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Poly(lactic acid)–multi-wall carbon nanotube conductive biopolymer nanocomposite vapour sensors

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ABSTRACT

Conductive biopolymer nanocomposites (CPC) have been prepared by dispersing multi-wall carbon nanotubes (CNT) "guest conducting filler" in biopolymer, poly(lactic acid) (PLA) "host matrix" via solution mixing to develop volatile organic compounds (VOC) sensors. CPC transducers were fabricated by spray layer by layer (sLbL) technique and the derived sensors chemo-resistive properties have been investigated by exposition to a set of organic vapours (chloroform, methanol, toluene and water) exhibiting different physical properties such as solubility, polarity and molecular size. The influence of both vapour nature and CNT content has been elucidated and explained on the basis of solubility parameters and percolation theory. The selectivity of PLA/CNT CPC towards vapours, was found to be well correlated to solubility parameters. Among all, chloroform was the vapour that led to the highest response of sensors. To determine the influence of crystallization on conductive network architecture and thus on chemo-resistive characteristics of PLA/CNT, a comparative study has been carried out before and after annealing of sensors. The modification induced by this thermal treatment on both surface morphology and bulk crystallinity of PLA/CNT CPC, has clearly evidenced by atomic force microscopy (AFM) and differential scanning calorimetry (DSC) are found to be responsible for important changes in vapour sensing behaviour.

1. Introduction

Insertion of conductive nanoparticles within insulating polymer matrices generates a new species of intelligent materials termed "*Conductive polymer nanocomposites (CPC)*". The direct transduction of chemical information into an electrical signal associated to existing low power microelectronics and sensing technology make CPC an attractive material. A drastic change in electrically properties can be observed while CPC are exposed to different environmental sollicitations such as chemical, thermal or mechanical [1–7]. CPC versatility comes from the wide variety of combinations of conductive fillers and insulating polymer matrices drew on for their development. Carbon nanotubes (CNT), firstly discovered by [8] and later reported by Iijima [9] in 1991, have an inimitable combination of mechanical, electrical, and thermal properties [10–12]. In results, carbon nanotubes have been found leading entrant in different research areas such as sensors [13–15], actuators [16], field-emitting flat panel displays [17] as well as energy and gas storage [18]. The well-known exceptional properties (large surface area, high electrical conductivity and low percolation thresholds when dispersed into polymer matrices) and surface chemistry of CNT make them superior candidate over conventional conductive fillers [19–22].

Concerning the CPC formulation, the key issue is to accomplish better dispersion of CNT within the polymer matrix. However, an individual network of CNT between partial aggregations of CNT bundles is the ideal state of conductive network within polymer matrix for sensing application [23]. Among various CPC processing methods, solution dispersion under sonication process is favoured because this process not only endow with ultra thin film but also appropriate dispersion of nanofiller [24–26]. Moreover the performance of vapour sensor depends on thickness of transducers, thus the spray layer by layer assembly technique is found very attractive method to control this parameter and to obtain well dispersed multilayers CPC films [27]. In addition, recently we investigated the influence of polymer grafting on CNT and better interaction between polymer and CNT, have enhanced sensitivity of CPC than bare CNT based CPC [26–30]. The additional driving parameters were also found to explain the ability to identify and discriminate particular vapour as: polarity of molecule, analyte molecular size [31–33], saturating pressure [34,35], solubility parameters, intermolecular interactions [36–38].

Besides synthetic polymer matrices, with respect to be favourable to environment, an immense interest has been

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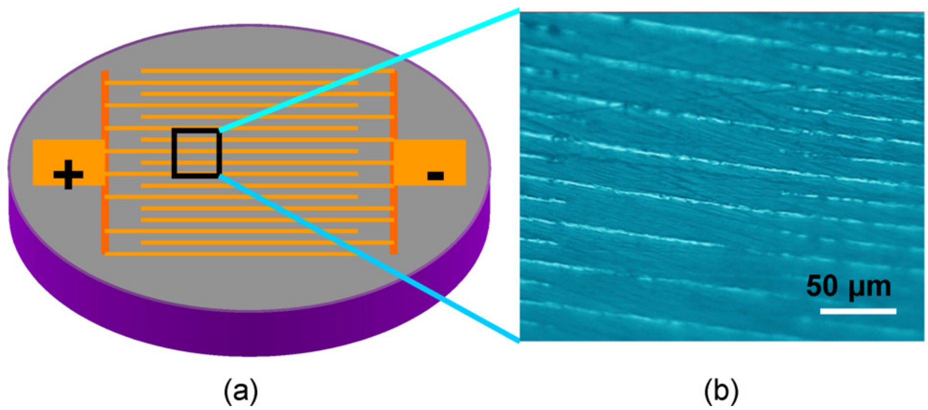

