ILSI 2021 Annual Symposium Session 3: Innovative Packaging

Transcript of the presentation, Renewable Materials Obtained from Agriculture and Aquaculture Residues in Costa Rica, the Experience of POLIUNA, Chemistry Department, Universidad Nacional,
Marianelly Esquivel Alfaro, Msc., National University of Costa Rica, Costa Rica

Thank you so much for being patient to share some of the work we do at our laboratory. At NSF, we work at the National University or Universidad Nacional. I work at the Polymer Science and Technology Laboratory. Those are some of our facilities. Costa Rica is a really small country, located in Central America. And we have five state universities and Universidad Nacional is one of them. And we work at the Chemistry department. This is the building, the new building of Chemistry. And we belong to the Faculty of Exact and Natural Sciences. So, I'm going to show a little about the work we do in the laboratory with residues. We have three main research areas; composite and nano composite materials, converging technologies, nano and bio technologies and we start Bio polymers like Collagen, Chitin-Chitosan, Starch and Cellulose. And we have this main objective of using residues. We use agriculture, different type of agriculture residues.

Today, I'm going to talk about, specifically about Pineapple and Aquaculture residues, mainly. [inaudible 00:01:13] About agriculture residues, I'd say the Pineapple case. Well, it's a big issue in our country because as you can see, this is a Pineapple plantation is a really extensive area cultivated with this plant. And Costa Rica is one of the main exporters of Pineapple, fresh Pineapple, worldwide. It represents an important economical activity, the main destination of these Pineapple, are USA and Europe, and for every fruit that you can get, you leave a complete plant or Pineapple in the field. I'm not talking about the [inaudible 00:02:14]. It's the plant that stays in the field. So that means there's a lot of biomass that stays in the field and gives some environmental issues.

Per hectare of Pineapple cultivation are produce 300 tons of Rastrojo. That is the leaves and the stem of the plant. And for 2018, it was more than 40,000 hectares plant. This biomass as a high volume and slow degradation. And the main processes applied are chemical drying and soil incorporation. This is the Pineapple Rastrojo in the field. The biomass, like I said, is a huge amount, is mainly composed by cellulose, hemicellulose and Lignin and the cellulose, I'm not going to talk about cellulose, but for the Pineapple leaf fiber, the main component is cellulose. So, it becomes an emergent source to obtain cellulose from agricultural residues. We have been extracting micro and nano cellulose and try to find some applications for those materials. Micro and nano cellulose have some properties like high mechanical strain, very absorbing, light, non-toxic, the fibers have a high aspect ratio and elevated surface area, and high thermal stability. Some applications we have been exploring are hydrogels, electronics, thinking about electronic paper filtration system for water purification films and composite materials.

Those are some pictures from the work we have been doing. For the Pineapple leaf extraction, we take the leaves. We, we usually focus our attention on the leaves, not the stem, and we do mechanical process that is called the [inaudible 00:04:39]. Then we do like a soaking process, and then we do a bleaching process, and we get this material that looks really similar to corn. From this material we extract micro cellulose. The micro cellulose extraction is made by controlled acid hydrolysis. So, you eliminate the amorphous regions, and you keep the crystalline regions. It's not an extensive hydrolysis, it's a mild hydrolysis. So, you keep these structures that has this crystalline and these amorphous parts.

We have been preparing micro cellulose and PLA composite materials. PLA is well-known polymer is aliphatic linear polyester and is compostable on the certain conditions of humidity and temperature and can be easily consumed by microorganisms. For the micro cellulose, we did a thermal analysis, you can see the thermal stability increases when you go from the PALF to micro cellulose for the infrared analysis. Usually, we focus on these areas to look if the Lignin and Hemicellulose was removed during the first process. And also, we do X-ray Defraction to analyze the crystallinity index. The idea is that when you go from PALF to MCC, the crystallinity index increases, it goes from 35 to 70%.

Also, here are some images of the Pineapple Rastrojo or leaf fiber. As you can see, we have the fibers, there's some because of the treatments we applied previously, and then we have the micro cellulose, as you can see, these are bundles of microfibers, and here you can see [inaudible 00:07:15]. And then we prepare these types of composite materials with different amounts of MCC and these materials, I don't know what I'm talking, I'm touching something. Let me see, I have this window, we applied some pre-treatment with Terbutanol and Polyethylene glycol, pre-treatment increase the nucleation capacity and interfacial interaction, as well as the compatibility about the thermal analysis, as much MTC is add to the material, the thermal stability increased and the range of temperature of [inaudible 00:08:15] between 290 to 400 Celsius degrees. Also, by DSE, it was showed that the melting heat decreases, and the crystallinity decreases and from DMA analysis, dynamical and mechanical analysis, storage models increased.

Also, we, we did this same images before and after do fracture, applying this mechanical treatment, before the fracture, you can see the surface and then you have these images after fracture, where you can see the fibers coming out of the matrix. This implies that maybe they interface between the fiber and matrix can be improved. In the case of nano cellulose, nano cellulose can be nano fibers NFC, which maintains the amorphous and the crystalline parts. The diameter is between 2 and 20 nanometers. And the length can exceed 10 micrometers it's a long fiber. And for the case of NCC, nano crystal cellulose [inaudible 00:09:35] expensive hydrolysis, you can separate the crystalline parts. The diameter is smaller than NFC, 8 to 20 nanometers, and the length can be from 100 to 600.

