

FEATURE

Beyond carbon fiber: What will be the fibers of choice for future composites?

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Glass fiber used to be the fiber of choice for reinforcing plastics. Just think of boats or of innovative cars in the 1950s like the Lotus Elite and Chevrolet Corvette. These days, carbon fibers are more and more used, especially in the aircraft and automotive industry. It makes you wonder which new fibers might be popular in composites in the future. Reinforced Plastics investigates a few possibilities.

Carbon fiber is an extremely strong, stiff and successful material. But it does have an Achilles heel. "Yes, we have to go beyond carbon fibers," says Professor Nicola Pugno from the Laboratory of Bio-Inspired & Graphene Nanomechanics in the University of Trento, Italy (http://www.ing.unitn.it/~pugno/). "I recently fractured my right shoulder due to the failure of a carbon fiber reinforced material."

His accident was caused by the carbon fiber reinforced frame of his bicycle suddenly breaking due to the poor toughness of carbon fiber. In principle you can negate that poor toughness with hybrid composites like carbon/Kevlar. But as Pugno points out: "Kevlar is



FIGURE 1

This brittle fracture of a mountain bike carbon frame happened under subcritical conditions (cycling at about 25 km/h on mountain grass). It caused Professor Pugno's shoulder dislocation (Photo: Nicola Pugno).

not as strong as carbon fiber. So if you use it to increase the toughness of the material, you are decreasing its strength. It is the kind of compromise we engineers are used to. But in nature you can find other solutions that are better. Spider silk for example."

Spider silk and limpet teeth

Nicola Pugno and his team have recently discovered the strongest biological material, stronger than spider silk and with a strength comparable to carbon fiber.

"Carbon fiber is basically the strongest material we have," Pugno says. "With a strength in the order of 6 GPa, it is six times the strength of high strength steel. So it is very strong but also very brittle. But in limpet teeth we have discovered a material with a strength at small scale in the order of 6 GPa." (http://rsif. royalsocietypublishing.org/content/12/105/20141326). This is currently the strongest known biological material. The previous record by the way was a kind of spider silk with a measured strength in the order of 4 GPa.

As opposed to carbon fiber, the limpet teeth material also has a high toughness, although spider silk still remains the biological material with the highest toughness: in the order of 300 J/g. Kevlar by comparison has a toughness in the order of 100 J/g.

That does not mean that spider silk is a good alternative for Kevlar in bulletproof vests by the way. Spider silk can indeed stop projectiles. But because spider silk will deform much more than Kevlar, the bullet, encased in spider silk, will probably still penetrate the skin of the wearer. Spider silk will stop the bullet, but too late to protect the wearer from injury.

"From carbon fiber you cannot even measure the toughness, since it is so brittle that the energy is not dissipated in its volume but on the surface," Pugno says. "So you have to use fracture toughness,

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dissipated per unit area instead of volume. This discrepancy in physical units shows the problem with carbon fibers. Designing products with carbon fiber is difficult and in my opinion still a risk."



FIGURE 2

Close-up of the brittle fracture of the mountain bike carbon frame bottom tube. According to the manufacturer this failure was "accidental" and not due to a defect, which according to Professor Pugno basically suggests the inability today to monitor and/or design safe carbon composites. The mission of Professor Pugno's lab is also to change this old conception and material design (Photo: Nicola Pugno).

The strength in limpet teeth is based on iron nanofibers. These were tested in traction. Single iron fibers would be even stronger. When discussing strength it is always important to mention the size scale at which the material is tested. "Spider silk is very strong because it is very thin," Pugno explains. "But if you make a roll of it, the strength decreases. This is for statistical reasons. The larger a structure, the larger the probability of finding the most critical defect. That is why nanoscale materials are stronger."

Carbon nanotubes can for example reach an ideal strength of 100 GPa, which would theoretically even be enough for making the cable of a space elevator. But the space elevator would require a cable tens of thousands of kilometers long. And then the probability of defects in the material is enormous. So in the real world we are nowhere near having a material strong enough for a space elevator yet.



