighboring electrolyte are incorporated into the polymer in order to maintain charge neutrality. Based on the direction of ionic flux, the structure swells or contracts as a response to oxidation state.[4] Despite the advantages associated with the high porosity of PPy, its conductivity is greatly affected on reduction (decreases by 2–3 orders of magnitude)[9]; therefore, PPy is considered to be low speed material, due to the relationship between conformational changes and diffusion of ions from electrolyte. The results reported for PPy-based mechanical actuators indicate a maximal strain of 39%, stress in the range from 22 MPa to 34 MPa, strain rate of 11% s^{-1},[10] and electrochemical linear actuation strain of 0.54%.[11] Advanced PPy-based trilayer device (PPy/porous membrane/PPy), with an active length of 35 mm, presents a periodic maximum tip deflection of 11 mm,[7] which corresponds to maximum tip deflection angle of 17.4°.

Meanwhile, when used as mechanical actuators, carbon nanotubes are characterized by fast responses associated with small strains. Production of inter-penetrating material,[11] multi-layer laminated configuration,[8] hybrid materials with metal nanoparticles, and polymer fibers[3,12] represent interesting strategies developed to circumvent limitations of the individual components and to improve the response of mechanical actuators. Composites have been intensely studied due to their multi-functionality and improved physical properties, as a result of synergistic interaction between components.[13] The fabrication of three-dimensional structures based on one-dimensional templates facilitates the improvement of surface area,[14] conductivity, and mechanical response. Similar efforts towards direct polymerization of conducting polymers (CP) on multi-walled carbon nanotubes (MWCNT) can generate promising composites for use as actuators.

As a result of strong interaction between carbon nanotubes and NH groups of PPy, homogeneous interaction between PPy and MWCNT is typically obtained on polymerization of pyrrole in the presence of MWCNT.[15] Chemical and electrochemical procedures along with the different parameters, such as polymerization conditions, type of electrolyte, and additives needed, have been established for the production of composites.[6,16] The coating of PPy on the surface of nanotubes represents a critical requirement for providing superior electrical response and high level of porosity. As a result, specific applications of these composite materials, such as in mechanical actuators, field emission devices, supercapacitors, batteries, and sensing devices, are favored.[5,13,17]

Due to the low solubility of PPy in common organic solvents, electrochemical synthesis is typically used for the production of hybrid actuators. However, large-scale production is limited due to the restriction of electrode dimensions used for deposition. We have circumvented this limitation by using interfacial polymerization for the large-scale preparation of materials with high-conductivity for use as mechanical actuators.

Interfacial polymerization is a method for chemical synthesis of conducting polymers wherein a dispersion of oxidant and monomers is established at the interface between water and oil phases. As a consequence, the polymerization is controlled by diffusion of components at interface. The resulting electroactive composite is used as an external actuator[2] (material is partially immersed in the electrolyte, i.e., aqueous solution of NaCl or KCl (1 mol L^{-1})) and mechanical motion results from the response of the composite to redox reactions and regular flux of ions from solution to the bulk of sample.

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*e-mail: helinando.oliveira@univasf.edu.br

EXPERIMENTAL

Materials and methods

Multi-walled carbon nanotubes and ferric chloride (Aldrich), and chloroform (Vetec) were used as received, while pyrrole (Aldrich) was distilled before use in the polymerization reaction.

Composites with different relative concentrations of pyrrole (0.4–0.8 mL) and MWCNT (0–1.5 mg) were synthesized. Best results for the application of the synthesized composite as mechanical actuators were obtained when 1.5 mg of MWCNT in water (15 mL) in the presence of ferric chloride (300 mg) was added to a dispersion of pyrrole (0.8 mL) in chloroform (15 mL).

The aqueous solution was slowly added dropwise to the chloroform solution and a two-phase structure was established, as shown in Figure 1a. After 24 hours (at rest) a thick film was observed at the interface (see Figure 1b). The resulting free-standing black film was carefully removed from the interface and dried in an oven at 60 °C for 24 hours. The thickness of films varied from 60 μm to 200 μm and its reasonable level of porosity was easily identified.

