



### ILSI 2021 Annual Symposium Session 3: Innovative Packaging

#### Transcript of the presentation, **The Road towards Fully Cellulosic Barrier Materials: Possible Alternatives to Plastics**, **Caroline Locre**, CTP - The Pulp and Paper Research & Technical Centre, France

As mentioned, I will talk to you about the road towards fully cellulosic barrier materials and possible alternatives to plastics. And of course, welcome questions at the end of the presentation. You should see my presentation now. So just to mention that two of the projects that I will mention during the presentation have received funding from the bio-based industry joint undertaking, under different grant agreements.

Before going into the subject itself, I wanted to say a few words in one slide about CTP. We are an industrial and technical center serving its industry which is a pulp and paper industry, with the goal of creating value to strengthen the positioning of pulp and paper industry all over the world. And to do that we try to contribute to the development of the product mix by working in new market, developing a new paper functionality and new process technologies, and working as well with the downstream sector for example, the food packaging sector. And we do that through advanced industrial research, which is exploratory some innovation technology transfer, food consultancy and expertise services, and analytical services as well.

So as mentioned today, I will try to give you a bit of context about the search for alternatives to plastic materials. Why we are looking for that now, and present to you two processes that we hope could lead to materials of the future and to hopefully fully cellulosic barrier materials. Those two processes are the wet lamination of Micro Fibrillated Cellulose and Chromatogeny, before concluding on this presentation.

So first a bit of context. You are probably all aware of current regulatory context of that is shifting more and more. And for example, the single use plastic directive is part of this concept, context, sorry, in which producer responsibility is extended reusable solution to single use plastics are supporting prediction targets are very ambitious and some bans on some materials are also implemented through this directive, this is one example. Another one is specific in France, the [inaudible 00:02:55] school, Egamlim which targets a balance of commercial populations in the agricultural sector. It also targets to promote healthy and sustainable food. And specifically in relation to plastics, it targets the decrease of plastic uses in the food sector. For example, through forbidding trays to cook reheat and serve food in collective catering, through forbidding plastic straws, through forbidding plastic bottles in school cafeterias. So those are strong actions from Europe, from different member of the Union that targets plastic packaging.

But that's not only coming through regulatory for a regulatory context. Pressure is also applied from consumers, for example, because more and more consumer awareness is rising in part due to a strong

media coverage of littering plastics in the ocean and swamp. And NGOs and foundation have more and more strong action to accelerate the transition to a circular economy. So, it's a trend that we see is really trying to shift away, or actually partly shift away from plastic materials.

One possibility to do that, and I'm not saying it's the only one of course, but it's one of the possibilities to go towards cellulosic materials. Because cellulose is a bio-based polymer, renewable, biodegradable, recyclable. So, a really strong contender to shift towards packaging that are part of the circular economy.

Unfortunately, if it were that easy, we would have done it a long ago to switch from, example from plastic bottles to paper bottles. This is just here one example among many others. And there's been a lot of communication recently in the media about the possibility to shift to paper bottles.

But it's not just about producing for example, the bottle that is made from paper, there is a lot of requirements to take into account to produce the packaging material. We won't describe them all here but are listed on this slide. This is not the goal of course, but it is just to tell you that it is very, very complex to create packaging material that answers requirements both for protecting the food, managing converting, sealing and recyclability, biodegradability, visual aspect, mechanical resistance, and so on. There are many, many factors to take into account.

If we go into more details in the barrier requirements, which is one of the requirements that's packaging has to answer, then we can see that there are many requirements in some food barrier, depending on the food that is packaged into the packaging material. Some food need barrier to be protected against water vapor, against oxygen, light, aromas, contaminants, and so on. So, the combination of the product that is package and their shelf life and needs to be taken into account in order to define the barrier specification that's needed for a packaging material.

All of these, to say that even if paper and board are very good in term of an environmental ranking, because as I said, it's a renewable, biodegradable, recyclable material. On its own before converting, barrier performances that are required for most food products, most food stuff are not achieved. And the cellulosic substrates need to be transformed and converted with barrier solution in order to achieve the requirements needed to be able to package food stuff for example. And here you can see on this graph that the vast majority of barrier that are used today on paper and board are extruded polymers mainly fossil based, [inaudible 00:08:09] based, sorry, aluminum, wax, silicone, fluorinated products. So, materials that are not sustainable or not integrated in the circular economy.

And the trends that we see more and more is how to try to phase out aluminum and polyethylene and to replace those barrier coatings was barrier layers with bio-based materials in order to have a bigger and better packaging, that are bio-based, composed as much as possible of fibers that could be recyclable in a paper recycling stream. How to remove fluorinated compounds from paper and board and really, the question that we, I think, are asked really often now is, is it possible to produce a 100% cellulosic packaging with the technologies today? And this is what I'm going to try to answer, or just give you hints about today.