Fig. 1. (a) Schematic drawing of cleaved capacitor and (b) top view (OM image) of cleaved capacitor used as electrode.

addressed for the development of biopolymer based composites. One side, PLA is a widely premeditated as biomaterial and biodegradable polymer [39–42], synthesized by the ring-opening polymerization of lactides and lactic acid monomers which are obtained from the fermentation of sugar feed stocks [43]. On the other side PLA is a semi-crystalline polymer with a low degree of crystallinity, a key parameter for the CPC development [42,43]. Regarding nanofiller filled composites, accumulating the CNT not only significantly increases the crystallinity of PLA but also amplifies the electrical conductivity [44]. Therefore, crystallization induced effects on chemo-resistive properties must be consider prior to final industrial application such as e-nose which can be used for disease detection quickly [45,46]. To understand the influence of crystallinity on vapour sensing phenomenon of polymer nanocomposite, PLA has been selected as polymer material for CPC formulation.

To our best knowledge, there is no report, which investigated the role of PLA/CNT CPC and its crystallinity towards vapour molecule sensing. In present study, PLA/CNT CPC based sensor were prepared via spray layer by layer technique using pre-dispersed CNT in PLA solution and novel potential of PLA/CNT CPC as smart material for vapour sensing have been revealed. Interestingly, influences of vapour nature, filler concentration and crystallization have been envisaged.

2. Experimental measurements

2.1. Materials

Poly(lactic acid) (PLA, L9000) was purchased from Biomer, Krailling (Germany). Multi-wall carbon nanotubes (Nanocyl 7000®) were kindly provided by Nanocyl (Belgium) synthesized via well established the catalytic carbon vapour deposition process having 90 wt% purity. Choloroform, methanol, and toluene were received from Aldrich, and styrene was obtained from Acros (France). All the solvents were used without any further purification.

2.2. Fabrication of sensors via spray layer by layer (sLbL) process

PLA based sensors were prepared by two-step process. Firstly CNT (4 mg and 6 mg which are corresponding to 2 wt% and 3 wt%) were dispersed in clear solution of PLA by dissolving 200 mg PLA in 20 ml chloroform followed by sonication at 30 °C for 60 min continuously. In a second step, the PLA/CNT suspension was sprayed onto home made electrodes (similar to that used by Freund and Lewis [46]). In brief, electrodes were prepared by mechanical cross-sectional cutting of commercial 22 nF ceramic capacitors which consist of a series of interdigitated metal lines (25 wt% Ag/75 wt% Pd), separated by 30 µm (Fig. 1). Prior to CPC deposition, these

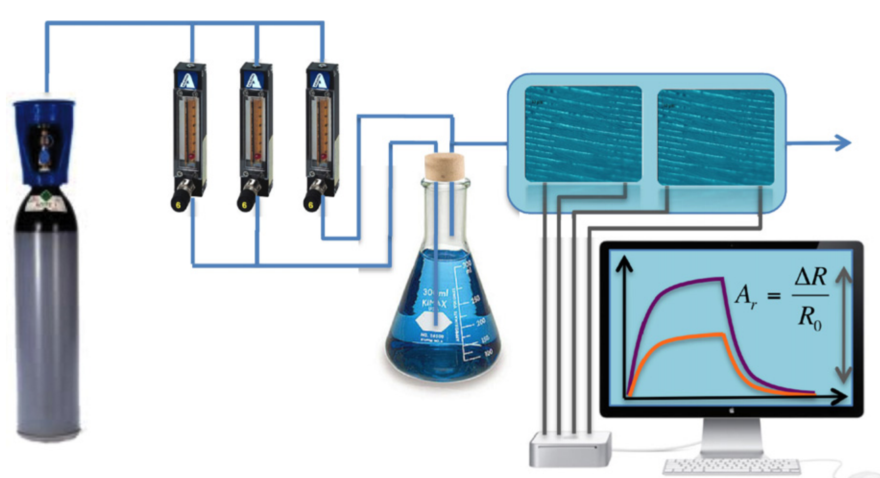

Fig. 2. Scheme of chemo-resistive vapour sensing device.