

STRONG OR FLUFFY NANOPAPERS: HOW TO UTILISE CELLULOSE NANOFIBRILS EFFECTIVELY?

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Apart from its wide application in the paper, textile and biomedical industry, cellulose is now an emerging alternative reinforcement to improve the properties of polymers. Numerous research focuses on the development of renewable nanocomposites. In this context, nanocellulose liberated from plant cell walls or produced by bacterial serves as excellent candidate due to its inherently nano-sized nature, high crystallinity and high Young's modulus. However, numerous cellulose-reinforced polymer nanocomposites reported in literature often failed to fully exploit the fibril tensile stiffness and strength, estimated to be 114 GPa and >2000 MPa, respectively. Nanofibrils can be compounded directly into polymers as reinforcement or used in paper form to produce laminated paperbased composites.

We will discuss the potential and limitations of nanocellulose as reinforcement for polymers. We compare the potential of (bacterial cellulose) nanopapers and freeze-dried (loose) cellulose nanofibrils as reinforcement for polymers. The impact of fibril network formation on the surface chemistry of the fibrils will be investigated. It was observed that dense nanofibril networks are difficult to infuse and impregnate with matrix systems, which allows only to utilise the nanopaper properties, Young's modulus and tensile strength, in composites as opposed to the properties of individual cellulose nanofibres. To address this drawback, we produced nanopapers from cellulose dispersions in organic solvents rather than water, which gives results in 'fluffy' nanopapers with much higher porosity. The higher paper porosity should result in an increased permeance of BC papers. Such nanopapers are much easier impregnated with a resin system resulting in composites in which the fibre properties are utilised to a greater extent.

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Douglas Coffin Miami University

In terms of tear strength, you didn't say anything about the tear of the other cellulose nanocomposites you made. Typically, we would expect low tear if you have really short fibre lengths and well-bonded fibres. Tear strength will be low because you can concentrate energy to really small scales. By leaving the matting in as you did, do you have something that can distribute the energy? Do you think there is a way in terms of any material with small nano materials to produce high tear?

Alexander Bismarck

Probably not, that is the simpler answer. You need to modify the paper material by introducing longer fibres. If you make a paper out of natural fibres, i.e. non-woven natural fibres, which carry the nanocellulose, this would give you better bonding and then this case after hornification, whether it be cold crystallisation or irreversible hydrogen bonding or something else, this material will be quite tear-resistant and can carry significant load even without a polymer matrix.

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Jukka Ketoja VTT Technical Research Centre of Finland Ltd

So, I continue about this very interesting material. The strain was quite high, about 60%. What do you think was the reason for achieving such a high strain?

Alexander Bismarck

The high strain is due to fact that you have in essence only very little nanomaterial in a hollow, amorphous matrix; the glucan matrix bonds well and transmits loads more effectively to the nanofibrils and allows for rearrangement of the nanofibrils giving you significantly higher strain. So, if you go to the mushroom and you pulp that material you get microscale fibres already which only consist of an amorphous glucan structure. We don't know much more yet about this material, but these fibres themselves are much more ductile than the crystalline cellulose.

I would like some feedback how would you get fungal papers more tear-resistant, I take ideas?

Martti Toivakka Åbo Akademi University

Can you comment on various ways to address the inherent moisture-sensitivity of nanocellulose based composites? If you don't modify the fibres, do you need to coat them or does the matrix need to be hydrophobic? How do you address that?

Alexander Bismarck

If I manage to embed my nanopapers within the matrix then they are moisture resistant. An example is the material in the Trabant car. The moisture uptake then is driven only by water diffusion into the material through a polymer matrix, which you can select. You will not completely retard moisture uptake but it will be extremely slow.

Together with Eero Kontturi we also developed a method to render nanopapers more hydrophobic. You take nanocellulose irrespectively of its origin, you disperse it in an organic medium in which you dissolve whatever polymer you are interested in, and we showed it for polystyrene and polyvinylidene fluoride (PVDF), and PVDF only because it contains fluorine, which you can easily detect, the dissolved polymer will adsorb irreversibly on the fibril surface. Even without chemical bond formation in this case, you will not be able to remove the polymer anymore. This modification also results in a retardation of moisture uptake. You modify nanocellulose physically by simple polymer adsorption and you can even use this material to make, for example, thermoplastic composites if

you manage to adsorb enough material, otherwise you need a layer of polymer to bind the fibril networks together, which works.