At CTP in the recent years, we have worked on two specific bio technologies that we hope are our barrier technologies of the future, and that bring a good barrier performance to papers and board substrates without adding plastic materials on top of it. The first one is called Micro Fibrillated Cellulose wet lamination and this technologies, this technology, sorry, is a process that deposited dry a layer of

MFC onto the surface of paper and board. I will go a bit more detail on the technologies right after. And the second technology is called Chromatogeny. And this one is a process that chemically modifies the cellulosic compounds. So, the cellulose substrates in order to turn it hydrophobic. But let's go into a bit more detail on MFC wet lamination first.

MFC or micro fibrillated cellulose is a product that is produced from cellulosic fibers, but these micro fibrils have small diameter and small length, they are really ready, and they can be used as a coating layer on both of paper and board in order to obtain an excellent barrier to grease, to oxygen, to contaminants and to aromas. As you can see here on this picture, right, you have an uncoated board, which has been put into contact with oil for 30 minutes. So of course, there is a big oil stain on board after contact and on right picture of the exact same board coated with a layer of micro fibrillated cellulose and after on this material, after 30 minutes of contact with oil, as you can see of the barrier is perfect. And there is no staining of the oil on the material.

So, the barrier is really excellent. And the advantage of micro fibrillated cellulose is that it is of course, cellulose. So, bio-based material, biodegradable is recyclable in a conventional paper recycling stream like paper and board. But with the additional advantage of being barrier. The drawbacks, however, of this MFC material is that it presents it's manufactured as a gel. So, it's as a very little solid content of about two to 4%. So, the rest is water, but it's highly viscous. So traditional coating processes that are used in the paper making industry are not adapted to apply it on papers and boards. And it was therefore necessary to find a new process, a new concept to be able to deposit this micro fibrillated cellulose layer on the paper or board substrate in order to obtain this barrier. And this is where the MFC wet lamination process came to light.

So, the idea is that the wet MFC film is formed by filtration of the MFC through a wire. And only once this MFC film is formed, then it is reported on the paper or board substrate. And since it is still wet, it naturally adheres to the paper substrates. So, there is no glue that is used to join the MFC layer to the paper or board layer. It's all-natural addition. And the paper on which MFC film has been applied is then simply dried before being re-winded.

And you have a MFC stratified paper at the end of the machine. This technology so as I said, is targeted to bring excellent grease, oxygen and contaminant barrier to paper and board. MFC are cellulose of very hydrophilic material. So, it does not bring either water barrier or what a vapor barrier. This is not a target of this kind of layer. And up to now, the technology has been developed at that scale to begin with. So, technology readiness level three, and is currently being at scaled at a pilot scale, sorry, on a small pilot machine, that's been installed that CTP at the end of 2019. So, a bit than a year ago. And it requires a full dedicated equipment to develop the process and produce sample for testing and proof of concept. And this MFC laminating material is afterwards fully compatible with further surface treatment to bring over barrier performances to it such as coating, laminating and so on.

To give you a bit more detail on how the material is produced at laboratory scale here, you have equipment that is used. And the idea is simply to filter an MFC suspension on wire, using some vacuum then to replicate this MFC film on a paper substrate, and then using a plating press. Let's just see here, in the middle to press the MFC film and paper to deliver between built in papers in order to join the two layers and then to finish drying the material using conductive drying under stress, for example, in a flat dryer or in a half moon dryer. And then when you peel the built-in paper, you have the remaining MFC wet laminated paper.

To go into a bit more detail about performances of the paper, because I mentioned we can reach excellent oxygen, grease and contaminant barrier. I show you the grease performance, but here you have on the right, the oxygen transmission rates that we can reach with an MFC covered paper and as you can see, with MFC laminated paper I'm using about 16 to 18 gram per square meter of MFC. Then we reach bio performance at 23 degree and 50% relative humidity, which is in the range of two to five. So quite a good performance. Bearing in mind that the initial substrate showed absolutely no barrier performance to oxygen at all.

The addition of the MFC film is possible both on mineral coatings paper or on directly paper itself, or board itself. It really depends on the surface chemistry of the material, but most paper and board should be an addition to with this demonstration. I also mentioned that the barrier to contaminants is excellent. And here we have done some evaluation of the transfer of contaminants through the barrier by using a donor sample that was spiked with selected substances. And here are the selected substances where [inaudible 00:18:15] and more surrogates, some mineral oil surrogates, and as you can see the migration of this contaminants, whereas reduced and through the barrier by more than 90% on the red, on the graph you see for migrations, without barrier. And in green, you see for migration through the MFC layer, which was significantly reduced.

So, that was MFC wet lamination. And as you can see here on this picture on the right, this is an MFC film that is being peeled from paper or board citric. So, this is what an MFC wet laminated material look like. The second process I would like to talk about today is chromatogeny. Chromatogeny is a green chemistry process that brings hydrophobicity to hydrophilic reactive substrates. These can be papers and boards. These can be lignocellulosic fibers, polyvinyl alcohol, starch, some minerals, for example, and it's a solvent free technology suitable for a reader to read processes. The first developments in the paper industry have been applied to papers and boards. And the idea of there is to bring water resistance to the material while keeping converting ability, recyclability, and biodegradability of the material.

