



HUMINS AS PROMISING MATERIAL FOR PRODUCING SUSTAINABLE POLYSSACHARIDE-DERIVED BUILDING MATERIALS

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Abstract

The chemical industry is pushed by public opinion and brand owners to a more sustainable resource utilization such as changing from fossil feedstocks to biomass which is a renewable resource. The major component of biomass are polysaccharides, so to drive the competitive utilization of (2nd generation) polysaccharides towards non-food applications and thereby creating biorefinery supply chains it is essential that all (side-)products are valorized at maximal added value. 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 FDCA biorefinery. Humins are obtained by acidic treatment of polysaccharides and show very interesting potential as a reactive, semi-ductile thermoset matrix to impregnate cellulosic fibers. These encouraging results assure an important future for humins as economic green matrix for the production of textile composite and wood impregnation for instances.

Keywords:

Biorefinery; Polysaccharide; Humins; Thermosets; Composites; HMF; FDCA

1 INTRODUCTION

One of the current efforts of both academic and industrial research focuses on the use of biomass as a renewable source for platform molecules. The major challenge is to find adequate sustainable alternative resources to fossil feedstocks. In this regard, lignocellulosic biomass is 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 top of value added molecules from carbohydrates [Werpy 2004], [Bozell 2010], [van Putten 2013], [Eerhart 2014], [Patil 2011], [Patil 2012].

The growing interest to develop sustainable biomass conversion processes at large scale has been exemplified by the SME Avantium, a CleanTech top 100 company. Avantium operates a pilot plant (24/7 since 2011) to convert carbohydrates into Alkoxymethylfurfural (RMF) compounds, further processed to a new class of furanic building blocks based on FDCA denoted as YXY. FDCA resembles the bulk chemical terephthalic acid and can be used as building blocks of polymers. We have shown that producing polyesters using FDCA and ethylene glycol polymers can be produced with strongly improved properties compared to PET [de Jong 2013], [Codou 2014], [van Berkel 2015].

Moreover, biorefineries are confronted with the valorization of some 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 [Patil 2011], [Patil 2012], [Hoang 2013], [Pin 2014].

In the case of Avantium's process two main classes of side compounds are produced: humins and levulinic acid/alkyl levulinates [Pin 2014], [Avantium 2015].

Despite humins are known for almost a century [Schweizer 1938], [Schweizer 1940] 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 [Hoang 2013]. Its valorization into higher added-value applications will be key for making economically feasible many biomass conversion processes. Recently we showed with initial work that humins can be successfully used as a matrix to produce composites [de Jong 2013], [Pin 2014]. 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 [Sevilla 2009]. The chemical structure of humins consists of furfural and hydroxymethylfurfural moieties also with carbohydrate, levulinic and alkoxyethylfurfural 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.

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. [van Zandvoort 2013] and schematized here on Fig. 1.

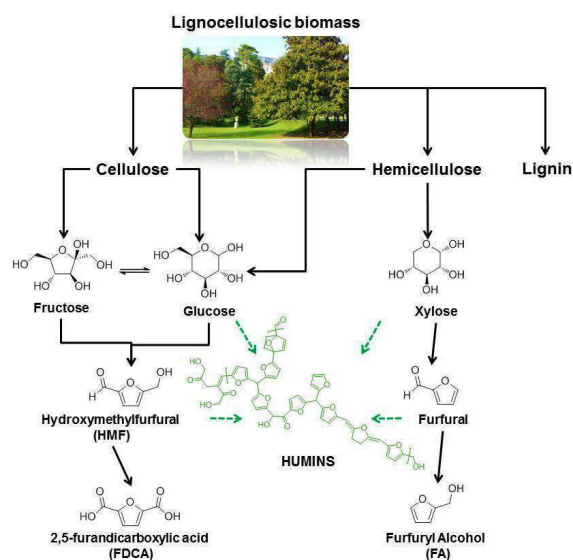


Fig. 1: Bio-derived platform and humins as condensation by-product

In the present work humins from Avantium's biorefinery derived from acid-catalyzed dehydration of fructose in methanol 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 reactivity. Solubility tests, FT-IR, UV, NMR, DSC and TGA have been 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 fibers or paper. Comparative studies with other furanic thermosets demonstrate that superior properties have been achieved compared to polyfurfuryl alcohol (PFA) and PFA/lignin composites [de Jong 2013], [Pin 2014].

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 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: $\geq 98\%$), sulfuric acid (purity: $\geq 96\%$) and maleic anhydride (MA) (purity: $\geq 99\%$) were purchased from Sigma-Aldrich and were used as received.

