Use of lignocellulosic materials and 3D printing for the development of structured monolithic carbon materials

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A B S T R A C T

In the present work, electrically conductive and mechanically resistant carbon structures were elaborated by 3D printing and subsequent pyrolysis using microfibrillated cellulose/lignosulfonate/cellulose powder (labeled as MFC/LS/CP) blends. The processability of MFC/LS/CP slurries by 3D printing was examined by rheological tests in both steady flow and thixotropic modes. The printed MFC/LS/CP pastes were self-standing, provided a high printing definition and were proved to be morphologically stable to air drying and the subsequent pyrolysis. Pyrolysis at a slow rate (0.2 °C/min) to a final temperature ranging between 400 and 1200 °C was used to manufacture MFC/LS/CP carbons. The TGA/DTG was applied to monitor the thermal degradation of MFC/LS/CP materials in blends as well as in a separated form. The resulting carbons were further characterized in terms of morphology, microstructure and physical properties (such as density, electrical conductivity and mechanical strength). At 900 °C, MFC/LS/CP carbons displayed a high electrical conductivity of 47.8 S/cm together with a low density of 0.74 g/cm^3 and a porosity of 0.58. They also achieved an elastic modulus of 6.62 GPa. Such interesting electrical and mechanical properties would lead to a promising application of MFC/LS/CP-derived biocarbons in energy storage devices as electrode materials in close future.

1. Introduction

Over the last decade, additive manufacturing progressively evolved from the laboratory/prototyping-to an industrial-process, capable of processing an ever increasing panel of structural and functional materials with various physical forms [1–3], i.e. from metallic/ceramic powders to food/biological hydrocolloids. Among available 3D printing technologies, paste/fused material extrusion emerged as one of the most versatile techniques for multi-material processing and it has been successfully used with carbon fiber-, carbon nanotubes- and graphene-reinforced polymer composites for both structural and electronic applications [4–8]. Indeed, the ability to combine materials with different functionalities in a single object paved the way to the additive manufacturing of new 3D printed structures embedding electronic devices [9,10]. Despite a relatively high conductivity (ranging from 0.01 to 4.76 S/cm [6–8]), carbon-polymer composites are adapted for the fabrication of resistive/antistatic patterns, whereas high conductivity silver-based conductive inks are the preferred system for the deposition of conductive paths and electrodes on insulating substrates. Thereafter, in most cases the fabrication of highly conducting 3D structures requires the combination of both conductive and structural materials [9].

In order to go beyond this limitation, the aim of this work was to manufacture monolithic carbon objects with both conductive and structural functionalities using 3D printing and lignocellulosic materials as carbon precursors. Lignocellulosic materials represent the most abundant polymer source in nature and have been widely used in medical, packaging, construction and energy industries. In energy storage devices, biomass was usually used as "inactive" component, such as binder in electrodes [11], reinforcing agent in gel-polymer electrolytes [11], separator [12] or nanoporous template in supercapacitors [13]. More recently, its carbonaceous chars, obtained after pyrolysis in inert atmosphere, have been successfully applied as an "active" electrode materials [14–16], although, no further interpretation concerning their development of electrical conductivity during pyrolysis was given.

Among few studies from the literature, Perepelkin [17] summarized an electrical resistivity decrease of nearly 12 orders of magnitude for biomass precursor heat-treated at 350 °C and 950 °C, despite the fact that biomass has been considered as non-graphitizing carbon precursor. McDonald-Wharry et al. [18] proposed a model called "distorted graphene triad" for describing the microstructure of non-graphitizing carbons. Such model is composed of 3 distinguish microstructures: regular graphite-like domains, distorted graphite regions and

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amorphous carbon phase. Rhim et *al.* [19] studied the electrical property development throughout the pyrolysis of microcrystalline cellulose (MCC) using a binary model (after compensation of porosity effect). The authors suggested that the increasing temperature leads to the continuous growth of conductive carbon clusters and upon a percolation threshold between 600 and 610 °C with a conductive phase volume fraction of 0.39, conductive phases begin to make contact so that the DC conductivity become detectable. In addition to the improvement of electrical property by increased pyrolysis temperatures, Kercher et al. [20] also reported the temperature-strengthened mechanical properties by studying the carbonization of fiberboards.

In the midst of various lignocellulosic materials, microfibrillated cellulose (MFC) and lignosulfonate (LS) have caught special attention for the elaboration of carbon precursor composites [19–21]. MFC are released from cellulose fibers via mechanical treatments with potential chemical treatment [12]. Thanks to their micro-scaled dimensions, MFC forms a dense fiber network with high strength [23]. LS is a water-soluble macro-polymer composed of a large quantity of cross-linked aromatic cycles (lignin phenyl propane units substituted with sulfonate groups) [24]. It is an industrial byproduct from the production of wood pulp using sulfite pulping. The composites elaborated from MFC/LS slurries are self-standing with MFC playing the role of mechanical reinforcement whereas LS ensures the carbon yield after pyrolysis (LS could achieve a high carbon yield up to 50% after 800 °C, compared to the 21% for MFC and the 3% for CP) [25,26]. However, a previous work [25] revealed that adding LS into MFC hydrogels led to either a disruption of the hydrogels' stability after 3D printing due to lack of viscosity (with 10%–30% LS), or a loss of shape definition because of the long restauration time (with 50% LS). Since LS is an essential component to the composite due to its large contribution to the carbon yield [26] that is important to ensure the thermal stability and conductivity of as-elaborated bio-carbons, one solution to improving the hydrogels' printability while keeping using a large quantity of LS in the formulation is to add appropriate additives. Cellulose and its derivatives were characterized to have a high viscosity and shear-thinning property [27] in their water suspensions. Thereby, the commercial cellulose powder (CP) was chosen as the additive in this work.

