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Preparation and properties of electrically conductive, flexible and transparent silver nanowire/poly (lactic acid) nanocomposites

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ABSTRACT

As the everyday use of petroleum-based products has raised environmental concerns, there is an urgent need to replace them with green materials. In this work, an eco-friendly, highly conductive, flexible silver nanowire/poly (lactic acid) film has been fabricated through a simple casting method by embedding the silver nanowires (AgNWs) below the surface of the poly lactic acid (PLA) matrix. The fabricated film has a high optical transparency of 89.5% with a sheet resistance of 64.8 Ω/□ and a figure of merit (FoM) of $4.92 \times 10^{-3}\ \Omega^{-1}$ which is comparable to that of indium tin oxide (ITO). These films demonstrate excellent flexibility, great adhesion, smooth surface with root mean square (RMS) roughness of 11.7 nm and high mechanical properties with tensile strength and Young's modulus of 39.8 (MPa) and 1.6 (GPa). The results obtained from different testing methods show that the AgNW/PLA nanocomposites are potential candidates in flexible electronics and optoelectronics.

1. Introduction

Recent developments in fabricating highly conductive nanoparticles, have opened a new prospect in future electronics [1–4]. The need for flexible, light weight, electrically conductive devices led to the generation of smart materials called conductive polymer nanocomposites (CPC) [5]. CPCs have a wide range of applications in sensors, photovoltaic cells, electrochemical capacitors, optical devices, diodes, highly stretchable transparent energy devices [6,7] and electromagnetic absorbers [8]. Beside flexibility and electrical conductivity, transparency is required in transparent conductive electrodes used in various types of optoelectronics including photovoltaic cells (PV cells), organic light emitting diodes (OLED), touch screens, highly stretchable transparent electrodes [9,10], highly flexible transparent conductors [2,3], highly stretchable electrodes [11–13] and liquid crystal displays [14]. Electrical conductivity could be achieved by the use of a wide range of conductive nanoparticles such as Ag, Au, Pd, Pt, CNTs and graphene [15–17]. Among all these conductive nanoparticles which have been extensively studied by researchers, silver nanowires could bring about electrical conductivity, flexibility and transparency all at the same time, as a result of silver having the highest electrical conductivity (6.3 × 107 S/m) among all the metals and the possibility of synthesizing 1-D nanowires that could be flexible and transparent [18,19]. AgNWs have unique electrical properties besides having outstanding thermal and optical characteristics and being highly resistant to corrosion [20–22]. Additionally, having antimicrobial properties make AgNWs more human friendly compared to other non-metallic conductive materials e.g., carbon nanotubes [23]. As a result, AgNWs are promising candidates in fabricating materials which need to be flexible, transparent and conductive [24]. Different methods have been used to synthesize AgNWs among which polyol method is the most popular due to simplicity and high efficiency [25]. As-synthesized AgNWs have high sheet resistances. However researchers utilized various techniques to reduce the sheet resistance of AgNW networks. Examples are thermal annealing, mechanical pressing and plasmonic nanowelding [4,9,12,26].

AgNWs have been introduced to many polymeric materials to make thin transparent films. These polymers have been used as matrices or protection layers. Examples are conductive polymers like: PEDOT:PSS [27,28], polycarbonate (PC) [29] and polyacrylate (PA) [30] or other polymers like: PET, PDMS, PVA, PU, PVDF [24,31,32]. As the continuous use of synthetic polymers makes serious environmental issues, there is an urgent need for replacing them with new eco-friendly substances. Lately, chitosan which is a biodegradable polymer has been studied by some researchers [21,33]. However it has many drawbacks including poor mechanical

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properties, high cost, incapable of being highly scalable, extreme sensitivity to ambience and low resistivity to chemicals [34]. Poly lactic acid (PLA) is a linear aliphatic thermoplastic polyester which is, renewable and an excellent alternative to the synthetic polymers ultimately derived from crude oil [35]. PLA is a bio-derived polymer as the monomers are obtained from the fermentation of agricultural products such as corn and sugar beet. These monomers called lactides and lactic acid monomers are synthesized to PLA through ring-opening polymerization [36]. PLA is also environmentally friendly and biodegradable since it degrades by microorganisms present in the environment. It also shows low toxicity and barrier properties making it more human friendly [37]. Moreover, PLA is a semi-crystalline polymer with a low degree of crystallinity, making it a suitable matrix in CPC development [5,38].

PLA composites have attracted much attention, recently [39]. However, using PLA as the host matrix for AgNWs has been rarely studied [40]. In this work, AgNW/PLA films have been prepared through a layer by layer casting for the first time. At first AgNWs have been synthesized through polyol method and a precise study has been carried out on the effect of reaction variables on morphological and structural parameters of the wires. The influence of time on diameter and morphology of the wires has been studied precisely. Additionally the effect of morphological parameters on transparency and conductivity of the AgNW networks have been investigated and new results have been obtained. Later PLA solution is cast on the AgNW networks, dried and then peeled off the glass. It will be illustrated in this study that by employing PLA as the host matrix, many of the drawbacks of bare AgNW networks like poor adhesion, surface roughness and poor mechanical properties will be resolved and surprisingly conductivity will be improved at the same time.