Humins are directly 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 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.

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

Resins preparation: The reference resin is based on PFA and consisted of 95% of FA and 5% of acid catalyst (MA) on weight basis. This quantity of catalyst was chosen as the optimal concentration, considering that humins will interact with the acidic catalyst and thus decrease the intrinsic FA reactivity.

To prepare PFA/Humins thermoset resin a 40/55/5 (w/w) FA/Humin/MA ratio has been used, 5% being the initiator part. Preceding the addition of the acidic initiator, the FA was mixed with humins at 105 °C for 20 min under mechanical stirring until a homogeneous, viscous, black liquid was formed. Then, the maleic anhydride (5% w/w) was introduced in two equal steps of 2.5% w/w. On the basis of differential scanning calorimetry (DSC) investigations (not shown here), introduction of viscous condensed humins into the system decreases the overall reactivity and shifts the polycondensation peak to a higher temperature compared to those of the pure FA/MA mixtures. After cooling to 80 °C, the last addition of 2.5% w/w initiator was done. Subsequently, the mixture was stirred for another 5min and cooled to room temperature.

In parallel, sulfuric acid has been tested as co-catalyst. The quantity of sulfuric acid has been fixed for this first experiment to 1 % (w/w) of pure acid ($\approx 96\%$) diluted in an aqueous solution of 20 % by weight. The quantity of sulfuric acid should be further tailored in function of the reached curing temperature.

A homogeneous, viscous, shiny, black resin was obtained in each case. The resins were stored in the fridge, and no phase separation was observed, even after several weeks.

The different cellulose composites were processed by impregnation of the above-mentioned resins with cellulose filter. After impregnation of the filter at room

temperature, the system was pressed and put in an oven for final curing at 160°C during 3 hours. After curing, the final cellulose/resin ratio was about 1/1.

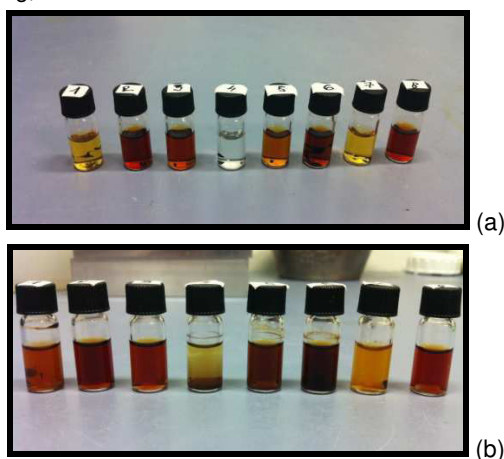


Fig. 2. Humins solutions in different solvents before (a) and after 20-90°C two heating-cooling cycles at 10°C.min⁻¹

2.2 Experimental techniques

Solubility tests have been done using Crystal16® multiple-reactor system. The solubilities of ~0.3 % solutions of humins in following solvents: isopropyl alcohol (IPA), acetic acid (AcOH), methyl levulinate (ML), diethyl ether (DEE), acetonitrile (AN), acetone (AcO), water, and methanol (MeOH) have been studied. The experimental vials containing teflon mini agitator followed the temperature program via an aluminum reactor block. Two heating-cooling cycles from 25-90°C at 10°C.min⁻¹ have been applied and the quantification of solubility has been done by turbidity measurement, in transmission mode.

Infrared Spectroscopy. A PerkinElmer Spectrum BX II spectrophotometer was used in attenuated total reflectance (ATR) mode with a diamond crystal. The spectrum of air was recorded as background. A total of 1000 scans with a resolution of 1 cm⁻¹ was recorded for each sample to obtain sufficient sensitivity.

2.3 Thermogravimetric analysis (TGA)

Thermogravimetric measurements were carried out on a TGA 851e from Mettler-Toledo. The microbalance has a precision of ± 0.1 µg. Samples of about 10 mg were placed into 70 µL alumina pans. The samples were heated at 10 °C min⁻¹ from 25 °C to 1000 °C under air and nitrogen gas flow of 50 mL.min⁻¹ to determine their thermal stability.

Tensile Tests. The stress-strain curves were recorded on an Instron 5565 apparatus in tensile mode with crosshead speed of 2 mm min⁻¹. After curing, the samples were cut into strips of around 100 × 10 × 0.25 (length × width × thickness) mm. The length between the clamps was fixed to 40 mm. For each composite, the average values and standard deviations of Young's modulus and tensile strength were calculated from seven measurements.

2.4 Rheometry

Rheological behavior of humins was followed using an Anton Paar rheometer. The measurements were operated on plate-plate geometries (25 mm diameter and 1 mm gap) with strain convection heating. The tests were carried out in isothermal programs at 40, 80 and 100°C in angular frequency mode with oscillation.

3 RESULTS AND DISCUSSION

3.1 Neat humins

Solubility

Humins being generated by condensation of intermediates formed during dehydration of carbohydrates is a solid macromolecular material with heterogeneous aromatic structure and very limited solubility in common solvents. Solubility of humins in various solvents was determined using Crystal16® analytical method (Tab 1. and Fig. 2).

Tab. 1: Humins solutions for solubility studies

No	Humins (mg) /	Solvent (1mL)
1	2.2	IPA
2	2.2	AcOH
3	1.8	ML
4	1.8	DEE
5	1.7	AN
6	2.9	AcO
7	1.4	H ₂ O
8	1.8	MeOH

As example in hot water only a small fraction, around 5%, of humins gave an approximately homogenous solution; in presence of acetone it seems that an extraction of lower molecular weight polymers occurs. Among the eight chosen solvents only three have shown good humins dissolution, i.e. methyl levulinate (100%) acetic acid (~80% at T>35°C) and methanol (~70%) (Fig. 2 and Fig. 3). IPA solvent arrives to extract some humins fractions at a temperature above 55°C. In contrast, in Diethyl Ether the humins are insoluble, though some yellowish small fraction is extracted.

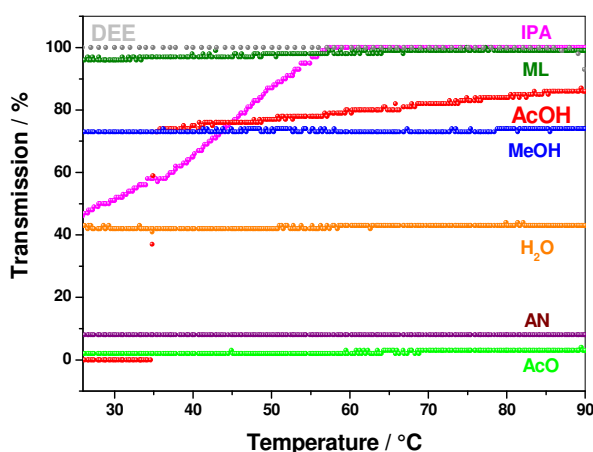


Fig. 3. Solubility as function of temperature for humins solutions at 20-90°C second heating, 10°C.min⁻¹

Rheological behavior

The rheological behavior of humins has been tested in isothermal conditions. Firstly, the temperature of 40°C was chosen to follow the flow behavior of humins at temperature of processing. Then, higher temperatures, of 80 and 100°C have been applied as limit of temperature of utilization, due to chemical changes occurring as presented in thermogravimetry studies.

Figure 4 compares the effect of temperature on the complex viscosity and the evolution of viscosity with

angular frequency. Obviously, the complex viscosity decreases drastically with temperature, with 2 decades from ~1200 Pa.s at 40°C to ~10 Pa.s at 80°C.

At 40°C we can observe a decrease of viscosity with the shear rate which is the sign of a shear thinning behavior. At 80°C and 100°C, the shear thinning behavior is less pronounced than at 40°C. At 100°C some irregularities appears on the curves which might be associated with volatilization of by products at such high temperature.

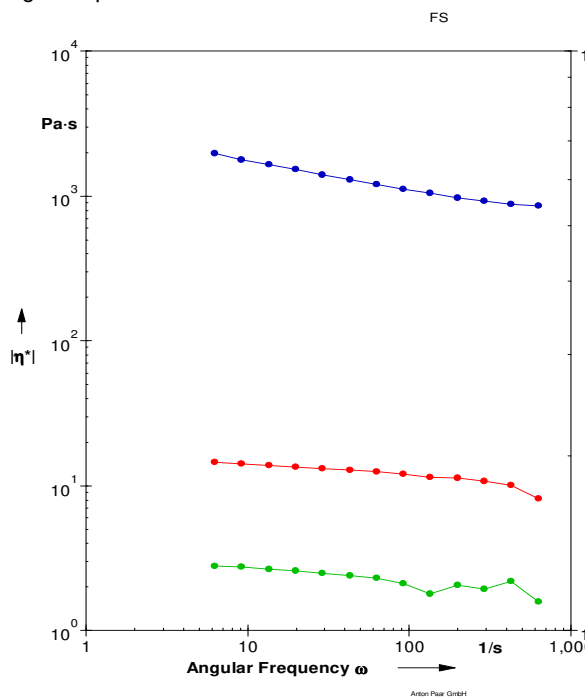


Fig. 4. Humins evolution of complex viscosity in function of frequency at 40, 80 and 100 °C

Thermal stability

Thermogravimetric analyses of humins were performed in both, nitrogen and air environments where the reaction medium favors the pyrolysis or the thermo-oxidative degradation process. The thermal decomposition temperature corresponding to 10% of weight loss ($T_{d90\%}$ on Fig. 5) is ~170°C.

As seen in Fig. 5 the derivative plots of weight loss curve (DTG) show evidence of several steps of degradation and the comparison of thermal degradation of humins in inert and reactive environments shows a significant difference with the reaction medium only in the second part of degradation, i.e. at $T > 480^\circ\text{C}$.

Based on the major DTG curves, the decomposition patterns under N_2 could be divided into 2 regions and that under air into 3 regions. The first region is almost identical for both media denoting a primary devolatilization and structural changes in the temperature range from 120-270 °C. During this step the sample lost around ~29.41 % of weight.

Under nitrogen, the second step of degradation occurs in 300-600°C temperature range. In these two steps of degradation, humins undergo dehydration, decarboxylation, decarbonylation together with the decomposition of the network structure. Some condensations/recombinations of formed fragments are possible, the final char yield being around ~38 %.

Under oxidative medium the second and the third decomposition steps appear as peaks in DTG curve at

about 300 – 400°C and 420 – 720°C respectively. In the last temperature range the humins thermo-oxidative degradation is very significant, the final residue being around 4.15%.

In conclusion, humins are very sensitive to thermal treatment, resulting thermal degradation involving complex chemical, thermolysis or thermo-oxidative mechanisms. To obtain a scenario of thermal scissions of networks, a deeper study of mechanism of degradation is needed.

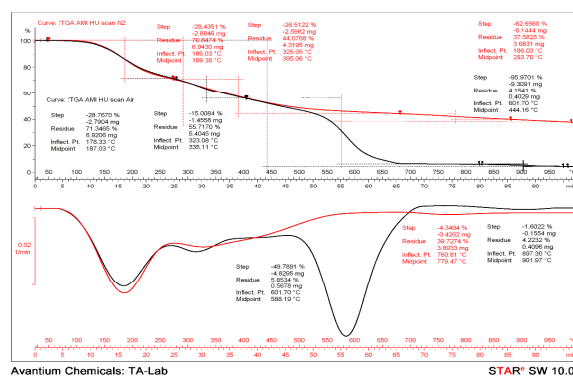


Fig. 5: Thermogravimetric analysis of humins under air (black) and under N_2 (red) systems at $10^\circ\text{C}\cdot\text{min}^{-1}$ relative weight loss (upper part of the Figure) and derivative weight loss (lower part)

3.2 PFA/Humins thermosets and composites

FT-IR Analysis of Humins and PFA/Humins Thermoset Resins

The fructose-based humins spectrum is shown in Figure 6. The molecular structure of humins is mainly derived from HMF and 5-methoxymethylfurfural (MMF). The peak at 1515 cm^{-1} is assigned to C=C stretching in furan rings while the peak at 1020 cm^{-1} corresponds to C-O stretching. In the same case as PFA, the composite peaks between 800 and 750 cm^{-1} are attributed to the out of plane C-H bending of the different substituted furans. According to Patil et al. [Patil 2011] the peak at 1712 cm^{-1} together with the peak around 1600 cm^{-1} in humins are characteristic of carbonyl group conjugated to an alkene group. Finally, it should be mentioned that the feature at 1665 cm^{-1} could arise from the C=O stretch of the MMF and HMF's aldehyde group.

The spectrum of the pre-polymerized 40/55H/5 resin corresponds approximately to the superposition of the signals from the PFA resin and those from the humins. Some features can be attributed to specific interactions between the PFA network and the humins. A new band develops at 868 cm^{-1} which is neither visible in the spectrum of PFA resin or in the spectrum of humins. The peaks appearing within this wave number region are generally attributed either to C-H wagging of methylene linkages or C-O stretching from Diels-Alder cycloadducts. This might indicate that novel kinds of interactions were created between the side chain oxygen groups of the humins and the furanic rings from the PFA. Moreover, clear-cut shoulders appear at 1714 and 1735 cm^{-1} in the carbonyl stretching region. The chemical environment of the carbonyl groups present in the aliphatic parts of the humins has been modified probably due to new interactions with the polyfurfuryl alcohol network. It should also be mentioned that the C-H out of plane bending of the furan rings appears at 798 and 738 cm^{-1} for the 40/55H/5 resin. These peaks are broader and slightly

shifted to higher wavenumbers compared to the PFA resin. It denotes a more complex network of furan rings due to interconnections between the two systems.

