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PLA-TiO_2 nanocomposites: Thermal, morphological, structural, and humidity sensing properties

Shoaib Mallick[a], Zubair Ahmad[b,*], Farid Touati[a], Jolly Bhadra[b], R.A. Shakoor[b], N.J. Al-Thani[b]

[a] Department of Electrical Engineering, College of Engineering, Qatar University, P.O. Box, 2713 Doha, Qatar
[b] Centre for Advanced Materials (CAM), Qatar University, P.O. Box, 2713 Doha, Qatar

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ABSTRACT

In this paper, the effect of TiO_2 ceramic nanoparticles on the thermal stability, morphology, molecular mass, structure and electrical properties of the polylactic acid-Titanium dioxide (PLA-TiO_2) composites, aimed for relative humidity (RH) sensing have been reported. PLA-TiO_2 nanocomposites films were developed through a spin coating process. The developed films were characterized by X-ray diffraction (XRD), Raman spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and electrochemical impedance spectroscopy analysis (EIS). To investigate the RH-dependent characteristics, the devices were prepared on pre-patterned ITO substrates. The capacitive and resistive response of the nanocomposite films were studied under RH levels ranging from 20–90%. The PLA-TiO_2 nano-sensing films, having modified surface by acetone etching, exhibited superior morphological and electrical performance when compared to PLA-TiO_2 pristine samples.

1. Introduction

Accurate and reliable humidity measurements have key importance in many industrial processes including food packaging, quality control, textile and modern electronic industry [1–4]. Various types of humidity sensors have been investigated including stress-based humidity sensors [5], capacitive humidity sensors [6], resistive humidity sensors [7], quartz microbalance humidity sensors (QCM) [8] and surface acoustic wave (SAW) humidity sensors (SAW) [9]. QCM and SAW sensors are expensive owing to the material requirements and fabrication process whereas both the capacitive and resistive type sensors are easy to make and can be fabricated using low-cost materials. The operating principles of capacitive humidity sensors are based on the change in dielectric constant of the sensing film with a change in a humidity level. Similarly, in resistive type humidity sensors the conductivity of the sensing film changes with alteration in humidity levels.

As far as the sensing materials are concerned, the development of polymer-base sensing materials is a hot topic of recent research and development [10]. Among the polymers, polylactic acid (PLA) has attracted attention of many researchers due to its salient advantages including good biocompatibility and excellent mechanical properties which makes it popular in medical implants, in food packing and in the biomaterials industry [11,12]. PLA is a biodegradable polymer derived from lactic acid, which can be produced from renewable resources such as sugar cane, corn, wheat and other starch products. The use of renewable resources means that such a sensor is sustainable and cost-effective. Zhang et al. [13] studied the thermal properties of PLA-fumed silica nanocomposites and reported that the addition of fumed silica nanoparticles into PLA polymeric matrix increases the glass transition temperature (Tg), which may improve the thermal stability of PLA. Among various inorganic nanoparticles choices, TiO_2 nanoparticles have a special peculiarity because of its good stability, UV resistance, high refractive index and excellent photo stability [14,15]. Luo et al. [16] synthesized the PLA-TiO_2 nanocomposites film applying grafting method and investigated the mechanical and physical properties of the PLA-TiO_2 nanocomposites. Zhang et al. [17] prepared the PLA-TiO_2 nanocomposites by van extruder technique and investigated the scattering mechanism under elongation. Marra, Antonella, et al. [18] studied the impact of functionalized TiO_2 nanoparticle on the structure, morphological, mechanical and thermal properties of PLA. The functionalization of TiO_2 nanoparticles with fluorocarbon enhanced the dispersion of nanoparticle, which improved the mechanical properties of PLA. Despite such investigations, to the best of our knowledge, there is not enough literature available on the TiO_2 dispersion mechanism and its impact on the electrical behaviour of PLA-TiO_2 nanocomposites for humidity sensing applications. The thermal stability of PLA-TiO_2 composite is improved due to addition of TiO_2 nanoparticles which is also studied by Zhuang et al. [19] they reported that the addition of

* Corresponding author.
E-mail address: zubairtarar@qu.edu.qa (Z. Ahmad).