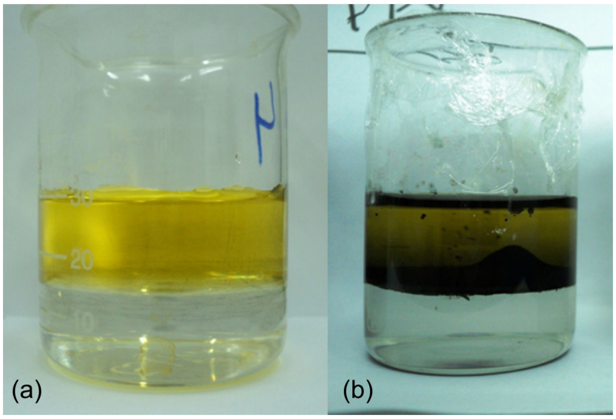

Figure 1. *Two phase system before (a) and after (b) polymerization (24-hour period)*

Scanning Electron Microscopy images were obtained using a SEM Vega 3XMU while differential scanning calorimeter curves (DSC-60 Shimadzu), FTIR spectra (IR Prestige-21; Fourier transform infrared spectrometer, Shimadzu), and impedance spectroscopy (Solartron 1260) were recorded to quantify the interaction between the components in the synthesized composite samples. Electrical responses of samples were analyzed in the absence of electrolyte with disposition of the composites (discs; diameter, 10 mm) as the dielectric between gold electrodes. An AC voltage (with no bias) of 100 mV was applied during EIS experiments.

Deformation profiles were recorded visually after the application of electrical stimulus with a Stanford Wave Generator model DS345.

RESULTS AND DISCUSSION

A high degree of rugosity, wherein the micrometer-sized wells are filled with nanometer-sized fibers, is observed for the surface of the synthesized PPy-MWCNT composite. These features are shown in Figures 2 and 3, wherein images at different magnifications identify the presence of fibrilar aggregates inside the surface cavities of the prepared composite.

High degree of rugosity, as identified in the SEM images, is associated with increase in the surface area, i.e., increased number of available sites for ion exchange, in the resulting device, and subsequently elevation in the degree of its dilation.

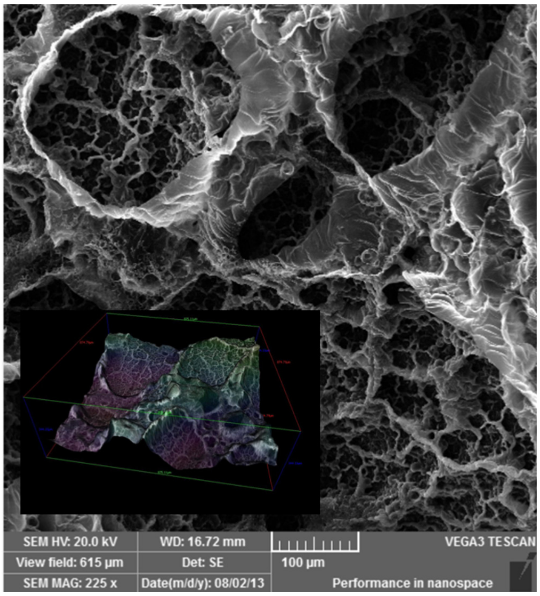

Figure 2. *SEM of surface of the synthesized composite PPy+MWCNT (inset: 3D view of the sample)*

