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Humins as promising material for producing sustainable carbohydrate-derived building materials

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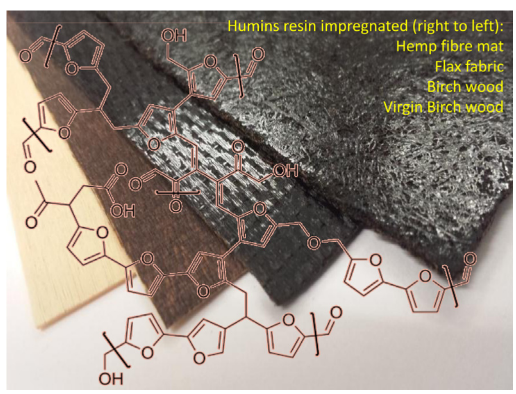
HIGHLIGHTS

- Humins are original unique macromolecules, sub-products during polysaccharide conversion.
- Furfuryl alcohol/humins resins with good viscosity, stability and curing behaviour were prepared.
- New thermosetting materials suitable for applications in a.o. building products were produced.

GRAPHICAL ABSTRACT



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ABSTRACT

Nowadays biobased building materials are used in various fields and for a wide range of applications such as polymers, fillers, coatings, adhesives, impregnation materials or high performance composites. This work focuses on humins, a biomacromolecular by-product of a HydroxyMethylFurfural/FuranDiCarboxylic Acid biorefinery. Humins are obtained by acidic treatment of polysaccharides and show very interesting potential as a reactive, semi-ductile thermoset matrix to impregnate cellulosic fibres. Therefore, humins have the essential characteristics to develop a new class of thermoset materials and composites, offering excellent possibilities to increase the renewable carbon content of the final products and improve its properties. A proper characterization of the neat humins in terms of solubility, flow behaviour and thermal resistance is essential in order to find the optimal parameters of processing humins solutions as well as co-reactive mixtures for impregnations or to prepare composites. In addition the study further indicates that humins enhance the modulus and the tensile strength of pure polyfurfurylalcohol resins. It was also shown that there is a difference in behaviour when sulfuric acid or maleic anhydride is used as initiator. The most optimal initiator will depend on application and preferred processing conditions. These encouraging results assure an important future for humins as economic green matrix for the production of composites and wood impregnation.

1. Introduction

One of the current efforts of both academic and industrial research focuses on the use of biomass as a renewable source for

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platform molecules. The major challenge is to find adequate sustainable alternative resources to fossil feedstocks. In this regard, also lignocellulosic biomass, i.e. the non-edible part of plants, can be an important source of fuels and chemicals. As an example, starting from (hemi-)celluloses, biorefineries can produce furan derivatives and levulinic acid (LA) which are positioned in the "top 12" of value added molecules from carbohydrates [1–8].

The growing interest to develop sustainable biomass conversion processes at large scale has been exemplified by the SME Avantium, a CleanTech top 100 company (http://www.cleantech.com/indexes/global-cleantech-100/). Avantium has developed the YXY Technology. The YXY technology platform produces a wide range of novel materials and products, all 100% biobased, by converting plant-based sugars into chemical building blocks, like Furanics and Levulinics, for plastics and other applications. YXY is a game-changing technology that offers biobased products and fuels with superior properties at market competitive prices [19]. The basic philosophy behind Avantium's YXY technology is to develop products from renewable sources that compete on price and performance and with a superior environmental footprint. A pilot plant is operating on a 24/7 basis since 2011 to convert carbohydrates into Alkoxymethylfurfural (RMF) compounds, further processed to a new class of furanic building blocks based on FuranDiCarboxylic Acid (FDCA) denoted as YXY [9,10]. FDCA resembles the bulk chemical terephthalic acid and can be used as building blocks of polymers such as polyesters, polyamides and polyurethanes. It was shown that producing the polyester PEF, using FDCA and mono-ethylene glycol, polymers can be produced with strongly improved properties compared to PET [10–12].

Moreover, biorefineries will be challenged to valorise the by-products accompanying glucose or fructose conversion into these molecules. For example, the synthesis of 5-hydroxymethylfurfural (HMF), 5-alkoxymethylfurfural and levulinic acid (LA) by acid catalyzed fructose dehydration, is complemented with the formation of substantial quantities of a black tarry by-product, a complex polyfuranic polymer, called humins [6,7,13–18]. In the case of the YXY process two main classes of side compounds are produced: humins and levulinic acid/alkyl levulinates [19,25]. Recently, the establishment of the company Synvina, a joint venture between Avantium and BASF was announced, its main target the building of the first commercial scale FDCA plant as well as launching FDCA and PEF to the market. This plant of around 25–50 ktonnes/year FDCA output will also produce 10's of ktonnes of humins.