Bob Pelton McMaster University

We have heard about nanopapers for quite a while now, do you know, are there any commercial applications? Is anyone using nanocellulose papers for anything?

Alexander Bismarck

I am not quite sure. Oji paper in Japan was apparently interested in nanopapers as a substrate for flexible electronics because you can make them transparent and because they have a very low thermal expansion coefficient, but I don't think it's for commercial scale. Normal papers are perfect but nanopapers are simply stronger and stiffer. I am not aware of commercial applications. But bacterial cellulose films, if you do not disintegrate them before making nanopaper but simply remove all bacteria, are commercially used as to replace damaged dura mater – the membrane covering the brain. They are also used to treat burn wounds as they hold a lot of water and keep bacteria away from the wound. Also, Loreal sells bacterial cellulose films (and even normal, NFC papers can be used) as face-masks and apparently Loreal will tell you it's the perfect moisturising agent, and once dry your skin becomes very tight.

Gil Garnier Monash University

I did not hear you mention nanocellulose or lignin and I suspect this is because you want a very high aspect ratio and, whenever you have pulp or deal with lignin, you chop a bit of fibre. So, am I correct, is that the issue? Can we do the same type of high-level material with nanocellulose from wood, and if so, what is the effect of aspect ratio on the properties of your material?

Alexander Bismarck

Lignin is indeed a very interesting subject. Orlando Rojas and Bill Sampson did some work on nanolignocellulose, so nanocellulose with a significant amount of lignin which obviously affects paper properties – reducing them, because fibril-fibril interactions are retarded. However, if you use the process of using animal to collect biomass and use the animal droppings as cellulose source, then when you pass manure through a fermenter you will by anaerobic digestion in a biogas plant remove the animal components, i.e. dead cells and mucous. It will also remove some of the cellulose and hemicellulose, but lignin remains. If you then pulp that

Discussion

material and grind it you need less energy to grind it into nanocellulose but you will obtain nanocellulose with up-concentrated lignin. The aspect ratio is still quite long but this material is probably, for the reason that you affect strength of a paper, not too interesting as a source for composites, but it's interesting as a particular stabiliser to effectively stabilise water and oil emulsions, which works really well.

But bacterial cellulose is free of lignin, and that is why we like bacterial cellulose, also bacterial cellulose fibrils are much longer – providing a larger aspect ratio – and the molecular weight of bacterial cellulose is much higher as compared to wood cellulose and has a higher crystallinity, resulting in better fibril properties. The fibrils have a ribbon form which results in paper in larger fibre-fibre bonds which in the presence of a bit moisture are also still quite flexible. To make better composites what we need are large nanocellulose paper sheets, which can be made as shown by VTT. But these nanocellulose sheets need to be free of flaws.

To use nanocellulose fibrils as direct reinforcement we need a process to produce high aspect ratio nanocellulose, cost effectively. But we cannot add much of them into polymers as the melt will become very viscous, which makes composite production difficult. If fibrils are too short, with a low aspect ratio, their length will always be below the critical length which negatively affects stress transfer. It is possible chemically modify the fibrils to improve adhesion but this adds cost. Will we be able to make cost effective composites compared to glass fibre or natural fibre composites with nanocellulose? Probably not but we can make thinner composites that have the properties needed and use them maybe for some electronic devices as printed circuit boards.

Gil Garnier

I have a comment: You are looking basically for a tear-resistant mechanism for your paper and I am concerned you are looking for the holy grail? As I explained we had the same problem. We developed some paper gowns for COVID protection, and we matched the requirement of a commercial gown except for tear. Then what we discover is where paper is a crack propagator then you need a mechanism to terminate cracks and then what we found is like you were going to put either a tape on the seam to prevent the crack occurring, or to have mesh inside like you did and that is brilliant idea. I think that is the holy grail we're after.

Alexander Bismarck

I think talking to the practitioners like Imanuel and Peter has already given some quite good ideas on how to utilise longer cellulose fibres, so now we need to go

back to the drawing board and think about the process, and how we can integrate them within fungal materials and bind it effectively.

Gil Garnier

But what you will have to do is to create a continuous mesh within the mesh that means you are going to need more than 8% of cellulose fibres to develop a continuous network and you need to have a bond that resists the tear.

Alexander Bismarck

I can live with 8% cellulose, if it's strong enough and gives me the tear properties and it's also still a biodegradable material.