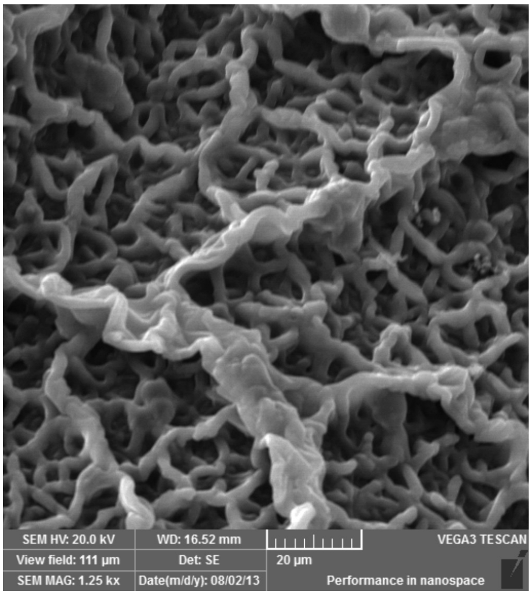

Figure 3. *SEM image of fibers inside the microscopic cavities*

FTIR spectra of PPy and PPy+MWCNT samples are shown in Figure 4. Characteristic peaks at 784 cm^{-1} and 1187 cm^{-1}, assigned to pyrrole ring vibrations,[18] and at 1547 cm^{-1}, assigned to C=C and C-C stretching bends, indicate the presence of PPy in the synthesized films. The inclusion of MWCNT in the composite is identified by the observed shift in the characteristic peaks to lower wavenumbers, such as from 1547 cm^{-1} to 1540 cm^{-1}; this establishes the presence of interaction between MWCNT and PPy during chemical polymerization.

The influence of MWCNT on the composite can be identified from the elevation of melting temperature from 78.06 °C (for neat PPy) to 88.65 °C (for the PPy+MWCNT composite). This elevation of melting point is associated with an increase in the enthalpy of fusion of the PPy+MWCNT composite and indicates the increasing crystalline nature of the composite (Figure 5).

Furthermore, the inclusion of MWCNT in the composite contributes to the improvement in its response to electrical stimuli, as detected by electrical impedance spectroscopy (see Figure 6). The inclusion of MWCNT in the composite results in the reduction in the

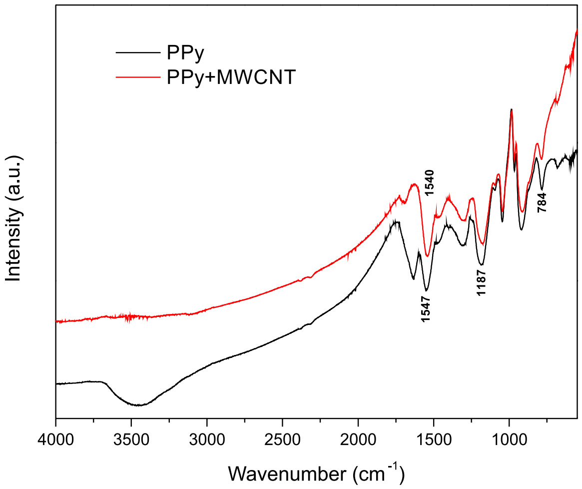

Figure 4. *FTIR spectra of polypyrrole (PPy) and PPy+MWCNT actuators*

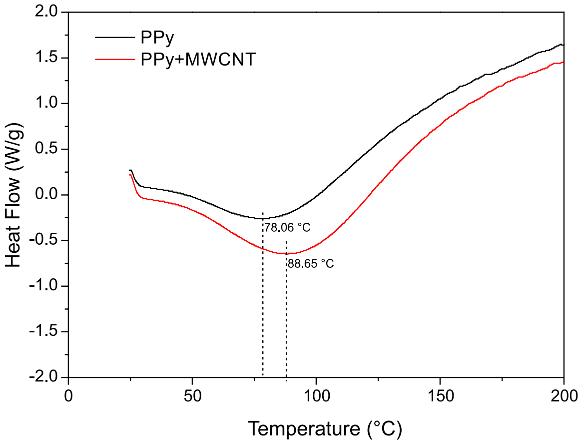

Figure 5. *DSC curves of neat polypyrrole (PPy) and composite PPy+MWCNT*

real part of impedance (at free and bounded charge frequency regions), an indication that additional conducting pathways are available. As a consequence, the capacitance measured at high frequency varies from 20.3 pF (for neat PPy) to 83.6 pF (for PPy+MWCNT) due to strong reduction in the IR drop of resulting material, characterized by superior electrical properties.

