Supplementary Information File for:

Sustainable Mesoporous carbon nanostructures derived from lignin for Early Detection Of Glucose.

Anne Beaucamp\textsuperscript{a,b}, Mario Culebras\textsuperscript{a,b,c}, Maurice N. Collins\textsuperscript{a,b,c}

\textsuperscript{a} School of Engineering, Bernal Institute, University of Limerick, Limerick

\textsuperscript{b} Bernal Institute and Department of Chemical Sciences, School of Natural Sciences, University of Limerick (UL), Limerick V94 T9PX, Ireland.

\textsuperscript{c} Advanced Materials and Bioengineering Research (AMBER) Centre, Ireland.
Figure S 1: Repeat Units of (a) AL, (b) PLA and (c) TPU (n=7)
Table S 1: Calculation of the Group Molar Attraction Constant $\sum n_i F_i$ for AL, PLA and TPU repeat units

<table>
<thead>
<tr>
<th></th>
<th>F_i *</th>
<th>AL</th>
<th>PLA</th>
<th>TPU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of groups n_i</td>
<td>$\sum n_i F_i$</td>
<td>Number of groups n_i</td>
<td>$\sum n_i F_i$</td>
<td>Number of groups n_i</td>
</tr>
<tr>
<td>-CH$_3$</td>
<td>0.3032</td>
<td>0 0</td>
<td>1 0.3032</td>
<td>0 0</td>
</tr>
<tr>
<td>-CH$_2$-</td>
<td>0.2689</td>
<td>2 0.5378</td>
<td>0 0</td>
<td>46 12.3694</td>
</tr>
<tr>
<td>&gt;CH-</td>
<td>0.1758</td>
<td>4 0.7032</td>
<td>1 0.1758</td>
<td>0 0</td>
</tr>
<tr>
<td>-CH-</td>
<td>0.2485</td>
<td>0 0</td>
<td>0 0</td>
<td>0 0</td>
</tr>
<tr>
<td>-O-CH$_3$</td>
<td>0.236</td>
<td>3 0.708</td>
<td>0 0</td>
<td>0 0</td>
</tr>
<tr>
<td>&gt;C=O</td>
<td>0.5376</td>
<td>0 0</td>
<td>0 0</td>
<td>0 0</td>
</tr>
<tr>
<td>-COO-</td>
<td>0.6677</td>
<td>0 0</td>
<td>1 0.6677</td>
<td>2 1.3354</td>
</tr>
<tr>
<td>-O-</td>
<td>0.2351</td>
<td>2 0.4702</td>
<td>0 0</td>
<td>1 0.2351</td>
</tr>
<tr>
<td>Aromatic CH</td>
<td>0.2395</td>
<td>5 1.1975</td>
<td>0 0</td>
<td>16 3.832</td>
</tr>
<tr>
<td>Aromatic C</td>
<td>0.2006</td>
<td>7 1.4042</td>
<td>0 0</td>
<td>8 1.6048</td>
</tr>
<tr>
<td>Aromatic Meta</td>
<td>0.0135</td>
<td>3 0.0405</td>
<td>0 0</td>
<td>0 0</td>
</tr>
<tr>
<td>Aromatic Para</td>
<td>0.0825</td>
<td>2 0.165</td>
<td>0 0</td>
<td>4 0.33</td>
</tr>
<tr>
<td>6-Membered Ring</td>
<td>-0.0479</td>
<td>2 -0.0958</td>
<td>0 0</td>
<td>4 -0.1916</td>
</tr>
<tr>
<td>-OH aromatic</td>
<td>0.3496</td>
<td>0 0</td>
<td>0 0</td>
<td>0 0</td>
</tr>
<tr>
<td>-OH aliphatic</td>
<td>0.4617</td>
<td>4 1.8468</td>
<td>0 0</td>
<td>0 0</td>
</tr>
<tr>
<td>-O-CO-O-</td>
<td>0.904</td>
<td>0 0</td>
<td>0 0</td>
<td>7 6.328</td>
</tr>
<tr>
<td>-O-CO-NH-</td>
<td>1.04</td>
<td>0 0</td>
<td>0 0</td>
<td>4 4.16</td>
</tr>
</tbody>
</table>
Table S2: Solubility parameter and enthalpy of mixing for AL, PLA and TPU blends: density was measured using a AccuPyc II 1340/ Gas Pycnometer working with Helium