The NFC extraction we applied for the Pineapple leaf fiber was mediated by TEMPO oxidation The TEMPO oxidation is specific process to oxidize the hydroxyl groups in carbon six. And then we apply grinding process with the Masuko grinder and homogenization, and then Microfluidization by this process. You can get these types of hydrogens and for the NCC, as I said before, the hydrolysis is an expensive hydrolysis. So, you get this suspension after dialysis, where you keep the crystal imports in, as the processes made by Sulfuric acid hydrolysis you get these Sulfonate groups on the surface that improves the water dispersion and keeps the negative charge in the surface of the [inaudible 00:10:55]. For the characterization we did AFM, SEM, FTIR. And also, we analyze size and set the potential for the case of NCC.

Those are some AFM images. Also, I put here to the size, this is for NFC, and this is for NCC. As you can see, the size of the fiber is different, so you have length about the one micrometer and width about three to five nanometers for the entity, the size is about 700 nanometers. And the set, the potential is minus 34. Like I said before, has negative charge also was applied. Same analysis is similar for the NFC. You can see this network of fibers and for the NCC, you can see the needle like small parts. From the thermal analysis as expected the thermal stability increases by [inaudible 00:12:18] NCC. It goes from 355 to 376. That is expected because you keep the crystalline parts and eliminate the amorphous parts. Also, we use this NCC material for starch [inaudible 00:12:46] to make composite materials. This starch is extracted from this Bitter cassava that is not used for eating. It's not edible. And here are some pictures around the optical and some images of the starch granules in these [inaudible 00:13:14]

Here are some images of the materials obtaining those were characterized also by thermal analysis. The range of a thermal decomposition is between 340 and 345, this small range, and for mechanical properties, as you can see as much NCC was at the Tensile strength increase, the maximum amount was 15%. And for the elastic models has a similar behavior more NCC higher elastic models and the higher amount was a 15% NCC also for these materials. It was made water solubility analysis, water vapor permeability and transmission and opacity also were applied some antimicrobial activity for some bacteria and some Fungi, and it give interesting results for application in inputs. Also, we prepared nano cellulose films here we applied two different methods, one with TEMPO oxidation as a pre-treatment. And then Ultaturrax is a homogenization process, and we get base suspension.

And also, we applied Masuko grinder, and you get this pulp is like, like the paper pulp. And then by microfluidization, you get these aggregates. We did a process to get this film similar to the process applied for paper. And we got these samples. This is bleach is quite transparent, and this is unbleached. So, it keeps the idea was to, to compare if it is necessary to apply a bleaching process. Also, this depends on the application we're looking of course, but the idea is to compare these materials, this process of microfluidization and Masuko grinding where maybe Nalco university I'm feeling one of our students went to Finland to, to do the process. Here you can see some AFM images. This is for NFC, and this is for the film prepare. I think this is the bleach material, and you can see the network formed by the nano particles.

Finally, I'm going to talk about briefly about agriculture residues. Mainly we work with a [inaudible 00:16:20] that becomes a residue in the aquaculture industry because [inaudible 00:16:26] without the shell. We apply on first Chitin is a polysaccharide really similar to the cellulose, and it has one third of thinners, one-third protein and one-third of Chitin. These Chitin can be extracted by eliminating the minerals by acid treatment and then pertain by alkaline treatment. We get this material, this is Chitin, and we have a pilot plant where we do this process. Then the Chitin is converted to Chitosan by deacetylation process in this reactor. So, we, we modify disruptor to get these functional groups. I mean, primary amino groups that makes that Chitosan can be soluble in a light acid medium, that has some advantage.

This is our pilot plant. We, we can process about 300 shells, per batch, and the yield is about 20 to 30% for the case of Chitin conversion to Chitosan. They yield is about 50 to 60% and per batch, we can process about five kilograms, some application for Chitin and Chitosan. Well, for Chitin, the applications are less, mainly have been applied as a Nematicide for soil preparation, and also from Chitosan you can make fibers-controlled release system. This is my chitosan, microparticles Chitosan based emulsions, like Flocculant agent for water treatment, because the amine group can be charged positively. Also, as a particle stabilizer, for example, for gold nano particles. And also, for Chitosan, you can get these films or three dimensional [inaudible 00:18:51] for the case of films can be made by casting. Actually, this is a composite between Chitosan and [inaudible 00:18:59] also structured in our laboratory.

And as you can see, it's a film transparent film, those are some images of the film. And also, you can get these tri-dimensional structures by lyophilization. And in this case, we studied the release of an antibiotic thinking that this material can be applied in, in the scheme for worms also for Chitosan another application, we have been exploring, are the nano bicycles, and also the Chitosan nano bicycles as like a mini reactor to get a gold nano particle. Here are some images of the [inaudible 00:19:51] gold nano particles that also can be applied for some applications, for example, [inaudible 00:20:01] detector of different substances that have been explored. And also, Chitosan you can get these types of beads. Those are beads between Chitosan and iron. Those beads were applied towards nickel removal in water. So has a lot of applications.

Thank you so much for your attention. I would like to thank to all the institutions that make possible the research that we do in our laboratory and as a conclusion, I can say that we have this great potential to use residues from agriculture and from agricultural residues to obtain these materials, renewable materials, to get different applications. Thank you so much.