FIGURE 3

Close-up of the brittle fracture of the mountain bike carbon frame bottom tube on the other side (Photo: Nicola Pugno).

Knots

Pugno and his team are trying to learn from nature how to produce materials with improved properties. For example they are trying to

reproduce spider silk and the limpet teeth composite. And they have created a record-breaking fiber with a toughness of 1000 J/g, simply by inserting a knot in a Dyneema fiber. "Dyneema is a good compromise between strength and toughness," Pugno explains. "The knot works as a sliding friction energy dissipater. We were inspired by what we observed in the junctions in spider webs. There you can see at the nanoscale a knot that dissipates energy." (http://journals.plos.org/plosone/article?id=10.1371/journal. pone.0093079). The previous record by the way was 900 J/g with a graphene and carbon nanotubes composite. Pugno and his team are pushing the record even higher, already achieving 1400 J/g in Zylon fibers with knots.

Unfortunately, putting a knot into carbon fiber does not increase its toughness, because in carbon fiber the knot concentrates the stress and reduces the fracture strength. "We are trying to use another friction mechanism in carbon fibers," Pugno says. "You can play with the interfaces in the composite. For example you can put graphene into the matrix. Then you increase the toughness and strength of the interfaces."



FIGURE 4

Close-up of the brittle fracture of the mountain bike carbon frame top tube (Photo: Nicola Pugno).

Flaw tolerance

Pugno's focus is more on increasing toughness than tensile strength.

"6 GPa is already a fantastically high number," he says. "It can be increased with carbon nanotubes for futuristic purposes like space elevator cables which would require around 30 GPa. But at the moment, the limiting factor of carbon fiber is not strength but toughness. We are unable to do as nature seems to suggest: make a material that has both high strength and toughness."

If a metal bicycle frame gets a high impact load, it will deform and thus dissipate a lot of energy, offering the rider some level of protection. A carbon fiber frame on the other hand offers virtually no energy dissipation and will immediately break.

"Materials that are very strong are less flaw tolerant and therefore more sensitive to the presence of defects," Pugno adds. "So if the carbon fiber is not perfect for some reason, the strength is not 6 GPa anymore and can even become lower than the strength of steel. Graphene for example has a strength of 100 GPa in theory. But if you remove just one atom, the strength already decreases to 80 GPa. If you lose another atom, you lose another 10 GPa. So you are rapidly approaching the strength of classical materials. That is the reason why today we are unable to produce macroscopic graphene with a strength much higher than the strength of steel. Even the ideal strength of steel is enormous: flawless steel would have a strength of 20 GPa. The limpet teeth we found are approaching that ideal strength. Generally speaking you can take the Young's modulus of a material and divide it by 10 to get its ideal strength. The Young's modulus of graphene is 1 TPa, so its ideal strength is around 100 GPa. Steel has a Young's modulus of 200 GPa, so its ideal strength is around 20 GPa. Then why are we at 1 GPa in real world applications? Because of defects, even in steel."

That is why you cannot compare the graphene produced in the laboratory in small quantities with the steel used in the real world.



FIGURE 5

Close-up of the brittle fracture of the mountain bike carbon frame top tube on the other side (Photo: Nicola Pugno).

The next great breakthrough

This means that if graphene is to compete with carbon fiber as a construction material, a method has to be found to produce it with less defects. "That is the key point of all materials science," Pugno says. "In some cases, defects are useful, for example for obtaining electrical properties. But for mechanical strength, defects are detrimental. So if someone asks me what the next great break-through in materials science will be, it is reducing or if possible removing defects. We are currently reducing those defects, but not at the rate we would like. A synergistic approach is to make materials more flaw tolerant. That is why we are trying to mimic nature. Our bones for example are full of defects, but they are no big problem."

So it is difficult to predict if and when graphene will be able to compete with carbon fiber. Moreover, since we are so far removed from the ideal strength in most materials, the next big breakthrough could theoretically come in any material: even steel for example. "We are already close to the ideal strength in materials like Dyneema or nylon," Pugno says. "In steel there is a lot of room for improvement, but it is difficult to achieve. Toughness is much simpler to increase."

