



	Experiment title : Effect of side chain length on structure and mechanical properties of starch triesters	Experiment number : 02-01-884
Beamline : D2AM	Date of experiment : From : 16/03/2017 to: 20/03/2017	Date of report : 11/2017
Shifts : 12	Local Contact : Isabelle Morfin	
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Report :

The objective of this experiment was threefold. First, this work was aimed at accurately characterizing the structure of starch palmitate materials by means of SAXS and WAXS in order to get access to the structure at different length scale in order to propose a structural representation. Second, the structural evolution as a function of the temperature has been also investigated using these techniques in order to understand and to explain the complex thermal behavior that it exhibit. Finally, a main part of this study was focused on the characterization of the strain-induced structural evolution upon uniaxial stretching of these materials. These data were compared with the thermomechanical properties characterization already carried out in the lab and they were aimed at highlighting the structure-property relationships of this type of materials.

At first, valuable results regarding the structure of the materials were obtained. As depicted in figure 1.b, starch ester diffractograms display a broad amorphous halo centered on $2\theta \approx 20^\circ$, and a broad reflection in the small angle region. The position of this reflection decreases as the alkyl chain length increases. This reflection in the small angle region is attributed to the distance between starch chains as illustrated by the structural model presented in Figure. 1a. in agreement with results reported in the literature for similar materials. In other words the structure consists in a planar arrangement of the starch backbone, with esters groups oriented perpendicularly to the starch chains

In the case of starch palmitate, two additional low intensity reflection at $2\theta = 6^\circ$ and $2\theta = 21.5^\circ$ respectively were observed, in addition to the broad amorphous halo and the $2\theta = 2.5^\circ$ reflection described previously (Figure. 1b).

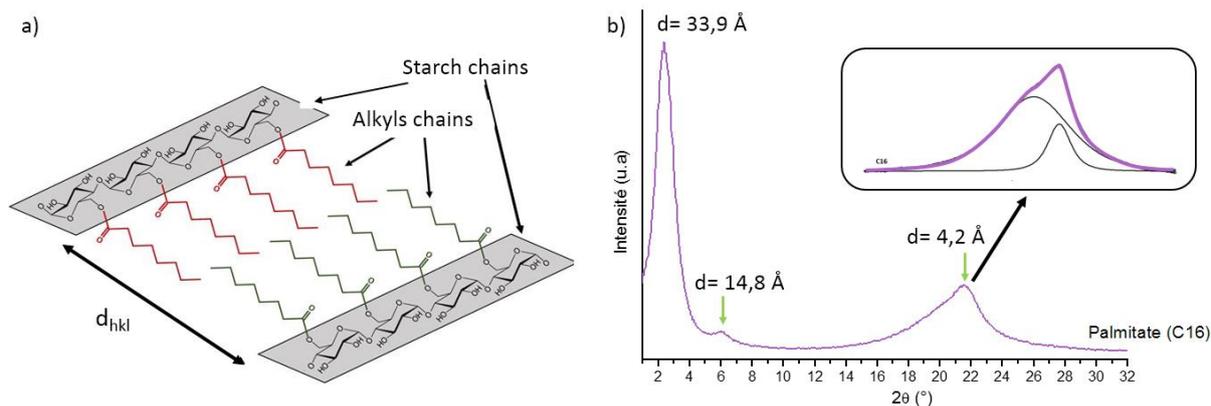


Figure 1: a) Scheme of spatial organization of starch chains and b) starch palmitate diffractogramme

The reflection at $2\theta = 21.5^\circ$, corresponding to a distance $d = 4.2 \text{ \AA}$, is attributed to an arrangement of the side alkyl chains in a α -hexagonal lattice. This result is in agreement with previous studies on poly(*n*-alkyl methacrylates) and poly(alkyl-*n*-alkyl) showing that alkyl side chains can crystallize in an α -hexagonal type cell. However for the reflection located at $2\theta = 6^\circ$ and corresponding to a distance $d = 14.8 \text{ \AA}$, no particular attribution was up to now mentioned in the literature to the best of our knowledge. The first hypothesis is that this reflection ($2\theta = 6^\circ$) corresponds to a second-order reflection of the principal peak observed at $2\theta = 2.5^\circ$ associated with the arrangement of the starch chains. Several studies show that there are mathematical relations, depending on the crystalline cell, between the position of the primary and secondary reflection. However, the application of mathematical relations for lamellar and hexagonal cells (which are most likely in our case) does not correspond to the experimental data. This second reflection at $2\theta = 6^\circ$ is therefore probably not a second reflection of the peak at $2\theta = 2.5^\circ$.

In order to understand its origin, heating and cooling temperature tests were carried out on these samples between -50 and 200°C at $10^\circ\text{C} / \text{min}$.