2. Experimental

2.1. Materials

PLA (Ingeo™ Biopolymer 2003D) was supplied from Nature Works, USA, with melt flow index of 6 g/10 min (210° C, 2.16 kg) and a density of 1.24 g/cm^3. It was a general purpose and transparent grade. Silver nitrate (AgNO3, 99.0%, Fluka), ethylene glycol (EG, 99.5%, Merck), silver chloride (AgCl, 99.5%, Sigma Aldrich), polyvinylpyrrolidone (PVP-Mw 40000 g/mol, DaeJung, South Korea) were used as-received. Chloroform, methanol, and acetone were all obtained from Merck. All solvents were used without any further purification.

2.2. Synthesis of silver nanowires

Several methods have been practiced by many researchers to synthesize silver nanowires. We followed a simple polyol method described by Hu et al. with some modifications [41]. To synthesize uniform AgNWs with a high yield, first 20 ml of PVP solution (298 mM in EG) was added to a three-necked round bottom flask. It was heated to 170 °C in 30 min and was refluxed through the whole reaction. For nucleation, 0.050 g of finely ground silver chloride (AgCl) was added to the flask. After 4 min, 10 ml silver nitrate (130 mM in EG) was injected to the reaction in a dropwise manner for 10 min. With the presence of PVP as the capping agent, silver seeds were restricted to an anisotropic growth in 1 dimension, resulting in the formation of wires. The cooking continued for another 30 min to let the wires grow completely. Magnetic stirring at 500 rpm was applied throughout the entire synthesis. The suspension cooled-down in room temperature for 45 min. After that 150 ml methanol was added to the suspension and it was centrifuged and washed with methanol four times at 8000RPM and 3 times at 4000RPM (after each centrifugation, 3 min ultrasonic bath was applied to the suspension). The supernatant containing EG, PVP, particles, and other impurities was discarded. Finally the precipitate of AgNWs was re-dispersed in 20 ml of methanol. Reactions were performed at three different reaction times and the effect of reaction time on morphology of the nanowires was studied. Three types of AgNWs were prepared according to this method. All the conditions were the same except for the cooking time which was 30 min for AgNWs type A, 60 min for type B and 90 min for type C. Differentiating the cooking time, led to different diameters of the wires and another aspect less observed in other studies that is changing the growth angle of the wires over time. All glassware used in the syntheses was washed several times by acetone and deionized water and then dried in hot air.

2.3. Fabrication of AgNW conductive networks and AgNW/PLA conductive films

The AgNW suspension in methanol with the concentration of approximately 10.0 mg/ml was diluted to approximately 1.0 mg/ml, which was a suitable concentration for subsequent processing. This was subjected to 10min low power ultrasonic treatment in a sonic bath. Films of 50mg/m^2-to 500 mg/m^2 silver nanowires were drop cast from suspension onto glass (Microscope slides −75 by 26 mm) and allowed to slowly dry on a shaking plate to prevent wire aggregation. The resulting networks were heated at 200 °C for 20 min to reduce sheet resistance. The morphology and electrical conductivity of prepared networks were studied separately. To fabricate PLA/AgNW films, PLA/chloroform solution (5 wt %) was cast on the networks. The wires embedded into the PLA and the networks became flatter, with the polymer filling the holes between the wires [42]. To remove the entrapped solvent, the nanocomposites films were dried at 50° C for 64 h under vacuum [43]. PLA needs to be thick enough so that the single wires and the wire−wire junctions sink in it to get a desirable conductivity; consequently the films have a thickness of about 50 μm [42].

2.4. Characterization

Different analysis techniques were employed to characterize AgNWs and evaluate AgNW/PLA film properties in this study.

Structural information of AgNWs and the surface and cross-sectional morphology of the films were characterized by using scanning electron microscopy (SEM, VEGA\\TESCAN, Czech Republic). The samples were coated with a thin layer (3−10 nm) of gold through sputter coating. For evaluating the fracture surface of the films, sample were immersed in liquid nitrogen for 15 min, slit by a sharp blade and then broken in nitrogen.

Statistical analysis on the AgNW diameter and length has been conducted using ImageJ software. Reported average diameters and lengths are based on the evaluation of 100 wires for an SEM image of each synthesis with a magnification of 35.00Kx.

The energy dispersive spectrometer (EDS, INCA, Oxford instruments, England) was utilized to examine the contents and dispersion of silver and other impurities of AgNWs and also to study the AgNW/PLA film elemental analysis.

The transmission electron microscope (TEM, Zeiss, EM10C, 80 KV) was used to measure and confirm the microstructure of AgNWs.

Sheet electrical resistance values were measured using a 4-point probe resistivity measurement system (4point probe, SNJ co., Iran). Each resistance was obtained as the mean over five locations.

The crystal structures and phase composition of AgNWs were analyzed by using an X-ray diffraction apparatus (XRD, Siemens, D5000, (λ = 1.5418 Å)-Germany); using Cu Kα radiation, with a