Pugno explains that he has tried to make an estimate of the ideal toughness of materials: "My current view, which is not in any textbook, is that it is the strength divided by density. So if you take the specific strength for example of Zylon it is somewhere in the order of 10,000 J/g. But classical Zylon fibers will only reach a toughness of 100 J/g. With knots we can increase this tenfold, but I think in principle another factor of 10 should be possible."

Graphene flagship

Graphene was first isolated in 2004 by the physicists Andre Geim and Konstantin Novoselov of the University of Manchester. It potentially has a lot of useful properties, like low weight, high strength and excellent electrical conductivity. The possible applications are endless. It can be put into a matrix to get a composite, it can be used to increase the toughness of carbon fiber composites, and it can be used to make electronic components like batteries, Epaper displays and solar cells.

There are already commercial applications of graphene, for example a tennis racket from Head. Pugno is involved in the "Graphene Flagschip" (http://graphene-flagship.eu/): an enormous $\in 1$ billion EU research initiative, launched in 2013 to take graphene out of the lab and into the European society within 10 years. If successful we should start seeing a lot of commercial applications by 2023.



FIGURE 6

A cellulose fiber seen through the electron microscope (Photo: Fredrik Lundell/KTH).

Super strong fibers from wood

Fibers made from biomass are an exciting alternative for the future. Fredrik Lundell and his team from the Wallenberg Wood Science Center and Linné Flow Centre at the Royal Swedish Institute of Technology KTH in Stockholm for example have managed to turn wood into fibers stronger than metal. "We used cellulose nanofibrils," he says. "Everyone knows the fibers that are used to make paper; they are made from cellulose. In the tree the cellulose molecules are structured into fibrils and those fibrils are in turn structured into fibers. We utilize the intermediate structural element."

Taking fibers apart and reassembling them

To make super strong cellulose fibers, the fibers as they come from the tree have to be taken apart. "They are pre-treated in order to decrease the strength of the bonds between the fibrils," Lundell says. "This can be done thermally or with different chemical methods. Then homogenizers are used to squeeze the fibers through small holes. Thanks to that they are disintegrated into fibrils. This is an energy consuming procedure, but recent developments have made it possible to do this at a lower cost." The fibrils are then mixed with water and sodium chloride or acid. "The fibrils are electrostatically charged, so they tend to repel each other," Lundell explains. "But if we add acid or positive ions, those negative charges cancel out. Then the fibrils can come closer together and create strong bonds."

Next, the mix is squeezed through a 1.1 mm hole. Compared to the size of the fibrils this is relatively big. The individual fibrils are about 1 μ m long and between 4 and 20 nm thick. A filament is about 5–20 μ m thick after drying, which is the final step of the process.

The resulting fibers are about as strong as the strongest fibers you can find in a tree, but they are continuous and not hollow, making them suitable for textile or composite applications. Lundell's filaments are more densely packed with fibrils than a fiber in paper or wood. That is because the original wood fiber is hollow: it is after all a cell wall. Lundell's filaments are also longer than the original wood fibers.

"Natural wood fibers have a very ordered structure where the fibrils are in layers with well defined orientations, spiraling around the fiber the way you would laminate a pole," Lundell explains. "In our filaments they are actually a bit more randomly orientated, but they have a mean alignment which is central. That way we get properties that few fibers in a tree have. And in the tree, different parts have different alignments. In some parts the tree wants to be stiff and strong, in others it wants to be more elastic. So evolution has ensured that the tree has a good distribution of fibril alignments: soft fibers in some places and stiff fibers in others."

Lundell's process negates this difference in soft and stiff fibers. So it does not matter which part of the tree is used as the raw material for the process. "We disassemble each fiber into fibrils and reassemble them into a filament with exactly the properties we want," he says.

