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Single walled carbon nanotube (SWNT)–polyimide nanocomposites as electrostrictive materials

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ABSTRACT

The combination of properties offered by polymer nanocomposites provides opportunities for going beyond structural reinforcement where engineered electroactive responses and enhanced electrical and dielectric properties would result in multifunctionality. In our study, we show that adding single walled carbon nanotubes (SWNTs) to a non-actuating polyimide (PI) can create an electromechanical actuation response in the nanocomposite. The neat polyimide does not show any actuation response under an applied electric field, whereas the SWNT–PI composites above the percolation threshold exhibit an electrostrictive behavior that is highly dependent on SWNT content. Both bending and thickness–extension strains are obtained at very low electric field magnitudes; the study also evaluates the effect of applied electric field magnitude, frequency and SWNT content on the actuation strain and strain rate. Dielectric spectroscopy and thermally stimulated current measurements reveal an enhanced polarization in the presence of SWNTs. This enhancement is key to the actuation mechanism and is thought to arise from a combination of three sources: SWNTs acting as extended electrodes within the polymer, interfacial polarization and noncovalent interactions between the SWNTs and the polymer.

1. Introduction

Incorporating carbon nanotubes (CNTs) in polymers offers a means of exploiting their superior mechanical [1] and electrical properties [2]. Although enhancements in properties have been shown for structural applications [3,4] and for electrostatic discharge [5], there have been fewer investigations on these nanocomposites as actuator materials. Improved electromechanical response in polymer nanocomposites, along with superior mechanical and electrical properties, can make them promising multifunctional materials for future engineering applications.

Some researchers have probed the electromechanical properties of individual or bundles of CNTs. Roth and Baughman investigated single walled carbon nanotubes (SWNTs) as actuators using an atomic force microscope, and found that the SWNTs exhibit an electromechanical coupling [6]. They observed a change in the length of the SWNT due to weakened carbon–carbon bonds, resulting from injection of electrons. In a separate study, Baughman et al. investigated actuation of SWNT sheets, or Bucky paper, in an electrolyte [7]. The actuation was electro-chemically driven, where a macroscopic bending displacement of the sheets was seen in a bimorph cantilever configuration. El-Hami and Matsushige used an AFM tip to apply a voltage across an aligned bundle of SWNTs, and observed a thickness expansion as a result [8]. They concluded that the nanotubes possessed an electrostrictive nature. Similarly, Guo and Guo predicted an axial electrostrictive response in SWNTs using density functional quantum mechanics calculations [9].

Other investigations have focused on the effect of CNTs on the electromechanical response of polymers. Kang et al. have demonstrated an enhancement in the response of a piezoelectric polyimide, (β-CN) 1,3-bis(3-aminophenoxy) benzene (APB) oxydiphthalic anhydride (ODPA), in the presence of SWNTs [10]. They investigated a series of poled SWNT–polyimide composites and quantified their piezoelectric response through thermally stimulated current (TSC) analysis as well as by direct measurement of the in-plane piezoelectric strain coefficient, d_{31}. In general, they observed an increase in d_{31} normalized by poling voltage from a value of 1 for pure polyimide to 1.2 for polyimide with 0.02 wt.% SWNT content. Levi et al. have demonstrated an increase in the piezoelectric properties of poly(vinylidene fluoridetrifluoroethylene) (PVDF-TrFE) due to SWNTs. The researchers observed an increase in the d_{31} value from 20 pC/N for the pure polymer film to 25 pC/N for 0.1 wt.% SWNT content composite. This enhancement has been attributed to an increase in the piezoelectric β-phase due to addition of SWNTs [11].

Effect of multiwalled carbon nanotubes (MWNTs) on the actuation stress response of a polysiloxane nematic elastomers has been studied [12]. The elastomer without MWNTs did not show

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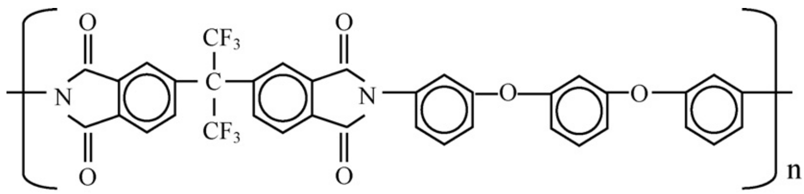

Fig. 1. Chemical structure of CP2 polyimide.

any actuation stress, while an increased stress response was seen in the 0.0085 wt.% and 0.02 wt.% MWNT composites under an applied electric field. The actuation was attributed to the torque experienced by the nanotubes due to the applied field. Similarly, in a study involving ionic polymer metal composites (IPMCs), an enhancement in the actuation stress was observed for 1 wt.% MWNT loading above which a decrease in response is seen due to inhomogeneous distribution of the MWNTs [13]. In a different study, Akle and Leo have demonstrated an increase in the strain and strain rate of a hybrid IPMC actuator by incorporating SWNTs in the electrodes, taking advantage of their conductive nature [14]. Zhang et al. have demonstrated enhancement in the electrostrictive response of MWNT–poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) composites compared to the pure copolymer, with MWNT content of 0.5 wt.% and 1 wt.% [15]. The authors reported an increase in both the mechanical and dielectric properties of these composites, which led to the enhanced strain response at a reduced electric field.

