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Supporting information

Surface modification of sized vegetal fibers through direct fluorination for eco-composites

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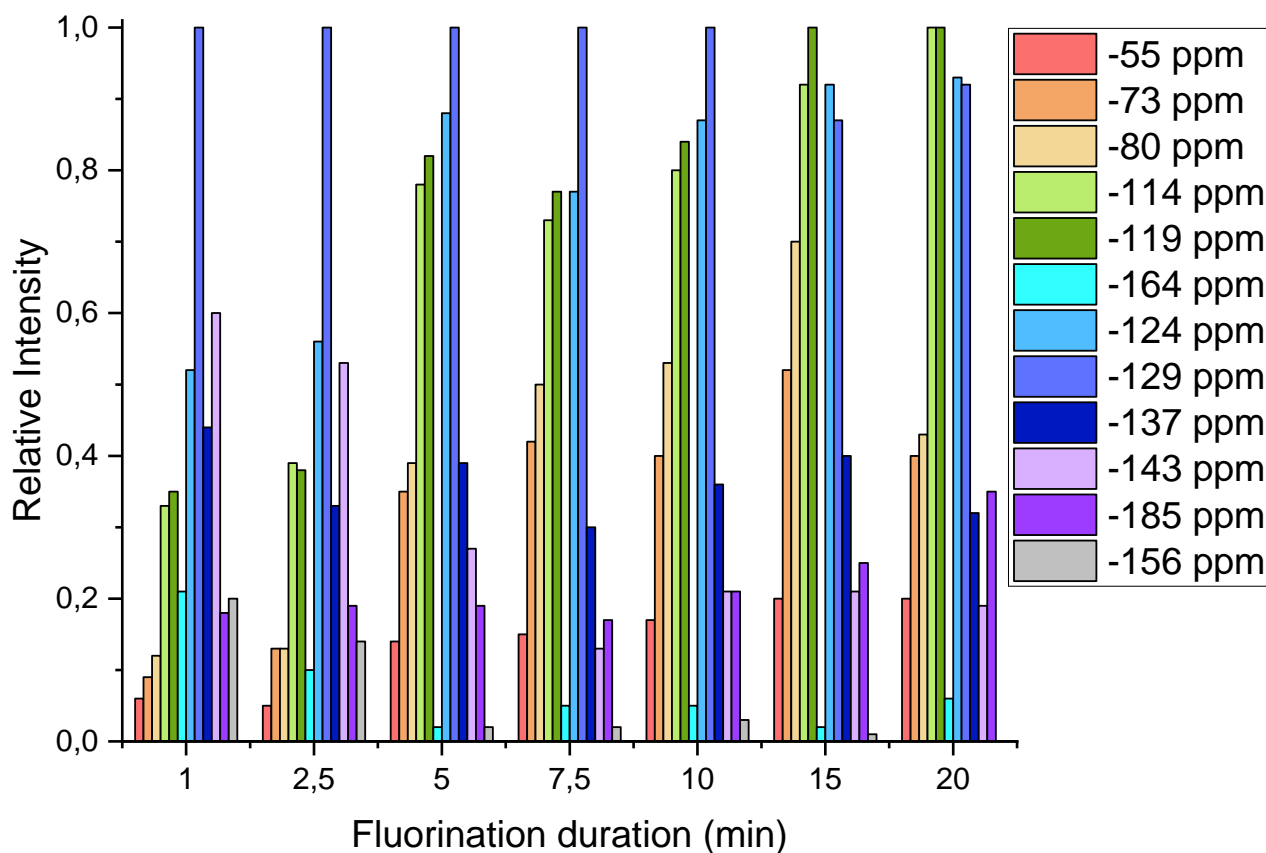


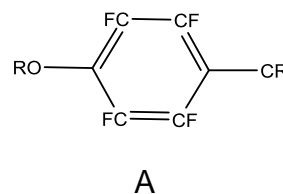
Fig. 1: Evolution of the relative intensity of ¹⁹F NMR bands versus fluorination

duration

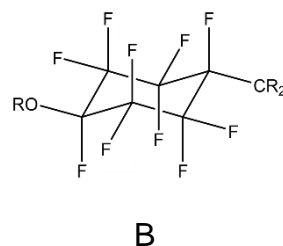
Thanks to the Fig. 1, the following conclusions could be done:

The presence of a band at -156 ppm confirms the existence of the chemical group (A) (presented on the right).

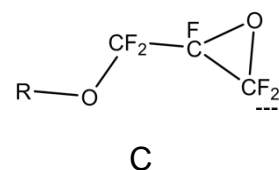
In addition, this band is present for 1 min and 2 min 30s of fluorination, but then its intensity is close to 0. This means that this group is only a “reaction intermediate” which will quickly react with fluorine to form another compound.



Bands at -124 ppm, -129 ppm and -137 ppm are linked with CH₂ of the 6 carbons ring (B). We can observe that these ones are all present, with a very high and stable intensity. This phenomenon induced these positions are very stable and not tend to be over-fluorinated. However, we can note the band at -124 ppm has a lower intensity for 1 min and 2 min 30s of fluorination. A hypothesis to explain this phenomenon could be axial positions of the ring are less reactive than equatorials ones. Indeed, -124ppm is linked to 4 fluorine nuclei, -129 and -134 bands are each related to 2 fluorine nuclei. Nevertheless, at no moment, -124 band is 2 times higher than -129 ppm or -134 ppm band. Another explanation could be an additional band “push” the other ones higher.