Multidisciplinary cooperation

The idea for this process came about because researchers from very different fields (like cellular chemistry and fluid mechanics) were



FIGURE 7

Artist's impression of the production of ultra-strong cellulose fibers: The cellulose nano-fibrils flow through a water channel and become accelerated by the inflow of additional water jets from the sides. The acceleration lets all fibrils align with the direction of flow, finally locking together as a strong fiber. (Image: DESY/Eberhard Reimann).

working closely together. The Wallenberg Wood Science Center studies new materials from wood, and the Linné Flow Centre concentrates on fluid mechanics.

"We have spent a lot of time talking, trying to understand each other and what we would like to accomplish," Lundell says. "Then we try to figure out how to use each other's knowledge to realize something no one has done before. So the key is to cooperate with open-minded people who will take the time to answer all your stupid questions."

From fluid mechanics they knew that in order to align fibrils, a stretching flow was needed, so they used a setup which was very good at creating a stretching flow.

Comparable to glass fibers

The strength of the resulting fibers should be comparable to the strength of glass fibers, as Lundell explains: "We are aiming at competing with glass fiber in terms of specific strength and stiffness and are confident we will reach that very soon. Probably, the stiffness will be better than glass fibers, the strength will be comparable and the strain at break will be larger than in glass fibers. We may even be able to reach the specific strength and stiffness of Kevlar. But getting beyond that will be tough. Wood fibrils are not as strong or stiff as carbon fibers."

So Lundell's fibers could become a viable alternative to fibers which are not derived from the biosphere. The advantages are clear. These fibers are burnable, so at the end of their life cycle, they can simply be burnt together with the resin they were laminated with. "And it is a renewable source of material," Lundell adds. "Even if you burn it, its carbon will be used to form new trees. So it is a closed loop. If you combine these fibers with biodegradable resin, you can even get a biodegradable composite."

What biodegrable resins would work best with these fibers is subject for further research. So if you have a biodegradable resin that might be suitable, do get in touch with Fredrik Lundell.



Test setup of the production of ultra-strong cellulose fibers (Photo: Karl Håkansson/KTH).

Further research

The process to make these super strong cellulose fibers seems not all that different from the process used to make paper. So you would think that scaling up the process to industrial levels should not be too difficult. **FEATURE**

"We are presently trying to figure this out," Lundell says. "We are quite positive we will be able to scale it up so we can produce large amounts of filaments and start testing them in composites, textiles and so forth. We hope to have all the information necessary to make commercial decisions in five years. Then we should be able to do a fair cost estimate and describe how to build an industrial system. Drying the filaments could be an economical bottleneck. So we are working on methods to reduce the amount of water that needs to be dried by heating."

As cost goes, competing with the relatively expensive Kevlar fibers in composites should not be a problem. The challenge however is to reduce the cost of Lundell's fibers to the point where they can compete with cotton in textiles.

Lundell explains that more research is also done to try and understand the fundamentals of the process so it can be used for more advanced structures: "For example: how do these fibrils behave in the process, how much can we align them, what do we need to do to align them to a certain degree, and how fast will the fibrils return to a dealigned state?"

And finally, Lundell and his team are looking to improve the process so the fibrils get more aligned, which will result in stronger filaments.

Nanocellulose foam

Biodegradable fibers probably won't take over within five or ten years. But they should start to offer an alternative that can compete with glass fibers and fossil fuel based fibers.

"Of course this also depends on regulations and how much of the cost for the total life cycle is charged to the customer," Lundell says. "The developments in nanocellulose are quite intense at the moment. A lot of different things are being done to modify nanocellulose and combine it with other materials. We have for example combined our cellulose fibrils with carbon nanotubes. Then we get conductive filaments. And there is a recent paper by our colleagues, who have made a dry nanocellulose foam, resulting in a very light material which is very much like a dry sponge. This can be used as a template for a Lithium-ion battery. I think that is very exciting."

That nanocellulose foam could also be used as the core material for sandwich panels. If you combine that core material with a battery, that would be nice function integration. In 10 or 20 years this might become a viable option.

Diamond nanothreads

Carbon nanotubes look promising and are already slowly entering real world applications. But another form of carbon is the hardest material known to man: diamond. Just imagine if you could laminate diamond fibers in composites.