The studies described above used already electroactive polymers as the matrix materials. In our study, we investigate the apparent creation of a coupled electromechanical response in a non-polar polymer with SWNTs. We also fully characterize the increase in electrical and dielectric properties of the SWNT–polyimide (PI) composite. Our data suggests that the use of SWNTs can create an actuation response in a non-electroactive polymer, which offers many advantages such as the possibility of rendering any polymer active.

2. Experimental

SWNTs used are laser-ablated SWNTs acquired from Rice University. Details on aspect ratio, solvent-based dispersion and processing are given in an earlier publication [16]. An aromatic colorless polyimide (PI), CP2 (see chemical structure in Fig. 1) is used as the polymer matrix material. The diamine and dianhydride used to prepare the CP2-PI are 1,3-bis(3-aminophenoxy) benzene (APB) and 2,2-bis (3,4-anhydrodicarboxyphenyl) hexafluoropropane (6FDA). The SWNT–PI composite is solution cast using in situ polymerization under sonication. The details of this procedure are given elsewhere [16].

Scanning electron microscopy (SEM) images are taken using a Zeiss 1530 high resolution, variable pressure FE SEM. The SWNT–PI composites are freeze-fractured. The conductive coating used for the SEM study is Pt–Pd.

For electrical and electromechanical measurements, the nanocomposite films are coated with a thin silver layer by a vapor deposition process. The thickness of the samples ranges from 30 to 60 μm, and that of the silver layer is kept at 100 nm. A QuadTech 7600 Precision LCR meter is used to measure AC electrical conductivity and dielectric constant of the nanocomposites in a parallel plate configuration over a range of frequencies (20 Hz to 1 MHz) and SWNT vol% (0, 0.05, 0.1, 0.2, 0.5, 1, 2). A Sun Systems EC1x environmental chamber is used to add temperature capability. The percolation threshold, concentration at which the material behavior changes from insulator to that of a conductor, is obtained from these measurements.

The electroded samples are cut into strips of 3 cm × 0.5 cm, which are then used for the electromechanical tests. Fig. 2 shows the experimental set-ups. For thickness actuation, a small area on the bottom face is constrained and the electric field is applied through the thickness (Fig. 2(a)). The change in thickness is measured by an Opto Acoustics dual channel 201 angstrom resolver. For the bending experiment, the top of the sample is sandwiched between glass plates with copper leads. This setup is then suspended vertically in an acrylic box chamber (Fig. 2(b)). The leads allow the application of electric field (DC or AC) to the strip. The bending of the sample is captured by a Photron Fastcam PCI R2 high-speed camera setup. An auxiliary light source is available for better visibility. The captured videos are analyzed using Photron image analysis software. This software allows measurement of the sample displacement by analyzing the sample position in successive video frames.

Thermally stimulated current (TSC) measurements are carried out using a Setaram TherMold TSC/RMA 9000. The polymer or polymer nanocomposite is poled by DC electric field around the glass transition temperature, T_g. The poling time is 20 min and is kept the same for all samples. The sample is then cooled rapidly to room temperature using liquid nitrogen and then re-heated slowly (2 °C/min)

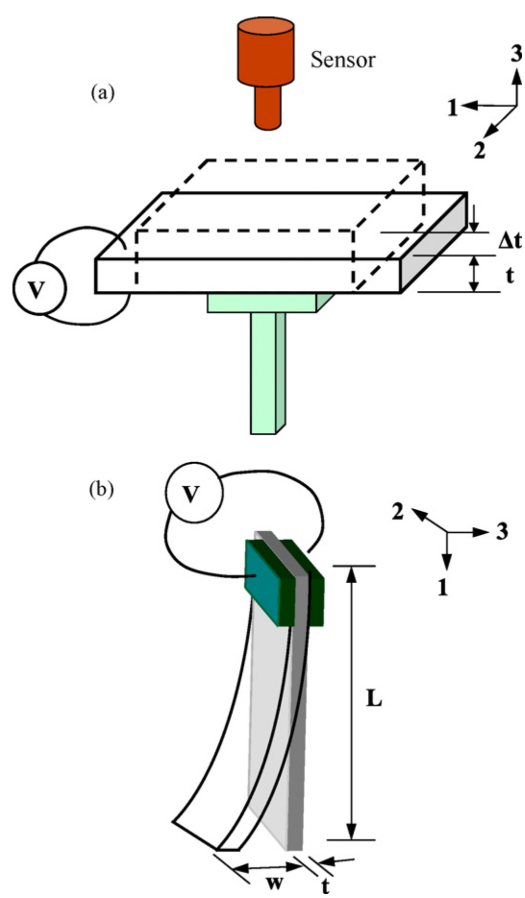

Fig. 2. (a) Thickness actuation and (b) bending actuation.