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TiO_2 nanoparticles reduce the mobility of PLA molecular chain which improve the thermal stability of PLA-TiO_2 composite.

In this paper, our aim is to study the effect of TiO_2 nanoparticles on the structural, thermal, morphological and electrical properties of the PLA for their potential applications in humidity sensors; TiO_2 nanocomposites humidity sensors. The PLA-TiO2 nanocomposite films were prepared through spin coating process. The morphology of the nanocomposite films were analysed by using FESEM and AFM techniques. Modifications in the sensing films were injected to enhance the porosity over the surface of PLA-TiO_2 nanocomposites. Finally, the performance of the PLA-TiO_2 nanocomposite films were investigated as moisture sensor in air. Our studies confirm that the PLA-TiO_2 nano-sensing films, having modified surface, exhibited superior morphological and electrical performance features when compared to PLA-TiO_2 pristine samples.

2. Experimental

Polylactic acid (PLA) and 99.99% trace metals basis titanium dioxide (TiO_2) nanoparticles (< 100 nm) were obtained from Sigma Aldrich. Specific surface area (SSA) of the TiO_2 nanoparticles was measured by using the Brunau–Emmet–Teller (BET) method using micromeritics ASAP 2420 surface and porosity analyzer and found to be 80.2240 m^2/g. The samples were degassed in nitrogen and the free space was measured using ultra-high purity (UHP) helium gas. The SSA was determined by a 5-point BET measurement with UHP nitrogen as the adsorbate and liquid nitrogen as the cryogen. The particle size distribution of TiO_2 nanoparticles has been estimated using atomic force microscopy (AFM) analysis and most of the TiO_2 nanoparticles lies in the range of 40–100 nm as shown in Fig. S-1, given in the supplementary file S. Interdigitated ITO/glass substrates of dimension 20 × 15 mm were purchased from Ossila. The cleaning of interdigitated ITO/glass electrode (substrate) was done by sonicating the substrate in soap water for 10 min and then rinsing it with distilled water. Then sonication with acetone and distilled water was performed respectively (10 min each) followed by nitrogen blow for sample drying. The PLA:TiO_2 nanocomposites films were prepared as depicted in Fig. 1(a). First, 2.0 wt% solution of PLA and ceramic TiO_2 nanoparticles were prepared in chloroform separately. Then, prepared solutions of the PLA and TiO_2 were mixed in the proportion of (1:2). The composite solution was then magnetically stirred for 2 h to ensure uniform composition. The composite solution was then deposited on the ITO/glass substrate using the spin coating technique. The optimized rotation speed and rotation time were 5000 rpm and 60 s, respectively. After deposition of the nanocomposite film on the ITO/glass substrate, wet etching of the sensing film was performed by placing ITO/glass substrate in acetone for 10 s. After etching in acetone the morphological and structural study of the developed surface morphology was performed by field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). Perkin- Elmer TGA (4000) used for TGA analysis, which measures the change in weight of a sample with respect to changes in temperature or time in a controlled environment. The DSC measurement was conducted on a Perkin-Elmer DSC (8500). The DSC and TGA were used to investigate the thermal stability and thermal weight loss of materials [20]. The thermal stability of the polymer nanocomposite material plays a key role in determining the conditions required for the device fabrication process and the applications in which the device can be employed. TGA and DSC analysis of PLA and PLA-TiO_2 composite were measured in nitrogen atmosphere. For the DSC analysis, the samples were scanned at the rate of 10 °C/min in the temperature range of 20–220 °C. An empty pan was used as the reference in both cases. The melting temperature (Tm) was evaluated from the DSC thermogram. The TGA of the annealed samples was performed in platinum crucibles with nitrogen gas pressure and flow rate of 3.0 bars and 20 mL/min, respectively. The dynamic measurements were made from 30 °C to 600 °C with a ramp rate of 10 °C/min. The XRD patterns were recorded using a EMPYREAN Advanced diffractometer operated at 45 kV and 40 mA with K-Alpha1 radiation of wavelength 1.540598 Å and K-Alpha2 radiation of wavelength 1.544426 Å with a scan speed of 1 s/step and a step size of 0.013°2θ.