A screw-pump based 3D printing technic was used as the principal forming method for elaborating MFC/LS/CP carbon precursor, owing to the fact that all pristine materials are water-processable and could form appropriate hydrogel for printing. The interest of using 3D printing in this work mainly consists in its flexibility to produce samples in various forms and dimensions in order to meet different characterization purposes. For instance, as the simplest form, monolines were printed only for tensile tests. More excitingly, electrodes could be directly printed using a two-head printer with one head firstly printing a web-like structure then another filling the web holes with other types of hydrogel (probably electrochemistry-strengthen components). As a result, 3D printing not only amplifies the potential applications of MFC/LS/CP as a printable hydrogel but also proposes an unexplored way to elaborate electrodes of next generation.

In addition to the thermal stability [28], biomass-derived carbons could acquire important porosity [29], interesting electrical property and mechanical strength with regard to their comparatively low density [30], making them a promising materials for electrodes in energy storage devices [31]. In the current work, the MFC/LS/CP hydrogel was firstly examined in hydrogel rheology. Later, the "green" carbons from MFC/LS/CP precursor were elaborated using 3D printing with subsequent pyrolysis and were characterized in terms of thermal stability, morphology, mechanical strength, electrical conductivity and microstructure evolution.

2. Materials and methods

2.1. Materials and hydrogel preparation

2% (w/w) MFC hydrogel was provided by FCBA (Saint Martin d'Hères, France). It was produced from bleached hardwood (birch) kraft pulp via a mechano-enzymatic protocol along with subsequent homogenization at high pressure. Sodium lignosulfonate (NaLS or simply LS) was purchased from Carl Roth GmbH + Co. KG (France). It is in the form of a brown powder with a sodium content reaching 9%. The elementary analysis of used MFC and LS could be found in a previous work [26]. High purity cellulose powder (CP) from cotton was purchased from Sigma-Aldrich (France) with a nominal particle size of 50 μm. All three materials were used as received.

Hydrogel was prepared by adding LS and CP powder into the 2% MFC hydrogel with a mass ratio of 1: 49: 14 corresponding to the dry matter of MFC: LS: CP, respectively. A commercial planetary blender (RP10, Proline) was used to homogenize the tri-component hydrogel.

2.2. Rheological tests

Rheological tests were conducted in two modes: simple shear mode for viscosity measurements and thixotropic mode for thixotropic tests. Regardless of modes, all rheological measurements were performed by using a rotational physical MCR 301 rheometer (Anton Paar) in a plate-cone configuration. A cone with 50 mm diameter and 1° angle was used and the gap was set to 1 mm. A transparent cover was used to prevent water evaporation during measurements. Temperature of the plate was maintained at 23 °C.

Viscosity measurements were carried out for all suspensions by repeating several cycles with shear rate ranging between 10^{-3} and 10^{3} s^{-1} with about 10 min relaxing time between each cycle. Four measuring points were set for decay with 10 s between each measuring point. Thixotropic measurements were carried out by maintaining the shear rate at 1000 s^{-1} for 20 s before a sudden drop to 0.1 s^{-1}. Samples' viscosity and stress responses were recorded as a function of time.

2.3. Elaboration of carbon precursors by 3D printing and subsequent air drying

MFC/LS/CP carbon precursors were elaborated using a fused deposition modeling (FDM) 3D printer (Leapfrog, Creatr HS model) equipped with a screw-pump paste extruder (Wasp, claystruder). The tri-component slurry was stored in a syringe with the plunger being pushed under a steady pressure (about 1 bar) and it passed through a dispensing screw-pump before being printed via a 0.5 mm needle. The printing speed, the width of filament as well as the layer height were set to 550 mm/min, 0.6 mm and 0.33 mm, respectively, in order to attain a good printing definition at a relatively high printing speed. Samples printed in various forms and patterns (such as cylinder, disc and web) were then air-dried at ambient temperature.

Only monolines of MFC/LS/CP mixture were printed using a 1 mm needle for bending test purpose. They were then air-dried in ambient temperature.

2.4. Pyrolysis and thermal characterization by TGA/DTG

Pyrolysis of printed and then dried composites was conducted in a tubular oven (Carbolite®, type 3216) under nitrogen flux. The heating program is shown in Table 1, with reference to Kercher at *al.* [20]. Chars at the exit of oven were washed by HCl solution to eliminate the mineral matters water by following the protocol of Takagi et al. [32].

The thermal stability of MFC/LS/CP composites was examined by thermogravimetric analysis (TGA) in a thermobalance (STA6000, Perkin Elmer) under nitrogen atmosphere. The temperature program has been detailed in an earlier work [26].