In a few decades, that might really be possible. A team of chemists from Penn State University in America has been able to synthesize diamond nanothreads.

"Getting some type of ordered structure from benzene has been a dream for me since I started being a scientist in the nineties," says Professor John Badding from Penn State University (http://bg. chem.psu.edu/publications.html). "Our expertise is in the use of pressure to control and synthesize materials. We were interested in whether we could induce a solid state reaction in benzene. People have been squeezing on benzene for nearly a hundred years. And we have been studying benzene under pressure for two decades. But a student got interested in this project and squeezed on benzene much more slowly than anyone had ever done before. We found that the benzene molecules then linked up in such a way, that the material had order in it."

To their surprise this ordered material turned out to be diamond nanothreads.

It is not sure if it is the slow compression or the slow release that is doing the trick. "We have not had the chance to figure all that out yet," Badding says. "There are so many research directions to go into. Right now our focus is on sorting out the structure at the level of the atom: the detailed atomic structure along the threads."

They are cooperating for that with Nobel Prize winning theoretical chemist Roald Hoffman from Cornel University. "He has just released a new paper that deals with the mechanism issue," Badding says. "The paper points out a number of different ways in which benzene could link together to make interesting thread materials. Now our challenge is to do experiments to probe the reaction as it happens and figure out how it might have happened."



FIGURE 9

Close-up of a diamond nanothread (Image: John Badding).

Linking up hexagons

A benzene molecule is a hexagon with six carbon atoms, linked up with "one and a half" bonds between them. And every one of those carbon atoms has one hydrogen atom linked to it on the outside. Under normal room temperature and pressure, benzene is a liquid, but in Penn State's high pressure reactor it freezes into a crystal.

You can imagine this frozen state as stacks of those hexagons. What happens during the slow compression or release is that the extra bonds inside such a hexagon break open and link up the hexagon with the hexagons above and below it, resulting in a long thread of hexagons.

"The chemistry of what can happen is very much controlled by the details of how these hexagons are stacked," Badding says. "That gives us a measure of control. One way in which the hexagons can react is called a 'Diehls-Alder' reaction. That is a cyclo-addition reaction: two molecules coming together to form a new ring. After the Diehls-Alder reaction you have gotten rid of two of the double bonds in the benzene. Is it then possible for a further reaction to happen to link up the third bonds? This is what professor Hoffman's paper focuses on." (http://pubs.acs.org/doi/ 10.1021/jacs.5b09053).



FIGURE 10 A longer view of a diamond nanothread. (Image: John Badding).

Lots of different carbon types

Diamond, graphite, carbon nanotubes, graphene, diamond threads, etc. there are many different variations of carbon now. "Carbon is a wonderful element for making lots of different structures," Badding says. "It is very versatile and can be hooked up and linked up in so many different ways. That is why life is based upon it and why it is the basis for the plastics industry. So it is no surprise that there are several different interesting forms of carbon."

These different forms can be classified with two parameters. The first parameter is dimensionality: is the material zero-dimensional little dots, one-dimensional threads or tubes, two-dimensional sheets, or a three-dimensional structure like graphite and diamond?

The second parameter is how the carbon atoms are connected together: is every carbon atom bonded to three neighbors or four? Carbon always wants to have four chemical bonds, but in graphite each carbon atom is only bonded to three other carbon atoms. That is called sp2 carbon or threefold carbon. In diamond on the other hand, each carbon atom is bonded to four other atoms. So diamond is sp3 carbon, or fourfold carbon.

The first carbon nanomaterial was C60, a zero-dimensional ball of sp2 carbon, first generated in 1985: these "buckyballs" resulted in a Nobel Prize in 1996. After C60 came carbon nanotubes, which are one-dimensional tubes of sp2 carbon. Later, graphene was discovered: a two-dimensional sheet of sp2 carbon.

