Thermal characterization and kinetic analysis of microfibrillated cellulose/lignosulfonate blends

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ABSTRACT

The water-processable microfibrillated cellulose (MFC) and sodium lignosulfonate (NaLS) system was used for the first time as carbon precursor. After drying and one-step pyrolysis up to 800 °C, the resulting bio carbonaceous char can acquire considerable electrical conductivity and porosity, making it a promising electrode material in energy storage devices. The present work characterizes MFC and NaLS separately as well as in blends in terms of morphology (SEM), structure (FTIR) and thermal stability (TG–MS). DTG patterns illustrate that MFC degrades in a narrow temperature range but at high reaction rates, whereas NaLS reacts more steadily in a larger temperature range. The thermal degradation rate of a MFC/NaLS blend differs from an additive weighted thermal degradation rate of each component: MFC and NaLS. The presence of sodium in the blends induced catalytic effects and made MFC decomposition to shift toward lower temperatures. This observation could be kinetically interpreted as a decrease of the MFC thermal degradation activation energies in the composites. The kinetics of MFC/NaLS blends is investigated by both model-free and mode-based methods, with the latter providing more appropriate Arrhenius parameters that allow reproducing the experimental curves.

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1. Introduction

Carbon materials derived from biomass are attracting increasing attentions nowadays for multiple reasons. Firstly, biomass carbon precursors, mainly wood components such as cellulose and lignin, are renewable sources and are thus eco-friendly and low-cost. Besides, synthesis methods for such carbons are comparatively simple, since for most of cases, one-step heat treatment in inert atmosphere is sufficient. Moreover, the resulting carbons from biomass precursors reach adequate electrical conductivity [1,2] and mechanical strength [3], together with a highly porous 3D structure, conferring a large number of possibilities such as to be employed as electrode materials in energy storage devices.

Cellulose is the most abundant organic polymer on Earth and consequently has been firstly investigated as a bio-carbon precursor. Currently, the development of novel isolation and homogenization methods makes it possible to extract cellulose microfibrils from wood pulp with dimensions in a scale of microm-

eters or even nanometers. The so-called microfibrillated cellulose (MFC), after extraction, is gel-like suspension, presenting shear-thinning and thixotropic characteristics [4,5]. Paper made from pure MFC is at least three times mechanically stronger than that made of traditional cellulose pulp [6], mainly owing to a larger number of hydrogen bonds. Synthesis of MFC carbons by one-step pyrolysis have been seldom reported, but analogue to that of cellulose, similar decomposition allure as a function of temperature is supposed to be achieved with a carbon yield up to 20% [7], depending on the heating rate. The final carbonized MFC paper maintains a web-like structure, ensuring the basic mechanical strength as well as potential electrical current pathways for further electrochemical applications [8–10].

Sodium lignosulfonate is a by-product from wood sulfite pulping process and is used as an industrial substituent of lignin for lignin-based carbon synthesis. Equally high carbon content (over 60%) and aromatic macromolecular structure but much lower manufacturing cost, compared to lignin, makes NaLS a promising bio-carbon precursor. Moreover, the brown-powder form of NaLS is water soluble and thus is water-processable. The printability of NaLS/MFC mixed solutions by a 3D extruder has been demonstrated in an earlier work [11]. 3D printing of such blends allows produc-

ing self-standing carbon precursors with various dimensions and forms in an easy way. However, unlike lignin, studies on the thermal analysis of NaLS are scarce in the literature and to the best of our knowledge [12–14], the decomposition process is far more complicated than that of lignin probably due to the extra sulfonate groups and the catalytic effect of inherent alkali species.

Pyrolysis of biomass is a rather complex process including multi-reaction steps through which various components decompose simultaneously. The coupled heat and mass transfer phenomena for thermally thick particles add complexity to the process. Any of these factors, such as sample composition, pyrolysis atmosphere, heating conditions, catalysts, heat and mass transfer limitations, could modify biomass pyrolysis pathways. Experimental thermogravimetric (TG) technics are commonly used to monitor the biomass thermal decomposition and provide mass-temperature data for the purpose of kinetic modelling [15]. Additional information on the decomposition reactions pathways can be obtained by coupling the TG apparatus to gas analyzers such as FTIR gas analyzer, µGC or mass spectrometer [15]. In the present work, a mass spectrometer was coupled with the TGA to acquire more information on the type of gases produced during the pyrolysis [12,13,16,17].