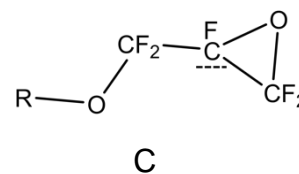


Bands at -114 and -119 are both linked to one F of the CF₂ group of the oxirane ring. Their intensities are very high at any time (and become higher ones from 15min of fluorination). This means, in the same way than CH₂ of B than those fluorine nuclei are very stable and not tend to be over-fluorinated. The intensity increases of these bands may be linked to the



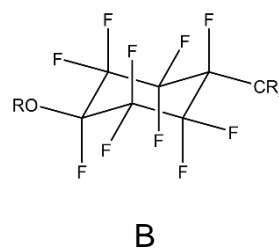
increase in the number of fluorinated groups.

By observing the -164 ppm band which corresponds to the CF group of the oxirane group, we can note it disappear quickly, and after 2min 30s its intensity is close to 0. This means this position is very reactive and is quickly over fluorinated. Consequently, this position is a privileged place of rupture.

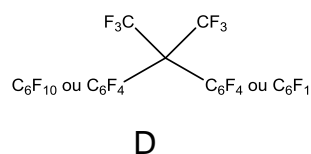


-185 is linked to one CF group of the 6 carbons ring (B). We can observe a constant intensity of these bands until 15 min of fluorination which indicates this position is fluorinated quickly and stable with the time.

-143 is linked to the other CF group of the 6 carbons ring (B), but is also share with one of the fluorine nuclei of (A). However, as shown previously, after 2min 30s of fluorination there is a very little quantity of (A) group. Consequently, we can suppose this band is only linked to the (B) group from 5min. Thereby, the same conclusion than -185 ppm band could be done. In addition, the final increase of this band is may be due to the apparition of new CHF groups.

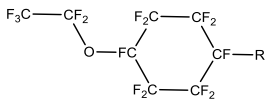
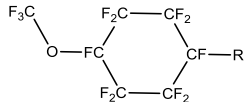
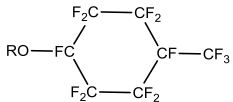


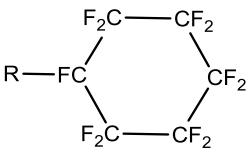
The corresponding band to group D is -55 ppm. Unfortunately, this one is also share with some other over fluorinated group. However, this group is composed of 6 fluorine nuclei and should have a very high intensity if this group is formed. But -55 band always has low intensity. This means this group is not very reactive and poorly formed, or highly reactive and quickly transform on CF₄.



If we are now looking on the over-fluorinated group list, it is possible to remove some of them from the list of observable candidates. Indeed, we have seen the aromatic ring is highly reactive, so it is quite unlikely to observe an overfluorinated group before the aromatic ring is perfluorinated. In addition, we observed CF of the oxirane ring is a privileged place of rupture. Consequently, the oxirane ring is unlikely to be present in an overfluorinated group. Finally, results showed C₆F₁₀ ring has a high stability, so a ring break is unlikely possible.

Thereby, only 4 chemical overfluorinated groups are remaining. (of course, other over-fluorinated groups may be formed, but they will be in minority).

<p>-80 ppm band is to the CF₂ positioned next to the non-oxirane oxygen and to the CF₃ of (E). However, after 2.5 min of fluorination an important increase of this band showed this compound is significantly formed.</p>	 <p style="text-align: center;">E</p>
<p>As said previously, -55 ppm band is also corresponding to the two CF₃ places between the two rings. Once again, again, an important intensity increases of this ring start from 5min, linked to an important formation of the (F) compound. In addition, if we compared the intensity of this band with the -80 ppm band (both divided by their number of fluorine nuclei), we see -80 ppm is a higher than the -55 ppm band. This show (F) compound is less form than (E) compound, proving once again, CF of the oxirane group is a privileged place of rupture.</p>	 <p style="text-align: center;">F</p>
<p>-73 ppm band, like both over fluorinated group, start an important intensity increase from 5min of fluorination. The</p>	

<p>intensity of this band is relatively important (close to the -80ppm band), so (G) compound is significantly formed, and the C between the two rings is another privileged place of rupture.</p>	<p>G</p>
<p>(H) compound add 1 fluorine band at -124 ppm. Unfortunately, this band also corresponds to axial fluorine atoms of the 6 carbons ring. However, as said previously, the -124ppm band intensity increase starts from 5min of fluorination. In addition, it's also at this time that the corresponding band to the other over-fluorinated compounds starts their intensity increase. Consequently, it's probably this compound that is responsible for the -124 band increase from 5min of fluorination.</p>	 <p style="text-align: center;">H</p>
<p>No band is visible between +120 ppm and +150 ppm. Consequently, I compound is not form.</p>	<p>R—OF</p> <p style="text-align: center;">I</p>