A different class of carbon nanomaterials is based on sp3 carbon. Adamantane is a zero-dimensional dot of sp3 carbon. It is essentially the smallest molecule that still has the same structure as diamond. Lots of people are presently trying to create graphane: a two-dimensional sheet of sp3 carbon. "That could be as strong as graphene or maybe even stronger," Badding says. "But people are not sure whether they have made it or not. It is a very interesting material. And then there is the one-dimensional form of sp3 carbon, which is what we are looking at in our nanothreads. We know that our nanothreads contain a lot of sp3 carbon but we are still trying to figure out if they are 100% sp3 carbon."



FIGURE 11 Diamond nanothreads are a one-dimensional form of sp3 carbon (Image: John Badding).

Translating it to the factory

Of course, the strength and stiffness of sp3 nanothreads have not been tested yet. But Vin Crespi already published a prediction of the strength of these materials as early as 2001. "He is on our team and happened to be at the meeting where we first discussed our experimental results," Badding adds. "He said maybe it is a nanothread. It was just coincidence that we had on our team the first person to predict these materials. He has looked at the strength of many different sp3 nanothreads and some of them could be as strong as sp2 nanotubes and maybe even stronger."

And it is expected that diamond nanothreads can be laminated with the same sort of resins as carbon fibers. But before we can even start thinking about producing sp3 nanothreads on an industrial level, a lot of problems have to be solved.

"Right now the pressures we are using to make these things are not practical for commercialization," Badding says. "In China for example they make large quantities of diamonds for abrasives and such industrially at a pressure of about 6 GPa. So it is economical at about 6 GPa. But we are using about 20 GPa in our synthesis, so we have to get the pressure down. But this is very early stage, fundamental research. People were all excited about the strength of carbon nanotubes in the nineties and now graphene. Commercialization just takes a long time."

All these carbon materials are in theory some of the strongest materials known to mankind. But one of the problems with sp2 carbon nanotubes has been that scaling them up for industrial purposes introduces a lot of defects into the material. Those defects prevent them from reaching their theoretical strength in real word applications. The same will be true for diamond nanothreads. But one idea to overcome this problem is the fact that sp3 threads can be cross-linked together. "So we could have chemical bonds between the threads which would decrease their defect sensitivity, but still keep them threadlike and flexible," Badding explains. "The sp3 bonded thread has hydrogen atoms off the side. If we got rid of two hydrogen atoms for example we could bond two threads together."

It will probably take decades to develop the process to the point where diamond nanothreads will find industrial applications. "When we look at sp2 carbon nanotubes: they have been around for 20 years and they are not in every car or building yet," Badding says. "It may take 50 years for sp2 nanotubes to find their applications. But knowing that they are out there, inspires people to look for applications. Over time very exciting possibilities will arise. And if sp2 nanotubes could be made perfectly, they would be extremely strong. Maybe one day someone will figure out how to do this. The same goes for our diamond nanothreads. But one of the most interesting things for us is not just the fact that a thread forms, but more generally how the thread was formed. This is a different approach to carbon nanomaterials. Nanotubes and bucky-balls were all made by gas phase reaction of carbon. And graphene is made by peeling apart graphite. But we are making our material with organic solid state chemistry. And we know that organic chemistry is very versatile. So we are wondering if this is a more general route to all kinds of interesting extended organic structures."

If they can figure out the exact mechanism that causes the diamond nanothreads to form, they may be able to control the reaction to make other molecules. Maybe in future this will result



FIGURE 12

"Tube 3.0" in a hex lattice: a diamond nanothread, first predicted by Vin Crespi. The black spheres are carbon, the pinkish spheres are hydrogen.

in a processing tool box to make molecules bespoke for the application you need.

"This is an exciting and to some extent new field," Badding says. "We may be able for example to make these structures conduct electricity."

Whereas sp2 types of carbon (like graphite) conduct electricity, perfect nanothreads (like diamond and other sp3 types of carbon) are not conductive. But there is a lot of research into diamond semiconductors. Because if you dope the diamond, you can turn it into a potentially useful semiconductor. "So if we introduce other atoms into the structure of our nanothreads, it could be an interesting electronic material," Badding says.