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Biobased thermoset resins: versatility and new horizons offered by furanics

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PURPOSE OF THE ABSTRACT

In the biorefinery processes, carbohydrates can be transformed into various building blocks via catalytic or enzymatic pathways. In particular, 5-hydroxymethylfurfural (HMF) and furfural are two platform chemicals which can be obtained from the dehydration of respectively C6 (fructose, glucose) and C5 (xylose) sugars. Furfural can be used as extractant, solvent, or fuel precursor, but more than 85% is converted to furfuryl alcohol (FA) by catalytic hydrogenation.

Polyfurfuryl alcohol (PFA) is a thermoset matrix prepared from the acid-catalyzed polymerization of FA. The high carbon content, chemical inertness and thermal stability of PFA have led to several applications in foundry molds and fire resistant or corrosive resistant materials. The thermal stability and thermomechanical properties of PFA can be for instance greatly improved by the addition and dispersion of silica nanoparticles presenting different morphologies [1-2]. Moreover, FA impregnation and its in-situ polymerization in wood increase significantly the wood durability. This eco-friendly process allows valorizing softwood into marine applications without employing tropical wood. However, this process requires utilization of protic polar solvents that can generate furan ring open structures in the cross-linked material. Results indicated that formation of open structures were favoured in the presence of solvents, thus leading to modification of the thermo-mechanical properties compared to PFA cross-linked without solvent. [3-4]

The 2,5-furandicarboxylic acid (FDCA) is obtained from controlled oxidation of HMF. FDCA can be condensed with various diols to prepare FDCA polyesters. Poly(ethylene furandicarboxylate) (PEF) is certainly the most pinpointed ones since it is the furanic analogue of the well-implemented poly(ethylene terephthalate) (PET). PEF can lead to multiple applications (i.e. bottles, cast films and fibers) since it possesses greatly improved barrier properties and attractive thermal and mechanical properties compared to PET. However, when sugars are dehydrated into HMF many side-products can be formed such as humins, a black and viscous co-product. Humins are carbonaceous heterogeneous polydisperse macromolecules. Therefore, the valorization of this macromolecular side-product would further improve both the environmental footprint and the process economics. The aforementioned humins consist of furan rings connected via aliphatic linkers, with oxygen-containing functional groups, such as carboxyl, carbonyl, and hydroxyl. We have shown that upon thermal treatment, the humins are very thermo-reactive. [5] They can be cross-linked leading to highly branched furanic networks with relatively high glass transition temperature.

Finally, these humins are also prone for being successfully valorized into thermosetting composites with improved mechanical properties.[6,7]

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS

furfuryl alcohol | humins | thermosets | structure/property relations

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