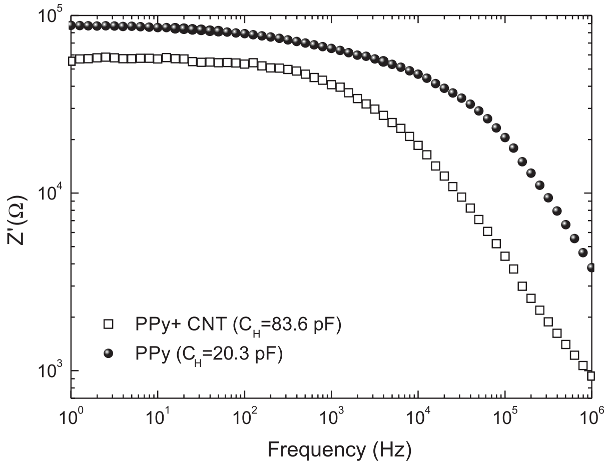

Figure 6. *Impedance of polypyrrole (PPy) and PPy+MWCNT actuators*

Taken together, the above observations are consistent with the presence of fibers on the surface of the synthesized composites, an indication that carbon nanotubes have served as a template for polymeric growth during the synthesis.

The behavior of resulting composites as mechanical actuators is evaluated by electrical excitation of films immersed in electrolyte (aqueous KCl or NaCl solution, 1 mol L^{-1}), and the applied frequencies vary between 1 Hz and 4 Hz. The resulting deformation of devices is maximized for neat PPy wherein the highest deflection is observed for the dynamic response at 2 Hz. Figure 7 shows a typical process of swelling (incorporation of ions from electrolyte to PPy) of PPy actuator after hundreds of oxidation/reduction cycles. The results indicate a maximum tip deflection angle of 12.44° (the corresponding value for composite PPy+MWCNT is 10.57°).

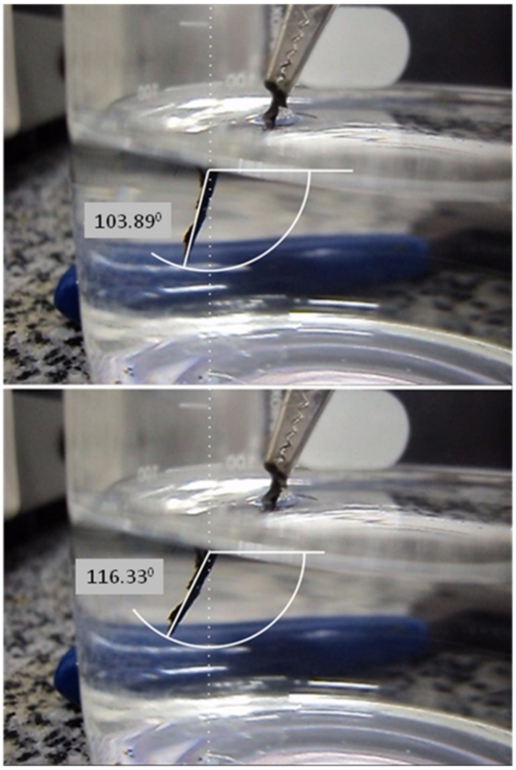

Figure 7. *Actuation of polypyrrole (PPy) film by external electrical excitation*

These results are in agreement with data reported previously,[19] i.e., a reduction in the strain of PPy+MWCNT actuators is induced by carbon nanotubes since a large strain is the result of changes in the volume of PPy (conformational changes in the polymeric backbone). In addition, the incorporation of increasing quantities of MWCNT contributes to the increased speed of response of the device[1] and is associated with superior electrical properties of resulting PPy+MWCNT, which prevents IR drop in the response of device.

An additional advantage related to the use of interfacial polymerization for production of PPy+MWCNT artificial muscles is the diversity of available geometries of interface between oil and water phase, allowing for the production of devices with specific geometries and for diverse applications such as electrically controlled organic devices for injection of fluids.

CONCLUSION

The chemical polymerization of polypyrrole (PPy) on templates of carbon nanotubes at the interface of water and oil represents a simple procedure for production of prototypes of artificial muscles with superior electrical properties. The intermediate strain of the resulting composite is associated with high admittance and capacitance, which contributes to the high speed of response to an external electrical field. The maximum tip deflection for single layer actuators (12.44° for PPy and 10.57° for PPy+MWCNT) are comparable to reported values obtained for complex ternary systems. This indicates that interfacial polymerization can be used for mass production of materials for application as mechanical actuators.

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