Contents lists available at ScienceDirect

Thin Solid Films

Poly(triarylamine) composites with carbon nanomaterials for highly transparent and conductive coatings

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ARTICLE INFO

ABSTRACT

We report on the fabrication of transparent, conductive, mechanically robust electrode composites of poly (triarylamine) (PTAA) doped with different concentrations of carbon nanotubes (CNTs) or graphene nanoplatelets (GNPs). Additionally, the effects of nanofiller surface modification with amines were characterized by comparing the transparency, conductivity, and mechanical properties to composites with unmodified nanofillers. The optimization of the concentrations and fabrication parameters resulted in films with high transparency, improved electrical conductivity, and superior mechanical properties.

Amine-functionalized nanofillers more readily dispersed into the matrix, and the addition of 1 wt% amine-CNTs resulted in a composite film with a conductivity of 1.1 S cm^{-1} and a transparency of 90–95% in the visible spectrum at a sub-100 nm thickness. At low doping concentrations, composites with amine-functionalized nanofillers exhibited a 100% increase in fracture energy compared to composites with unmodified nanofillers, an effect attributed to increased plasticity of the doped polymer. These findings have applications in many electronic devices that utilize organic semiconducting layers, such as organic light emitting diodes and perovskite photovoltaics.

1. Introduction

Poly(triarylamine) (PTAA) is an organic semiconducting polymer that exhibits high transparency and relatively high hole mobility, making it an attractive hole-transport material in optoelectronic applications such as organic light emitting diodes and perovskite photovoltaic devices [1–5]. Notably, PTAA was used as the hole transport layer in the world-record, 22.1% efficiency perovskite solar cell [6]. Its principal advantages compared to other traditional semiconducting polymers are its stability in air, resistance to degradation by exposure to UV light or moisture, and ability to be annealed at low temperatures, making it amenable to high-throughput roll-to-roll processing [7].

During the last decade, carbon nanomaterials—e.g., carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs)—have been incorporated into semiconducting polymers such as poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [8] and poly(3-hexylthiophene) (P3HT) [9], increasing their electrical conductivity by several orders of magnitude while retaining their transparency. The electrical conductivity of these composites depends on the polymer matrix, as well as the nanofiller material (e.g., CNTs or GNPs) and its main geometric characteristics (e.g., single or multi-walled CNTs, graphene monolayers, or GNPs). For example, P3HT composites with 5 and 30 wt% single-walled CNTs (SWCNTs) were reported to exhibit conductivities of 10^{-3} and 10^{-1} S cm^{-1}, respectively [10], while Nafion doped with 18 wt% SWCNTs was reported to have a conductivity of nearly 40 S cm^{-1} [11]. PEDOT:PSS, one of the most studied semiconducting polymers in composites due to its high electrical conductivity, exhibited increased conductivities of 400 S cm^{-1} with 35 wt% CNTs [12], and up to 637 S cm^{-1} with the addition of 1–5 wt% graphene [13]. However, to date no composites utilizing PTAA as the polymer matrix have been studied.

One common application for these composite materials is in thermoelectric devices; however, in this application optical transparency is not a concern and high particle loading (e.g., 80 wt%) resulting in opaque films has been reported [10]. Optoelectronic applications require high transparency, though, which is controlled by the polymer as

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well as the type and quantity of nanoparticle added. Typically, nanoparticle concentrations higher than 5–10 wt% result in a significantly decreased transparency due to increased agglomeration. And while the intrinsic optical characteristics of the materials comprising the composite play a role in determining its transparency, the most important parameter is the degree of dispersion of the nanofiller—i.e., if the filler does not disperse well, it forms aggregates that block the transmission of light [14].

Poor dispersion of CNTs or GNPs in polymer matrices remains a significant challenge and can result in low electrical conductivity if the formation of a percolated network is inhibited. Typically, composites incorporate unfunctionalized nanofillers which are not easily dispersed. Under stress, these composites with poor dispersion can undergo fracture—usually induced at the carbon–carbon interfaces due to their lack of covalent bonding and weak van der Waals interactions—resulting in a decrease in electrical conductivity [15,16]. However, the selective chemical functionalization of the nanofiller surface can increase the degree of dispersion within the composite, forming intermolecular interactions (e.g., hydrogen bonds) between the nanoparticles and matrix and enhancing its toughness.

We report a facile method for manufacturing PTAA composites doped with different concentrations of CNTs and GNPs in an effort to obtain a stable, transparent, and highly conductive film capable of replacing brittle oxides (e.g. indium tin oxide) [17] and scarce [18] or unstable metals (e.g. silver nanowires) [19] used in electrical applications, such as transparent electrodes, light emitting diodes, and thermoelectric or photovoltaic devices. Unmodified and amine-functionalized carbon nanofillers have been studied in order to analyze the effect of chemical functionalization on the degree of dispersion and the mechanical properties of the composites. The optical transparency and electrical conductivity were measured to ensure the primary goal of a transparent conductive film was achieved. The mechanical resilience of the composite films was determined by double cantilever beam (DCB) testing, which measures the fracture energy (or fracture resistance) of the layer.

