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Short communication

Conductive 3D microstructures by direct 3D printing of polymer/carbon nanotube nanocomposites *via* liquid deposition modeling

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ABSTRACT

In this work, a new three-dimensional (3D) printing system based on liquid deposition modeling (LDM) is developed for the fabrication of conductive 3D nanocomposite-based microstructures with arbitrary shapes. This technology consists in the additive multilayer deposition of polymeric nanocomposite liquid dispersions based on poly(lactic acid) (PLA) and multi-walled carbon nanotubes (MWCNTs) by means of a home-modified low-cost commercial benchtop 3D printer. Electrical and rheological measurements on the nanocomposite at increasing MWCNT and PLA concentrations are used to find the optimal processing conditions and the printability windows for these systems. In addition, examples of conductive 3D microstructures directly formed upon 3D printing of such PLA/MWCNT-based nanocomposite dispersions are presented. The results of our study open the way to the direct deposition of intrinsically conductive polymer-based 3D microstructures by means of a low-cost LDM 3D printing technique.

1. Introduction

Three-dimensional (3D) printing is a fabrication technology that consists in the creation of a 3D object starting from a digital model. 3D printing technologies have evolved very rapidly in recent years and have shifted apart from their traditional application field, namely rapid prototyping. Indeed, 3D printing is now being used routinely in a variety of manufacturing sectors ranging from aerospace and automotive to bioengineering [1,2]. At present, stereolithography, selective laser sintering, selective laser melting and fused deposition modeling (FDM) are among the most widely employed and investigated additive manufacturing methods both in academia and in industrial environments [3]. The various 3D printing technologies differ in terms of cost, maximum spatial resolution and type of materials used. In particular, for the first three methods, 3D features with a very high spatial resolution (in the order of a few μm at most) have been demonstrated but at the expense of relatively high equipment costs and the need of specialized personnel to operate them [3,4]. On the other hand, FDM has recently become fairly popular especially among non-specialized personnel as it represents a very cost effective approach to produce 3D objects with a relatively good resolution, which can approach 40 μm [5]. However, being a thermally-driven process that requires melting of a thermoplastic filament prior to the additive deposition of the extruded feature, it exhibits some limitations related to the materials to deposit, as only relatively few polymers possess the right thermal and rheological properties to be easily processable with this technology (with poly(lactic acid) – PLA and acrylonitrile–butadiene–styrene – ABS being among the most widely employed) [6]. Recently, the FDM approach was shown to allow a high degree of orientation of short reinforcing fibers in polymer-based composites during filament extrusion, resulting in 3D printed components with unique structural properties that can significantly exceed those of traditional compression molded samples [7]. In addition, the potential of the FDM technology for the fabrication of electronic sensors was recently demonstrated by 3D-printing solid filaments obtained starting from a dispersion of conductive carbon black into a solution of a commercial formulation of poly(caprolactone) (PCL) in dichloromethane (DCM) followed by evaporation of the solvent to form the solid filament to be extruded in a table-top FDM 3D printer [8]. Even though the approach presented in this work clearly allows the possibility to 3D-print objects with embedded sensors and electronic functionalities in a relatively simple fashion, it still requires the additional step of the production of a solid (nano)composite filament to be heated and melted in order to be processed with a standard FDM 3D printer.

Very recently solvent-cast 3D printing has emerged as a versatile and cost-effective strategy to overcome some of the limits imposed by the FDM approach [9]. This relatively new technology consists in the additive deposition of material layers directly from a solution in

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a volatile solvent. By means of this technology, the production of freeform structures, scaffolds and other self-standing microstructures was recently demonstrated using a computer-controlled robot moving along the *x*, *y* and *z* axes a dispensing apparatus equipped with a 100 μm inner-diameter extruding nozzle, starting from a concentrated solution of PLA in DCM [9]. In addition, by sputtering a metallic layer a few tens of μm thick onto the 3D printed structure, electrically conducting objects could also be obtained. However, no examples of the fabrication of intrinsically conductive 3D microstructures *via* direct 3D printing of conductive polymer-based nanocomposite materials from liquid dispersion have so far been reported in the literature, notwithstanding their enormous technological potential for application in fields such as microelectronics and biomedical engineering, where this approach would allow the direct fabrication of conductive microstructures with tailored 3D architectures in a low-cost and highly versatile fashion.

In the effort to address this issue, a 3D printing technique is developed in this work for the fabrication of conductive 3D microstructures with arbitrary shapes *via* the deposition of a new conductive nanocomposite from liquid dispersion by means of a low-cost commercial benchtop 3D printer equipped with a syringe dispenser (see Supplementary data). This method, that will be called liquid deposition modeling (LDM) throughout the text in analogy to the FDM approach introduced earlier, is based on the direct deposition of a homogeneous dispersion of multiwall carbon nanotubes (MWCNTs) in PLA using a high volatility solvent (i.e., DCM) as dispersion medium to ensure fast evaporation during wet filament deposition and rapid formation of rigid 3D microstructures. A thorough electrical characterization of the nanocomposite at increasing MWCNT concentrations is performed to evaluate the percolation threshold to achieve electrical conductivity. In addition, the rheological behavior of the nanocomposite dispersion is experimentally investigated at varying solid (PLA) content and a printability window for this system is identified based on the shear-rate of the material at the extrusion nozzle. Finally, examples of conductive 3D microstructures directly formed upon LDM of such MWCNT-based nanocomposite dispersion are presented. Conductive features as small as 100 μm can be reproducibly obtained with this method, indicating the high reliability of our approach. LDM clearly lends itself to the possibility of incorporating different types of structural and functional (nano)fillers in the 3D printed extruded feature without the need of producing a solid (nano)composite filament, thus presenting clear benefits compared to the more common FDM approach.