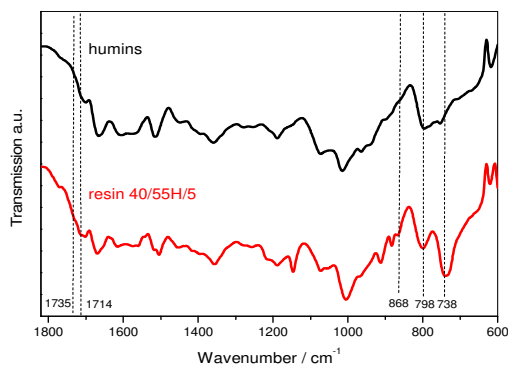


Fig. 6: IR spectra of humins (black) and 40/55H/5 cured resins (red).

Mechanical properties of PFA/Humins composites

Different fibre and lignocellulosic matrices were impregnated by the humins resins resulting in very appealing composites (Fig. 7). To assess physical characteristics the final Whatman composites after impregnation and curing at 160°C were compared to the pure PFA and 40/55H/5 as reference in Fig. 8.

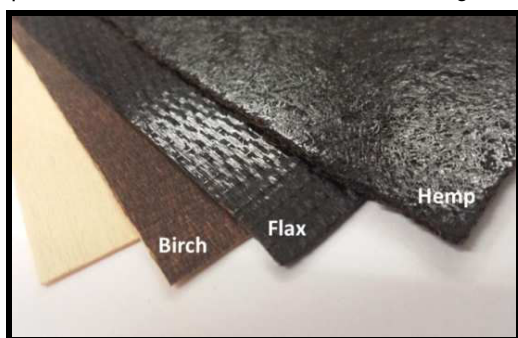


Fig. 7. Impregnation tests on textile fibers and wood.

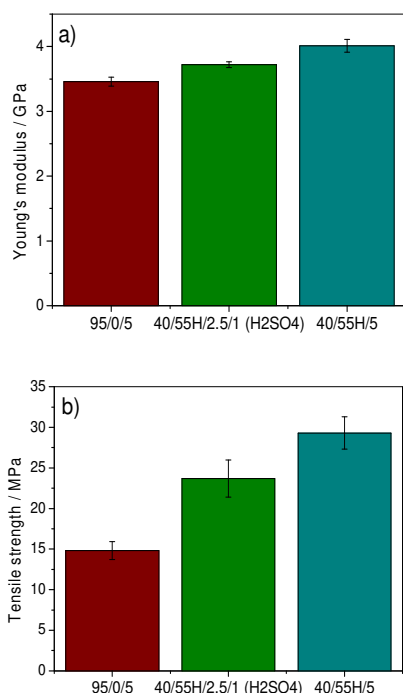


Fig. 8: Influence of sulfuric acid as co-catalyst for resin curing on Young's modulus (a) and tensile strength (b).

The composite with the resin 40/55H/2.5/1 (H₂SO₄) exhibits an average mechanical behaviour between the two references of pure PFA (95/0/5) and humins resins. The Young modulus is very close to the 40/55H/5 composite which demonstrates the importance of the first pre-curing stage with the 2.5% of MA. The tensile strength is quite a bit lower, at around 24 MPa (Fig. 8b). However, the final result is better than for biocomposites processed with neat PFA, and thus showing good omen for several applications. Furthermore, some qualitative tests with a higher content of sulphuric acid have been performed and reveal a good potential of curing for these kinds of resins, at room temperature.

4 CONCLUSIONS

This work shows that humins as by-products from bioprocessing 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. In the first part, we have shown that the proper characterization of the neat humins in terms of solubility, flow behavior 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 the second part, the work gives a short view on the obtained chemical structures after co-reacting with furanic PFA. The study indicates that humins enhance the interfacial adhesion between cellulose and polyfurfuryl alcohol based resins by increasing the modulus and the tensile strength. It can therefore be concluded that incorporating large amounts of humins in PFA resins together with cellulosic fibres/matrix result in biocomposites having great potential for building applications such as plywood, boards, flooring, decking, etc.

5 ACKNOWLEDGMENTS

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