Between 30 and 200°C no significant evolution of the broad amorphous halo is visible but a shift to higher angles and a widening of the peak at $2\theta = 2.5^\circ$ is observed. Moreover, between 30 and 50°C , the disappearance of the two reflections at $2\theta = 6^\circ$ and $2\theta = 21.5^\circ$ is observed. Concerning the peak at $2\theta = 21.5^\circ$, its disappearance can probably be explained by the melting of the crystals of the α -hexagonal phase which takes place between these two temperatures as it had been put in evidence in our laboratory by DSC analysis.

When the temperature decreases below the room temperature only the peak at $2\theta = 6^\circ$ reappears. In order to confirm these results, several successive heating-cooling cycles were carried out. The reflection located at $2\theta = 21.5^\circ$ is only present in the initial state of the film and disappears definitively once the sample heated above 50°C . The peak at $2\theta = 6^\circ$ reappearing during cooling below room temperature, several cooling rates were tested to see if this would have an impact on the presence and / or the appearance temperature of this peak.

As the different experiments have shown, the cooling rate has no influence on the formation or on the temperature of reoccurrence of the peak at $2\theta = 6^\circ$. Furthermore, it appears that the temperature of reappearance of this peak seems correlated with the melting temperature characteristic of the crystal structure of the alkyl chains.

To conclude, it seems that the peak at $2\theta = 21.5^\circ$ is attributed to a α -hexagonal structure of the alkyl chains. Concerning the peak at $2\theta = 6^\circ$ its attribution is more complex but could be due to a local pseudo-organization of the side chains, and more specifically to planes linked to the alkyl chains, parallel to the planes containing the starch chains (Figure 2.a). This hypothesis is reinforced by the azimuthal integrations of the peaks at $2\theta = 2.5^\circ$ and 6° of a stretched sample (Figure 2.b). Indeed, the planes containing the starch chains (reflection at $2\theta = 2.5^\circ$) and the reflection relative to the interpenetration of the alkyl chains (reflection at $2\theta = 6^\circ$) are actually oriented in the same direction and parallel to the draw axis.

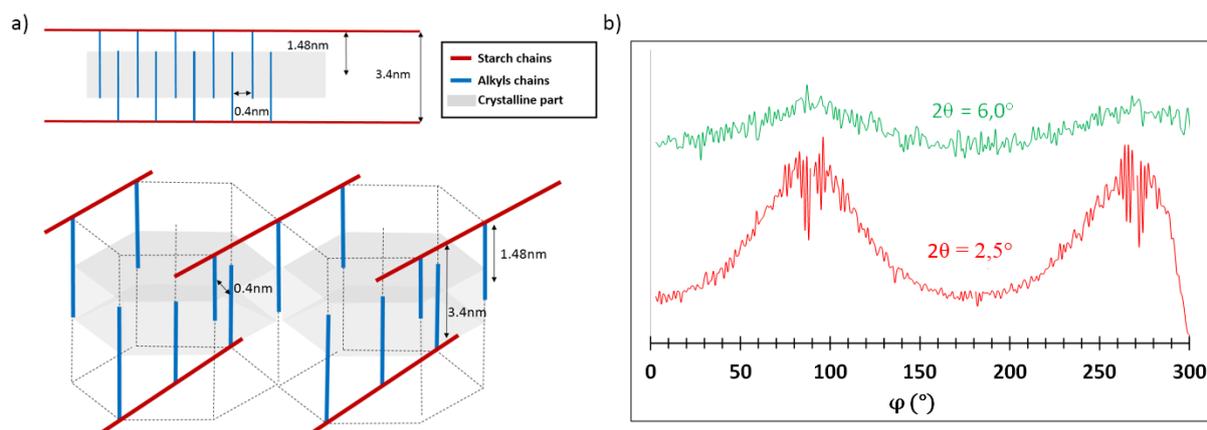


Figure 2: a) Scheme of spatial organization of starch palmitate and b) starch palmitate azimuthal integrations of the peaks at $2\theta = 2.5^\circ$ and 6°

Finally the stretching experiments allowed us to determine the evolution of the macromolecular orientation of these materials during the stretching test. Indeed, as seen above (Figure 2.b), after stretching an orientation of the starch chains and planes containing the interpenetration of the alkyl chains was observed in parallel to the draw axis. Moreover, an orientation of the side alkyl chains perpendicularly to the draw axis could also be highlighted.

Overall, we are satisfied from this experiment. We used the allocated beamtime to successfully explain the complex structure and thermal behavior and observe the strain-induced structural evolution upon uniaxial stretching of these materials. Besides the possibility to use the WOS detector for these experiments has revealed crucial and highly valuable.

A publication dealing with the result on the structural characterization is actually in preparation.