2. Experimental

MWCNTs were purchased from Nanocyl, Belgium (Nanocyl NC 3100, purity >95%, 9.5 nm average diameter and 1.5 μm average length). PLA pellets were supplied by Futura Elettronica, Italy. DCM was purchased from Sigma–Aldrich, Italy. All products were used as received. For the preparation of the nanocomposite dispersions at increasing MWCNT concentration, a 3 wt% stock solution of PLA in DCM was prepared under magnetic stirring at room temperature for 3 h. After complete dissolution of PLA, the desired amount of MWCNTs (ranging from 0.5 wt% to 10 wt% in PLA) was dispersed in the PLA/DCM solution using the following procedure [10]: addition of the MWCNTs, 30 min magnetic stirring at 950 rpm, 1 h ultrasonic bath (Starsonic 90) at room temperature, 30 min ultrasonication with a Sonic & Materials VCX130 sonicator tip (20 kHz, 130 W, oscillation amplitude 80%). This last step was carried out in an ice bath in order to prevent DCM evaporation and to minimize undesired exothermic phenomena resulting from the ultrasonication process. A similar procedure was employed for the preparation of nanocomposite dispersions at increasing PLA concentrations in DCM. In this case, a 1 wt% MWCNT concentration in PLA was employed and the PLA content in DCM was progressively varied (25 wt%, 30 wt% and 35 wt%). To perform electrical measurements, 25 mm × 75 mm thin film samples with a thickness ranging between 40 and 100 μm were prepared by drop-casting each nanocomposite dispersion with a given MWCNT concentration on a glass substrate. Upon drying in a ventilated oven, a solid self-standing nanocomposite film was obtained. The electrical conductivity of the nanocomposite films was measured using a four-point probe apparatus connected to a Keithley 2612 digital source-measure unit. A current scan between 0.01 and 0.1 A was applied on each sample with 50 steps and a settling time of 1 s for each measured step. The electrical conductivity of the nanocomposites was then calculated from resistance measurements [11]. Characterization of the rheological properties of the nanocomposite dispersions at increasing PLA concentrations (1 wt% MWCNT in PLA) was performed using a Rheometrics DSR200 rheometer with a 25 mm plate–cone configuration at 25 °C. Steady shear tests on the MWCNT/PLA/DCM dispersions were performed for 3 min in the 0–4500 Pa range. Optical microscopy was employed to evaluate the microstructural features of the 3D-printed architectures using an Olympus BX-60 reflected-light optical microscope with bright-field (BF) and dark-field (DF) imaging equipped with an Infinity 2 digital camera. Scanning electron microscopy (SEM) was performed on 3D-printed nanocomposite-based microstructures with a Carl Zeiss EVO 50 Extended Pressure scanning electron microscope (acceleration voltage of 15.00–17.50 kV) to evaluate their surface morphology and the 3D architecture (samples were sputtered with a gold coating prior to SEM analysis). A low-cost home-assembled 3Drag 1.2 benchtop printer (Futura Elettronica, Italy) was used for LDM-based 3D printing of the conductive nanocomposite microstructures (see Supplementary data for details on the 3D printer setup).

3. Results and discussion

In this work, the high electrical conductivity of MWCNTs was exploited to impart conductive character to the final MWCNT/PLA nanocomposite. To determine the effect of the addition of MWCNTs to the PLA matrix, the volume electrical conductivity σ of MWCNT/PLA nanocomposites was evaluated from resistance measurements on solvent-cast nanocomposite films with increasing MWCNT content (0.5–10 wt%). As shown in Fig. 1a, conductivity σ is found to increase substantially with respect to pristine PLA already upon addition of 0.5 wt% MWCNTs. Furthermore, a progressive increase in σ is observed for increasing MWCNT concentrations following a typical percolation behavior, until values in the range 10–100 S/m are reached for highly concentrated (5–10 wt%) MWCNT/PLA nanocomposites. Similar values of electrical conductivity were obtained on analogous nanocomposite systems based on MWCNTs and PLA matrix [12,13].

Achieving a uniform homogeneous dispersion of MWCNTs within a polymeric matrix is a key factor for the development of printable MWCNT-based nanocomposites because of the high tendency of MWCNTs to form bundles and aggregates [14] that may cause clogging of the printing nozzle and flux instability during the printing process. Therefore, an appropriate MWCNT concentration is required to obtain a nanocomposite material that is simultaneously conductive and 3D printable. The fracture surface of cryo-fractured 3D printed MWCNT/PLA nanocomposites containing 10 wt% of MWCNTs obtained from SEM analysis is shown in Fig. 1b. As evident from the SEM micrograph, a good level of dispersion and distribution of MWCNTs (white dots in the image) is achieved in the PLA matrix without the formation of any noticeable