The electrical characterization of humidity sensors was carried out in a humidity-controlled sealed chamber (dimensions 60 cm x 80 cm). The inlet and outlet valves connections were provided in the closed chamber so that humid and dry air flows inside the chamber. To increase the relative humidity level (RH) inside the chamber, the chamber was connected with commercially available Philips Respironics humidifier. The reduction in RH level inside the chamber was maintained by flowing nitrogen gas. The MS5308 LCR meter measured the capacitance and resistance of the fabricated sensors at different RH levels. The RS-6109 humidity meter was used as a reference humidity sensor and placed inside the closed chamber to monitor the RH levels and temperature. Fig. 1(b) shows the schematic diagram of the characterization setup employed in in this work.

3. Results and discussion

3.1. Thermal analysis

The Tm of pure PLA and PLA-TiO_2 nanocomposite is presented in Fig. 2(a). The Tm for PLA in TiO_2 composites and PLA alone were found to be 144.34 °C and 149.60 °C, respectively. This decrease in melting temperature of the PLA nanocomposite is due to the fact that TiO_2 nanoparticles disrupt the regularity of the PLA chain structures and increases the spacing between the chains. The exothermic peaks of the PLA crystallization temperature Tc and glass Transition temperature Tg were 108.5 °C and 50.9 °C, respectively. However, these peaks were not apparent for the PLA-TiO_2 nanocomposite. This may be due to the fact that the TiO_2 nanoparticles disrupt the PLA chain structure and increase the spacing between the PLA molecular chain hence the Tg and Tc for PLA disappear in the composite film [21]. In Fig. 2(b), the TGA curve shows the thermal weight loss of PLA-TiO_2 nanocomposite and pure PLA. It can be observed that the initial onset decomposition temperature of pure PLA and PLA-TiO_2 nanocomposite are ~ 200 °C and ~ 160 °C, respectively. However, their maximum onset values occurred at ~ 345.45 °C and ~ 304.10 °C, respectively (see Fig.-S2). The first step of weight loss that started below 50 °C might be related to vaporization of the solvent or moisture, which remains even after drying the samples at room temperature. Fig. 2(b) shows that the final weight loss of the polymer nanocomposite remained well below as compared to the PLA alone, this is because of remaining of the TiO_2 particles.

3.2. Morphological analysis

The morphological properties of a sensing film play a vital role in determining the sensitivity of a sensor. For instance, in humidity sensing, the adsorption of water vapour within the polymer matrix increases as the porosity of the polymer film increases. The water entrapment is directly proportional to porosity. The AFM is used to study the surface topography of the sensing film whereas the FESEM is used to investigate the dispersion of TiO_2 nanoparticles within the PLA matrix. The FESEM images in Fig. 3(a) and (b) show the dispersion of TiO_2 nanoparticles on the surface of the PLA-TiO_2 nanocomposite film before and after acetone etching. After etching, TiO_2 nanoparticles agglomeration is reduced and the nanoparticles become more uniformly dispersed.

Fig. 3(c) represents the AFM image of the PLA-TiO_2 nanocomposite before acetone etching. It is observed that the surface of the composite film is not uniform (due to the agglomeration of nanoparticles in PLA matrix) and rms roughness of the film was found to be 112.55 nm. However, Fig. 3(d) shows that after etching with acetone, TiO_2 nanoparticles seems to be well scattered (due to the etching of the PLA) and form more porous surface. The rms surface roughness of the etched