2. Experimental details

2.1. Materials

PTAA with M_n 7000–10,000 g mol^{-1} was supplied by Solaris Chem Inc. (St.-Lazare, QC, Canada). Unmodified (NC3150) and amine-functionalized (NC3152) CNTs were supplied by Nanocyl (Sambreville, Belgium). The CNTs had an average length of < 1 μm and an average diameter of 10 nm. GNPs (powder grade M25) with an average thickness of 6–8 nm and an average lateral size of 20 μm were provided by XG Sciences, Inc. (Lansing, MI, USA). Amine-functionalized GNPs with a thickness of 4–6 nm and an average lateral size of 5 μm were supplied by Cheaptubes (Grafton, VT, USA). Prior work has shown that this difference in size between the unmodified and amine-functionalized GNPs should not significantly alter their ability to be dispersed in solution [20]; however, the larger flakes can be expected to provide improved mechanical reinforcement [21]. All nanofillers were used as received.

Solutions of PTAA with different concentrations of nanofillers (i.e, CNTs, GNPs, amine-CNTs, or amine-GNPs) in 1,2-dichlorobenzene (ODCB, Sigma Aldrich, St. Louis, MO, USA) were made as follows. Dispersion of the nanofillers was achieved by ultrasonication, using a probe sonicator at an amplitude of 30% and a frequency of 3 Hz in an ice water bath to prevent extensive heating and damage of the nanofillers. It was found that different concentrations of each nanofiller were required for good dispersion. The time to achieve a suitable dispersion for all nanofillers varied as a function of concentration, from 15 min for lower concentrations up to 2 h for the highest concentrations. PTAA was subsequently added at a concentration between 10 and 20 mg mL^{-1}. After addition of PTAA, the solutions were dispersed

further by an additional 15 min of ultrasonication.

Finally, the PTAA/carbon nanomaterial composite films were fabricated by spin coating the solutions on clean glass substrates (22 × 22 mm) in either a one-step (500 rpm for 60 s) or two-step process (500 rpm for 30 s, followed by 2000 rpm for 60 s). These films were subsequently dried in an oven at 100 °C for 1 h. In the case of composites doped with GNPs, the concentrations studied ranged from 1 to 20 wt%, while in contrast, the CNT concentrations ranged from 0.3 to 2 wt%. The relatively lower concentrations studied for CNTs when compared to GNPs were due to the higher specific surface area of CNTs—i.e., ~ 500 m^2 g^{-1} compared to ~ 150 m^2 g^{-1} for GNPs—which hinders dispersion and thereby limits the maximum concentration of the nanofiller which can result in a well-dispersed solution. It should also be noted that the concentrations of carbon nanomaterials present in the films were assumed to be approximately the same as those in solution.

2.2. Characterization

Film thicknesses were measured using a stylus profilometer (Bruker Dektak 150 profilometer, Billerica, MA, USA).

The effects of the nanofiller dispersion on the morphology of the surface of the PTAA films were compared with a Field Emission Gun Scanning Electron Microscope (FEG-SEM, Philips Nova NanoSEM FEI 230, Amsterdam, Netherlands). All samples were coated with a thin Pt layer (5–10 nm) to reduce surface charging.

Transparencies of the composite films were measured by UV/Vis/NIR spectroscopy (Agilent Cary 6000i, Santa Clara, CA, USA) with a wavelength range from 300 to 800 nm and a 1 nm step size. The composite films were deposited directly on glass and a blank glass slide was used as a background.

Electrical conductivities were determined with a purpose-built four-point probe and a Keithley 2410 SourceMeter (Keithley Instruments, Cleveland, OH, USA). The applied voltage was swept from − 1 to 1 V with a step of 0.2 V. The electrical current measured was in the range of 10^{-5} to 10 μA. All measured samples followed Ohm's law, and the electrical conductivity was calculated using the current–voltage (J–V) curves.

The mechanical properties of the films were measured by double cantilever beam testing (DCB) using a method previously discussed in detail elsewhere [22–24]. DCB specimens were prepared by coating one glass substrate (25 × 35 × 1 mm) with the composite film. Another glass substrate (with the same dimensions) was adhered to the film using epoxy glue (EPO-TEK 353ND, Epoxy Technology, Inc., Billerica, MA, USA). Prior to the epoxy coating, a 5 nm Ti/200 nm Al film stack was then deposited as a barrier between the epoxy and PTAA composite films. A ~5–10 mm notch was made in the film with a razor blade to initiate stable fracture and subsequent propagation into the weakest layer. The specimen was then loaded in tension with a delamination adhesion testing system (DTS Company, Menlo Park, CA, USA) until new fracture initiated and subsequently propagated, at which point the specimen was unloaded. This load-unload cycling was repeated until the crack growth had propagated at least 15 mm through the sample. The calculations to determine the fracture energy are explained in detail in previous work [24,25].

3. Results and discussion

3.1. Film transparency and morphology

In optoelectronic devices, absorption by the front electrode and charge transport layers is undesirable because it results in efficiency losses; therefore, it was critical that our PTAA composites were highly transparent. We first measured the transmission spectra of undoped PTAA films with thicknesses ranging from 10 to 50 nm to determine the baseline transparency (Fig. 1a). The film thicknesses were controlled by