It doesn't change those properties, and it can also be applied to coated papers for example, polyvinyl alcohol coated paper in order to protect the water sensitive barrier. As you may know, polyvinyl alcohol is also a hydrophilic material, very soluble with water. So, to protect this barrier from moisture, still keeping the recyclability and biodegradability performance of the material.

So, the basic principle of chromatogeny is to use a reaction of fatty acid chlorides with hydroxyl group in order to obtain such esters that are grafted on the paper. So, the idea is there to protect the water sensitive material by grafting fatty alkyl chain starting from a fatty acid chloride on the surface of the layer of what contains hydroxyl group. Here you can see that the fatty acid chloride reacts with the hydroxyl group and as the board is formed with the material. And to do that the fatty acid chloride is deposited as a liquid on the material in the range of 0.2 to 0.5 gram per square meter.

So really a very, very low amount of fatty acid chloride which is enough to get this ultra-fast solvent free reaction and hydrophobic paper. So, as you can see here on these two examples, this is a paper that's been treated using chromatogeny and has been first coated with polyvinyl alcohol and then grafted using chromatogeny. And we see that it is perfectly hydrophobic. So, the water rolls on the surface of the material without wetting it. And the oil here, it keeps the barrier to grease and the oil does not penetrate into the substrate.

Chromatogeny has been developed now up to industrial scale specifically in South Korea, where there are two industrial machines. The first one was started in 2015, the second one started in 2018. And before that it was invented in 1997. So, it took quite a few years to bring it first to large scale, and then to vital scale in 2012, in 2010, sorry, before moving on for different projects to bring it towards industrial scale.

The main target and market of these technologies are uncoated papers and boards. So, the idea there is to really improve the water resistance of cellulosic based material. For example, to manufacturer waterproof paper, here of some examples of markets, but in the invention for such material such as simply corrugated board that would be resistant to rain, some health and medical paper, filters, paper that can be used for agriculture, for working outside, but don't get wet. Paper that selectivity absorb oil, but not water. Those are all applications that can be [inaudible 00:23:41]. As for polyvinyl alcohol coated papers and board. It can be crafted with chromatogeny. The idea is to develop medium and high barrier performances for this material. And here we can imagine applications such as release papers, this is actually the target of the industrial machines in Korea. Baking paper, sacks and bags, cups, for example, can also be an application. So, there are plenty of ideas and markets for such a material with those performances.

And speaking of performances here of grafted papers and boards. Here are some numbers of the barrier performances, and over performances that can be reached. As you can see on uncoated papers the idea is really to improve the hydrophobicity of the material. So, to really lower water absorption capacity, and to bring a high-water contact angle of the material. And on coated PVOH coated paper and board, then the water absorption capacity is even more significant, in reducing, we have an excellent barrier to water, excellent water repellency. We keep the excellent grease barrier of the polyvinyl alcohol, and we get actually at 23 degree and 50% relative humidity, quite good water vapor barrier, which unfortunately is not that good in typical conditions. So, these are things that should still be improved. And this material thanks to the pool in the narco layer is also excellent barrier to oxygen and mineral oil.

And as I mentioned earlier, this does not change the recyclability, biodegradability, salability, printability of, of the altered paper substrate. And food conduct compliance is ongoing. So, we are investigating this. To conclude on these two processes. I would like to mention two European projects in which we have worked on these different processes. The first one is Sherpack it finished last year so it ran from 2017 to 2020. And in that project, the idea was to develop a renewable, biodegradable and recyclable flexible paper-based packaging materials.

In that project wet lamination of micro fibrillated cellulose where it's used in combination with coating of bio polymer in order to reach both oxygen contaminants and water and water vapor barrier performances needed for such packaging. And the second project is called CelluWiz and is ongoing. And there, the idea is to target high barrier, all cellulose packaging materials. So, using both MFC wet lamination and chromatogeny grafting to produce three different proof of concept that you can see here that are clamshells, cups and trays. You can find more information on these two projects on their websites.

So, as you saw, we have different technologies processes that could bring interesting barrier performances to paper and board substrates without requiring the use of plastic materials. These are chromatogeny and MFC wet lamination, which targets different barrier performances of water for chromatogeny, grease, oxygen and contaminants for wet lamination that can be used in combination with different barrier coatings to bring additional barrier performances, for example, to water vapor,

because this is not really targeted by those two technologies. And that in the future this is really the objective could really be combined together in order to bring all the necessary barrier performances to paper and board substrates in order to reproduce fully cellulosic barrier materials that don't require the use of polymers and to possibly replace some of the polymers that are currently in use are on the market.

So, to conclude, I would like to say that we really hope that paper and board are one of the packaging materials of the future due to its strong skill for circular economy, for answering an environmental concern, being bio-based, biodegradable, recyclable, being safe to put in contact with food and being easy to transform and convert in order to form packaging. Thank you very much for your attention during this presentation. And I'll be happy to take a few questions.