<table>
<thead>
<tr>
<th>Samples</th>
<th>Volumic Mass ρ (kg.m⁻³)</th>
<th>Group Molar Constant $\sum n_i F_i$ ((J.m³)¹/² mol⁻¹)</th>
<th>Solubility Parameter δ (MPa¹/²)</th>
<th>Enthalpy of Mixing per unit of volume (J.m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>1325 *</td>
<td>6.9774</td>
<td>21.91</td>
<td>-</td>
</tr>
<tr>
<td>PLA</td>
<td>1250</td>
<td>1.14</td>
<td>19.91</td>
<td>-</td>
</tr>
<tr>
<td>TPU</td>
<td>1220</td>
<td>30.00</td>
<td>22.59</td>
<td>-</td>
</tr>
<tr>
<td>AL/PLA 50-50 (%vol)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
</tr>
<tr>
<td>AL/TPU 50-50 (%vol)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Figure S 2: Schematics of the synthesis of the AL-PLA CNF. The images were obtained by Helium Ion Microscopy (left) and TEM (right).
Figure S 3: N$_2$ adsorption-desorption isotherm (a) and Desorption pore width distribution (b) of (green) AL-PLA derived CnF; (red) AL-TPU derived CnF and (blue) AL-PLA derived CnF, treated subsequently with nitric acid.
Figure S 4: a) CV of porous AL-PLA CnF at 50mV.s⁻¹, in 0.05 mol.L⁻¹ N₂ saturated PBS at various pH values. b) Evolution of the cathodic peak intensity with varying pH. Inset of b) Plot of $E'_{0}$ vs pH.

Table S 3 : XPS Analysis Results on AL-PLA and AL-PLA with HNO₃ treatment.

<table>
<thead>
<tr>
<th></th>
<th>Atomic Content</th>
<th>Species vs Carbon ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>AL-PLA</td>
<td>91.2</td>
<td>5.4</td>
</tr>
<tr>
<td>AL-PLA at 90 °C</td>
<td>92.2</td>
<td>5.8</td>
</tr>
<tr>
<td>AL-PLA with HNO₃ Treatment at 90 °C</td>
<td>66.2</td>
<td>25.9</td>
</tr>
</tbody>
</table>
Annexe 1 : Determination of the Miscibility of AL with PLA and TPU

Gibbs free energy can be determined to evaluate miscibility of AL with TPU and PLA, as we reported previously \(^1\). A negative Gibbs free energy of mixing is necessary for polymers to be miscible as follows:

\[
\Delta G_m = \Delta H_m - T\Delta S_m; \Delta G_m < 0 \quad (S1)
\]

For a two components system \(\Delta H_m\) can be expressed \(^2\) as a function of the volume fraction \(\varphi_1\) and \(\varphi_2\) of the each components:

\[
\Delta H_m = (\delta_1 - \delta_2)^2 \varphi_1 \varphi_2 V_S \quad (S2)
\]

With \(V_S\), Volume of the system and \(\delta_1\) and \(\delta_2\) the respective solubility parameters of the polymers, expressed in in \((\text{MJ.m}^{-3})^{1/2}\) or \((\text{MPa})^{1/2}\).

Given the second principle of thermodynamics, the entropy can only increased during mixing so \(\Delta S_m > 0\). The magnitude of \(\Delta S_m\) is governed by the specific interaction between the specific polymers and by their molecular weight. High molecular weight polymers tend to present a low mixing entropy. So \(\Delta S_m \approx 0\). Therefore, the condition for polymer miscibility with \(\Delta G_m < 0\) is \(\Delta H_m \approx 0\). This condition is found to be true when the solubility parameters of the polymers are close in value.

Solubility parameters can be estimated using the group contribution method, which was introduced by Small. \(^3\) Each functional group has a contribution \(F_i\) to the total molar attraction of the polymer. \(F_i\) is defined as a function of the cohesive energy \(E_i\) and the molar volume \(V_i\) of a functional group by the equation,

\[
F_i = (E_i V_i)^{1/2} \quad (S3)
\]

With \(E_i\) in J.mol\(^{-1}\), \(V_i\) in m\(^3\).mol\(^{-1}\) and \(F_i\) in \((\text{J.m}^3)^{1/2}\).mol\(^{-1}\).

The solubility parameter \(\delta\) of a polymer is calculated as follows:
\[
\delta = \frac{\rho \sum n_i F_i}{M}
\]  

\( (S4) \)  

With \( \rho \) and \( M \) density of the polymer in kg.m\(^{-3}\) and molar mass in kg.mol\(^{-1}\) of a repeat unit, respectively and \( \sum n_i F_i \) the sum of all the molar group contribution for a repeat unit, in (J.m\(^3\))\(^{1/2}\).mol\(^{-1}\). \(^2\)

The repeat units for AL, TPU and PLA can be found in Figure S1. The structure of AL repeat units is described in \(^1\). As a hardwood lignin, AL presents an equal distribution between Synapyl and Guaiacyl groups with a majority of \(\beta\)-O-4 linkages. Details of the group molar attraction constant calculation can be found in Table S1.

The solubility of AL, PLA and TPU and the mixing enthalpy were calculated using \(( S1 \) and \( S2 \) and are displayed in Table S2. The respective enthalpy of mixing of PLA and TPU blends show strong miscibility between TPU and AL while PLA is immiscible with the lignin.
References: