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BIO-INSPIRED MATERIAL

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Chair: Joel Panek

FRC Chair and WestRock Company

Joel Panek

Unfortunately, Silvia is unable to be here in person today. But fortunately, we have Zoom now, so she will be joining us remotely to give her presentation. It is traditional to a have keynote presented by a person from a local university, who is not necessarily associated with the paper industry and it's intended to be kind of a thought-provoking start to the symposium and so with that I will hand it over to Silvia and thank you.

Silvia Vignolini

I would like to apologise as this is the first time that I am giving a remote talk in a conference that it is essentially, maximum of 3 kilometres far away from where I am now. As I am COVID positive I am sad not to join you in person and get to know you, but hopefully next time. I'm going to talk about biomimetics in the context of colouration. The activities of my group are mainly focused on understanding how biopolymers, such as polysaccharides, interact in nature and to mimic such architectures to produce optical appearance and colouration.

Pigmentation is used from packaging materials to paints, to cosmetics to food. So pigments are everywhere around us and because they are such an important part of our communication, we do not even think about the possibility of having a world without colour. We have evolved as animals to communicate through colour.

However, the problem is that the way colour is produced now is not essentially sustainable in terms of not only materials, but also methodologies. So my vision is to look at how nature can produce colours and imitate it, possibly using the same materials. Interestingly, when you look at the brightest colours that you have in nature, they are not obtained by use of pigments, but they are achieved by so-called photonic structures. Photonic structures can be achieved by structuring materials on the same scale of the light's wavelength. With such structures, light undergoes a phenomenon called interference, so that it is possible to generate colour without standard absorption, but also with any transparent material. And for the common knowledge, the easiest way to achieve that is the soap bubble. The soap bubble is essentially composed of a thin layer of water and soap, and because of this thin layer, you can obtain interference effects and colouration despite starting with a transparent material such as water.

The same concepts, but with a bit more complex architecture, are exploited in nature to make colours. In many different species different materials are used to make colours, because now the colouration is no longer a property of the chemistry of the material, but it's a property of how the material is structured. So you can have colour out of a chitosan-protein complex like in a lot of weevils' scales or using melanin embedded in keratin (as in birds' feathers). Mammals exploit collagen that is a protein that is also in our skin, and in plants use other waxes and cellulose. I am particularly interested in this cellulose. In plants photonic structure are often achieved with a helicoidal structure.

And this helicoidal structure is similar to the one of wood cells, that you probably are much more familiar with. Here fibres are aligned in pseudo layers which are twisted at a slightly different angle from each other in a continuous way. When the dimensionality of this helicoidal structure (so called pitch) is of the order of the light wavelength, you can get this blue colouration. This was really fascinating and when we started this work, we were looking more from the biological angle on how different plants evolve such helicoidal architecture. We studied, for example, plants that have or do not have this type of helicoidal structure, but also plants instead that have the architecture, but come from different families far away in the phylogenetic tree. Finally, we worked with the biologists and trying to modify genetically plants where you have this helicoidal arrangement and try to modify it. And finally, we have been also looking at the development of helicoidal architecture in plants. I was always fascinated by the fact that some plants, only a few of them, can actually even modify the handedness of this helicoidal structure, meaning the direction, the twist in which they can rotate so they can have both right-handed and left-handed plants. So this is more or less where I started. Obviously, by looking in nature, we wanted to mimic the same type of architecture for colouration.

Using cellulose also in the context of colour can be extremely advantageous: it's an abundant biopolymer, it is also edible, it's biocompatible, and at the end it's a regular commercially edible material.

My group is mainly working with cellulose nanocrystal that has the crystalline part from cellulose that is extracted from the plants, which are known to self-assemble into coloured chiral nematic architecture and this colour chiral nematic architecture essentially comes from the characteristics of the cellulose nanocrystal, as a liquid crystal colloidal system. What does it mean? It means that when you have them in water suspension (they are stable because they are charged during this hydrolysis preparation) as the water is evaporated they start to interact and form a chiral nematic structure, meaning that they again form the helicoidal architecture that is similar to the one observed in plants. When the water is completely removed, the system is becoming kinetically arrested (meaning that we cannot really reorient anymore the cellulose nanocrystals), so when you remove the water completely, you are essentially freezing the system into this helicoidal arrangement and compressing what is called the pitch, so that you obtain pitch of the order of few hundreds nanometre and therefore you can get colouration in the visible range, as for the plants.

I think many people have worked in his field and looked at the property of cellulose nanocrystals for almost 30 years, it is well known that this helicoidal self-assembly is happening and that it is possible to control the colour of the film by changing its characteristics. What my group has contributed to in this field is the understanding more of this origin of the chirality of the mesophase and this comes back because we were obsessed about how the chiral is transmitted in the system of the plant.

So we started to look at this problem of how is it possible to transmit the chirality of the helicoidal structure starting from the chirality of the cellulose. Is this something connected? Because often in the literature of the cellulose nanocrystal state, that chirality is obtained because of the strain in the chain of the cellulose in the crystal impact of the cellulose is such that it determines the chiral structure observed in the cellulose nanocrystals. However, despite several works proving the chirality of the cellulose nanocrystal itself, there is actually not a good systematic study that essentially connects the dots between these two points. Also because if you remember the two slides that I showed you here, when you can look at the cellulose nanocrystal you can immediately observe that it is really difficult to determine on such colloids a specific chirality, and despite several works showing that you can have some crystals where you can have a sort of a chiral twisting, explaining the twisting of the mesophase from only few observed individual building block is an unopened problem.

So, we actually started to focus on really what is the building block chirality and how can we characterise it in terms their shape. The shape of the whole system

is completely different one from the other, when you look at cellulose nanocrystals. So one of my PhD students did an amazing piece of work also using machine learning, looking at how you can trace the size of the cellulose nanocrystal and extract parameters that are important. In this case, it is important for the self-assembly. He discovered that one of the parameters which is important is the rectangularity parameter.

This rectangularity parameter is pretty straightforward. It just tells you what the difference is between the area of the nanocrystal that you are measuring and the area of a square that fits in terms of size and that has the same length and average width of the system. By doing so, and by looking at different types of a huge amount of data on different TEM images, the samples were essentially characterised by three to four different types of families of particles, going from aggregate bundles to isolated crystals. By sonicating the suspension we started to see how populations can change, we see less bundles and more isolated crystals, sonicating more we start to see distorted crystals. However, all these different particles, they can also coexist in the same suspension, so what essentially we look at is really large set of data characterised and categorised this different part.

By changing, for example, concentration and the sonication level of the suspension but maintaining all the other parameters the same, we looked how the population were evolving and we started to think that the helicoidal organisation is driven by crystalline bundles, so there is a specific population that it's determining the twisting power of suspension. So by adding bundles to a normal suspension and trying to look how the suspension evolved in terms of colour we observed that by increasing the concentration of these bundles you decrease the size of the pitch. You observed that the colloids are behaving in the same ways as molecular liquid crystals.

Many people so far have worked to exploit the cellulose nanocrystal mainly in the context of colouration to make coloured film on few centimetres scale and by doing the self-assembly by evaporation. To make this process viable in industrial applications, we needed to try to approach methods that are industrially available. Therefore, we thought about using a Roll-to-Roll machine, which is convenient because if we were are able to produce cellulose nanocrystal film with colouration on a large scale.

So by adjusting the suspension, we were able to really fabricate film of order of several metres and once you can obtain a coloured film, this can be directly used as a packaging once you have adjusted the mechanical property of the film, but also once ground this could be used as a readily available pigment. The advantage of this method is that in this case we can essentially only use cellulose nanocrystal, and by changing the property of the suspension, you can achieve different type of colouration from blue to green to red spanning the ultraviolet and the infrared region of the spectrum.

Once you have suspension, you can also exploit them for printing so these are examples of inkjet printing system with CNC. Moreover, it is also possible to make pigments that are completely matte so that they look similar to the pigment that you would use to colour your clothes, where the colour does not change with function of the direction that you are looking. To make these we use microfluidics. Again, we use the same cellulose nanocrystal suspension that we were exploiting previously but now we use it in to a microfluidic system and we have the self-assembly happening in confinement in a oil dispersion. This method essentially allows us to obtain hierarchical structure of particles where their helicoidal architecture is maintained in the wall of the particle itself and essentially because of this type of helicoidal architecture we are really able to obtain this independent angular colouration that it is really desirable in the context of pigments.

In context, we can also do the complete opposite. We can change using cellulose nanocrystal and magnetic field. It is possible to tune the orientation of the helicoidal structure in different places on a plane, and so this is essentially the way that you can make holograms and this picture that I am showing you here is animated, if essentially it is just a perfectly flat film, that seems to be in 3-dimensions.

We can use cellulose also to make a really important colour: white. So, this white colouration can be achived by using special sized crystal particle of cellulose. In short we make white pigments by changing the particular size of the cellulose fibres. We are not in the order of cellulose nanocrystals

I think it is interesting to exploit more this cellulose nano building block that can be obtained essentially from every source of vegetation waste, including food waste or cotton waste. Exploiting these building blocks and combining them with advance manufacturing technique we can produce optical material. To take a step forward now we are collaborating with several people doing life cycle assessment for our cellulose pigments and also of the cellulose nanocrystal themselves, so that we can somehow close the diagram and create materials that are really truly sustainable from sustainable resources. With this, I hope that I kept my time and didn’t lose track, and I would like to thank you for your attention and thank the people in my group who actually made this possible.

DISCUSSION CONTRIBUTIONS

Gil Garnier Monash University

Are you able to relate the CNC rectangularity parameter to the phase of liquid crystal, and can you bring the effect of rectangularity in the context of the diameter and the length of the cellulose crystal?

Silvia Vignolini

Thank you for your question, I did not give too many details on this point but we can connect rectangularity with the diameter and the length of the crystal in a polydisperse suspension. We actually did that. We looked at the rectangularity in different suspensions: specifically we compared the suspensions where we have changed the sonication dose. To make sure that we are comparing the suspensions where only the characteristic of the morphology of the crystals is changed, and nothing else, we adjust their ionic strength [pointing to graph]. This is a good graph that shows how the rectangularity is changed when you change the dose. And the different squares with different rectangularity values essentially correspond to the regions where you have a different class of crystallites as we define them in the talk. When you start with a standard suspension (as it comes from the hydrolysis process) and as we obtain crystals with a wide range of rectangularities that it is covering, if you see in this graph, more or less all the different ranges. So, you have single crystallites, but also a lot of aggregating bundles, and bundles and some distorted single-crystals. By performing sonication you break the bundles so you change the rectangularity; however you still have a distribution of typologies. But, here for example, when you have a lot of sonication, you almost don't have any more aggregated nanocrystal in these two areas but you might start to see more distorted nanocrystals because you are damaging the individual colloids. So, the amount of this rectangularity depends on the suspension that you have. And in the paper, we have provided in the supplementary data that you actually can download, you can even download the program to calculate the rectangularity on your nanocrystal suspension, but you have to do it on good TEM images. So obviously, the better your TEM, the better your results are.

Discussion

Ryen Frazier North Carolina State University

You mentioned the economic and sustainability assessments. I am curious if you have done any work related to the cost of all of this and how it compares to what already exists or is used? What do you think it will require for the consumer buy-in from the sustainability point of view?

Silvia Vignolini

So, the main cost in terms of CO_2 emission comes from the cellulose nanocrystal extraction. There is only one calculation that measures the CO_2 production for CMC and it is done on parameters that I think have been calculated by the first publication on what is the impact of CMC. And by looking at that, we actually got really bad news because the CO_2 released per kg of CNC is 29.6 kg CO_2/kg of CNC. This is worse than, for example, titanium dioxide, which is relevant in the context of pigments for pigment. And the problem of doing a proper life cycle analysis of the system is to know the exact condition of the different steps of fabrication: in terms of chemical processes, water and energy consumption and but also waste. Bigger company producers of CNC like Celluloforce, for example, do not provide this information, and their estimation of the life cycle assessment, it is as good as the data that you start with. So, we encountered lots of problems on trying to evaluate this, but then finally, now we start to talk with Prof Wadood Ahmad in FP Innovation who is sharing data and processes so that we can provide a much better assessment of CO_2 production in CNC. Once we have these values sorted, we can estimate the CO_2 consumption to make the pigment much easier as we have all the information in house.

Alexander Bismarck University of Vienna

Relating to the crystalline fraction used to control the pitch of the liquid crystalline phase – what is the perfect size to control the pitch and what is the rectangularity that you need to control the pitch?

Silvia Vignolini

It depends a lot on the suspension; it's not like a fixed number. So, the standard size of cellulose nonocrystal in length is within 80 to 150 nanometres (you have a log-normal distribution). In this case the rectangularity between 0.5 and 0.75, so if you want, they are like three or four crystals together forming these bundles.

These are the one that they can drive the twisting of the mesophase. The more bundles you have the shorter the pitch. The message here is that it does not matter too much about the rectangularity of the nanocrystal; what matters is the number of bundles in suspension, which are the ones we define with rectangularity in the quadrant in the graph.