FIRST STAGE OF GROWTH OF LIGNIN FILMS ON A SOLID SURFACE

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Lignins are natural polymers occurring in plant cell walls and represent, after cellulose, the most abundant polymer in nature. These phenolic polymers are embedded in a polysaccharide network composed of cellulose and hemicellulose. As a consequence, plant cell wall is a heterogeneous and composite structure containing several types of polymers differing in their chemical structure and macromolecular organisation. Its complex architecture is still under investigation.

It is now well established that lignins are polymerised in a polysaccharidic medium. Accordingly the structure of the plant cell wall can be considered as two interpenetrated networks: one composed by phenolics polymers, i.e lignins, and the other by polysaccharidics polymers. One of the main difficulty of studying interpenetrated networks is to determine the **organisation of both polymer networks in the vicinity of the wall**.

In order to gain a better understanding of the lignification process, we design a chemical architecture that mimes such process and choose to use neutron reflectivity to study the system. This technique allows the determination of each polymer surface organisation at the nanoscale level. The discrimination between the two polymers is performed by deuteration of one polymer. Taking advantage of the difference in neutron length density between deuterium and hydrogen, specific information will be obtained on both polymers. The architecture is described on figure 1 : a silicon wafer is grafted with polysaccharides (pectins) and peroxidase (enzyme which catalyse the polymerisation) via a spacer – amino propyl arm. Then DHPs (dehydrogenation polymer models lignin) are polymerised at the wafer surface, either from hydrogenated monomers, either from deuterated monomers. The resulting structures were studied by neutron reflectivity to determine the organisation of the phenolic polymer grown within the polysaccharidic structure.

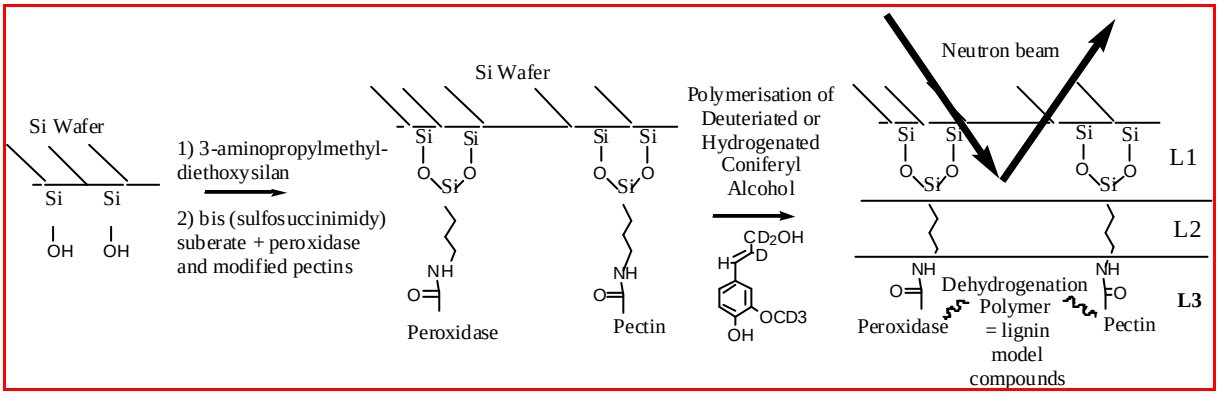

Figure 1. Grafting of the Silicon Wafer and polymerisation of Coniferyl alcohol.

Polymerisation was first performed with hydrogenated monomers in D_2O allowing the determination of the overall organisation of both polymers at the surface. This will give us the total amount of polymer in each layer, without knowing the specific percentage of each polymer. The reaction was then achieved using deuterated monomers in a mixture D_2O/H_2O (44%/56%) which have roughly the same neutron length density than the pectin and the peroxidase. In this last case, the neutrons reflectivity becomes only sensitive to the deuterated lignin monomers which allow the examination of their location within the blend.