Wood components have been largely investigated in terms of kinetics [18–22] but neither for NaLS nor for the mixtures of NaLS and MFC, to the best of our knowledge. Two main mathematical approaches are currently used to obtain kinetic parameters of biomass based on its TG results: model-based and model-free (isoconversional) method [23–25]. The former is based on a parallel reactions scheme for which the complex decomposition process of biomass during pyrolysis could be divided into a set of independent and parallel reactions, each of which is related to the decomposition of one single "pseudo-component" [18,23,26]. Therefore, the total conversion (or conversion rate) of the biomass is the linear weighted combination of its different pseudo-components. The conversion rate of each pseudo-component presents an Arrhenius dependence on temperature [27] and depends simultaneously on the selected reaction model [28]. The Arrhenius triplet, including pre-exponential factor A_i, the activation energy E_i of each pseudo-component, and the selection of the reaction model are determined by minimizing the difference between the modelled TG data and the experimental ones [18,23,26].

Model-free method (isoconversional) allows predicting Arrhenius parameters without previous assumption of a reaction mechanism [15,21,29]. It is based on an isoconversional hypothesis, which stipulates that the reaction rate at a given extent of conversion depends only on the temperature [15,21,29]. The first empirical isoconversional equation was proposed by Kujirali et al. [30] to evaluate the temperature dependence of materials decomposed under isothermal conditions. Later and since the 1960s, in non-isothermal kinetics, both differential and integral isoconversional methods have been developed. The latter is more often used although the resulting temperature integral does not have an exact analytical solution in closed form. In practical, the temperature integral can be approximated by using different empirical formulas [15], which accounts for the variety of integral methods.

Both model-based and model-free methods have their own advantages and shortcomings. Kinetic triplets (for the same material degrading under same conditions) that are determined by model fitting approach are not always consistent when different reaction functions are used [25,31,32]. Due to "kinetic compensation effect" [33], since Arrhenius parameters are highly correlated with the reaction model, they can be forcibly adjusted to accommodate any selected model and thus result a suitable fitting to the experimental curve. However, model fitting method still provides the closet modelling results to the experimental curve owing to its regression nature. When it comes to isoconversional approach,

there is no concern about the model selection influence, but the Arrhenius parameters obtained from such method could also be confusing if different approximation formulas are used for temperature integral. Consequently, some researchers [23,24] suggest to combine the power of both methods in terms of kinetic analysis and in the present work, such a combined routine is also used.

The current study evaluates the thermal behaviors of NaLS/MFC system and proposes for the first time a complete kinetic model for such composites. The modelling approaches will be detailed in Section 2.4.

2. Materials and methods

2.1. Materials

2% (w/w) MFC hydrogel was supplied by FCBA (Saint Martin d'Heres, France). It was produced from birch kraft pulp following a mechano-enzymatic protocol with subsequent homogenization at high pressure. NaLS, in the form of brown powder, was purchased from Carl Roth GmbH + Co. KG (France) with Na content reaching 9 wt.% (see Appendix A and B for more detailed elemental analysis results). Various quantities of NaLS were added into a known quantity of the 2% MFC hydrogels, followed by an agitation step, in order to obtain a series of mixed suspensions with various NaLS/MFC mass ratios. MFC and MFC/NaLS films are made from corresponding suspensions by one-step casting.

2.2. Morphological and structural characterization

Morphological characterization was performed on the MFC film, NaLS powder as well as one composite of 33% MFC and 66% NaLS using scanning electron microscopy (FEI-Quanta 2000, ESEM^{TM}). Chemical structure characterization is conducted with a Perkin Elmer FT-IR spectrometer (Perkin Elmer, USA). Each sample was embedded in a KBr pellet and spectra were recorded in the wave number range of 4000–600 cm^{-1} with a resolution of 2 cm^{-1} and an accumulation of 32 scans per analysis. Absorption spectra were obtained using ATR mode and then normalized to one cellulose band at 1110 cm^{-1}.

2.3. Thermal characterization by TG–MS

Thermogravimetric experiments are performed in a SETARAM TG92 thermobalance under helium atmosphere. A quadrupole mass spectrometer (OmniStar, PFEIFFER, Germany) is coupled to the TG analyzer through a transfer line heated at 180 °C. Paper-formed samples are previously cut into tiny fragments and the mass of each sample is controlled to be less than 12 mg in order to avoid mass and heat transfer limitations during pyrolysis. TG data are recorded for all samples in a temperature range from 150 °C to 800 °C at heating rate of 5 °C/min. Extra runs at heating rates of 2.5, 10 and 15 °C/min were performed only on pure MFC and NaLS samples for the isoconversional kinetic analysis. Mass spectra were recorded under electron ionization (70 eV) within the m/z 1–200 range. However, only important molecules were selected for the interpretation. The recorded intensities are normalized to those of helium and to the initial sample mass. Each TG–MS experiment is duplicated in order to ensure the reproducibility of the results.

2.4. Kinetic analysis

2.4.1. Model-based approach

The conversion degree of a matter is defined in Eq. (1) as a function of the initial mass (m_0), the final mass (m_f) and the current mass (m), derived from the TG data of the sample. The total conversion (or conversion rate) of biomass is the sum of those of its