Despite humins are known for almost a century [20,21], and as product resulting from prolonged sugar degradation reactions in the caramelisation process, its main application is still limited to energy and heat applications such as burning and gasification [13]. Its valorisation into higher added-value applications will be key for making biomass conversion processes economically feasible many. Recently we showed with initial work that humins can be successfully used as a matrix to produce composites [18,22]. The polyfuranic structure of humins and its high functionality are important structural factors that should be considered and even exploited in order to develop interesting biobased thermosets materials or as a matrix for impregnations and composites.

Humins are heterogeneous amorphous biomacromolecules, considered to have the idealized morphology of spherical core-shell architecture [22]. The chemical structure of humins consists of furfural and hydroxymethylfurfural moieties also with carbohydrate, levulinate and alkoxymethylfurfural chains linked together into macromolecules by ether, acetal bonds or aliphatic linkages. The nature of terminal groups could be of carboxylic, ketone, aldehyde and/or hydroxyl nature. Also the presence of certain solvents such as acids or alcohols during the carbohydrate dehydration reactions could instigate the appearance of other functional groups such as alkoxy and ester groups [4,5,15,16,23,24].

The mechanism of the humins formation is supposed to be an acid catalyzed condensation between its intermediates formed and possibly also with the starting carbohydrate during their transformation to HMF/MMF/LA, leading to a network of furan rings. A model structure by furan rings connected via alkylene moieties is proposed by van Zandvoort et al. [15–17] and schematized here on Fig. 1.

In the present work, humins from Avantium's biorefinery derived from acid-catalyzed dehydration of fructose in methanol produced in YXY's pilot plant were studied as resin components. Understanding the nature and the properties of humins is one of the objectives to evaluate its application potential. Various investigations were employed to gain more knowledge on its behaviour and reactivity. Solubility tests, Fourier Transform-InfraRed (FT-IR) spectroscopy, UV spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy, Differential Scanning Calorimetry (DSC) and ThermoGravimetric Analysis (TGA) have proven to be very useful to show the capacity of humins to auto-crosslink, or to lead to resins or composites after various chemical modifications to resins or foams.

The influence of humins structure and chemical compositions on chemical reactivity has shown that this material is very versatile, permitting the development of thermosets with very promising properties for impregnation of wood, natural fibres or paper. Comparative studies with other furanic thermosets demonstrate that superior properties have been achieved compared to polyfurfuryl alcohol (PFA) and PFA/lignin composites [18–22].

The temperature of resin curing is a key issue for a successful industrial introduction. It was shown that using co-catalysis with a strong acid can reduce the temperature of curing. This investigation is particularly useful for the "2 steps" resin curing strategy. Indeed, after the first introduction of 1/2 the amount of catalyst and the pre-heating, the resin was cooled down and then a second batch of the same or different co-catalyst was added at room temperature. The present work highlights the crucial role of resin composition, time and temperature on structural and morphological changes of resins and properties of obtained composites.

2. Experimental section

2.1. Materials

Furfuryl alcohol (FA) (purity: ⩾98%), sulfuric acid (purity: ⩾96%), maleic anhydride (MA) (purity: ⩾99%), isopropyl alcohol (IPA), acetic acid (AcOH), methyl levulinate (ML), diethyl ether (DEE), acetonitrile (AN), acetone (AcO), and methanol (MeOH) all analytical reagents were purchased from Sigma-Aldrich and were used as received.

Humins were produced by Avantium Chemicals at their Pilot Plant in Geleen, The Netherlands, by acidic conversion of fructose in methanol solvent. These humins were distilled under high vacuum to reach low 5-hydroxymethylfurfural (HMF) and 5-methoxymethylfurfural (MMF) content (<5% by weight). The humins composition obtained by elemental analysis (ICP) is approximately 60 wt.% C, 32 wt.% O, and 5 wt.% H. Their heating value is around 23 MJ/kg. Humins have the appearance of very viscous, shiny, black bitumen. Humins complex viscosities at 60 °C are around 69–254 Pa.s, depending on the batch composition. These values were determined in accordance with ASTM D7175 using an Anton Paar MCR 102 rheometer at 10 Hz.

Cellulose composites were made with Whatman 40 filter paper having a diameter of 110 mm and a weight of 900 mg.