Experimental reflectivity spectrum were recorded for twelve hours and fitted by model reflectivity curves calculated by the standard optical method (figure 2). Best fits between the calculated and experimental spectra were obtained by minimizing χ^2. A three layer model which can be represented according to the scheme reported in the figure 1 was used (L1:silicium oxide, L2: spacer –amino propyl arm, L3: peroxidase/pectin/DHPs). The width and densities of these three layers are resumed in table 1.

In the experiment without matching, the layer 3 consists of a very dense layer. In the second experiment where signals of all components except DHPs are matched, the layer 2 has an apparent volume fraction of 0 : the DHPs are thus all located in L3 which correspond to the peroxidase and pectin layer. Thus, the L2 layer is mainly formed of pectin and peroxydase. The polymerisation of DHPs only occurs in the last layer L3. It can be deduced that the polymerisation stop the diffusion of the lignin monomer within the L2. This result evidences an important process in the lignin polymerisation within the cell walls : it is an even process starting from the outer part of the wall to the inner part. Polymerisation is only able to proceed in the buffer direction and not on the wafer side.

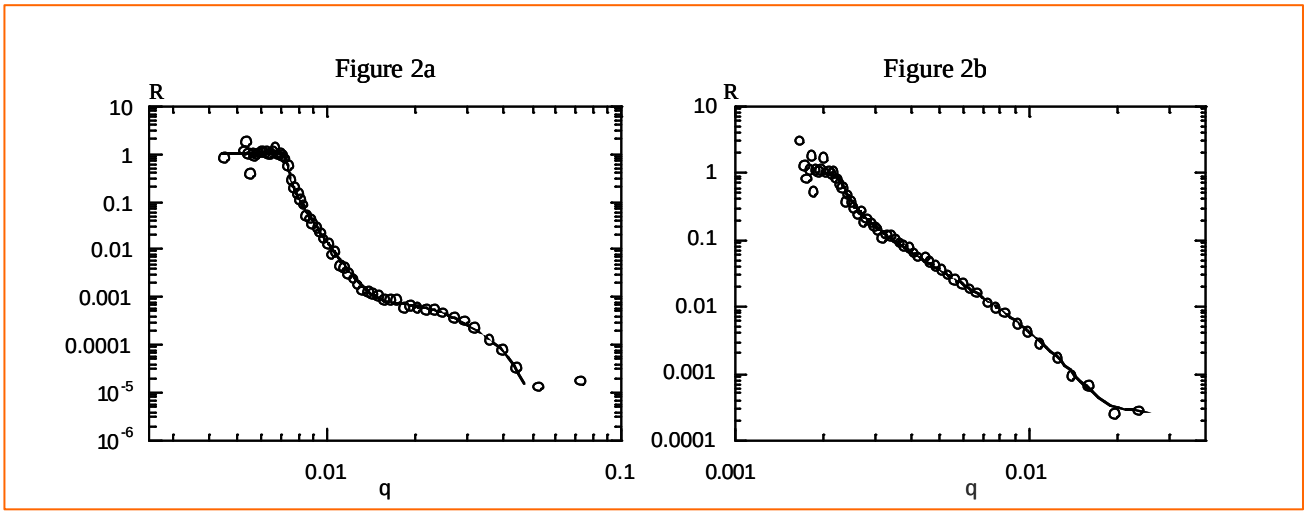

Figure 2. experimental reflectivity spectra (circle) and fit (straight line) for H coniferyl alcohol polymerisation (figure 2a) and for D coniferyl alcohol (figure 2b).

Table 1. Thickness and volume fraction fitted using a the three layer model.

	H Coniferyl alcohol		D Coniferyl alcohol	
	Thickness (Å)	Volume fraction	Thickness (Å)	Volume fraction
L1	15	0,8	25	0,7
L2	45	0,22	60	0
L3	40	0,7	55	0,3

Conclusion

In this preliminary experiment we have designed a new model architecture of the lignin polymerisation. We have shown that using neutrons reflectivity and isotopic effect, we are able to determine the distribution of phenolic polymer within the polysaccharidics network. Future work will be focused on the study of the influence of the structure of the pectins (molar mass, level of methylesterification) on the final structure of the DHPs network. Other physicochemical parameters will be also studied.