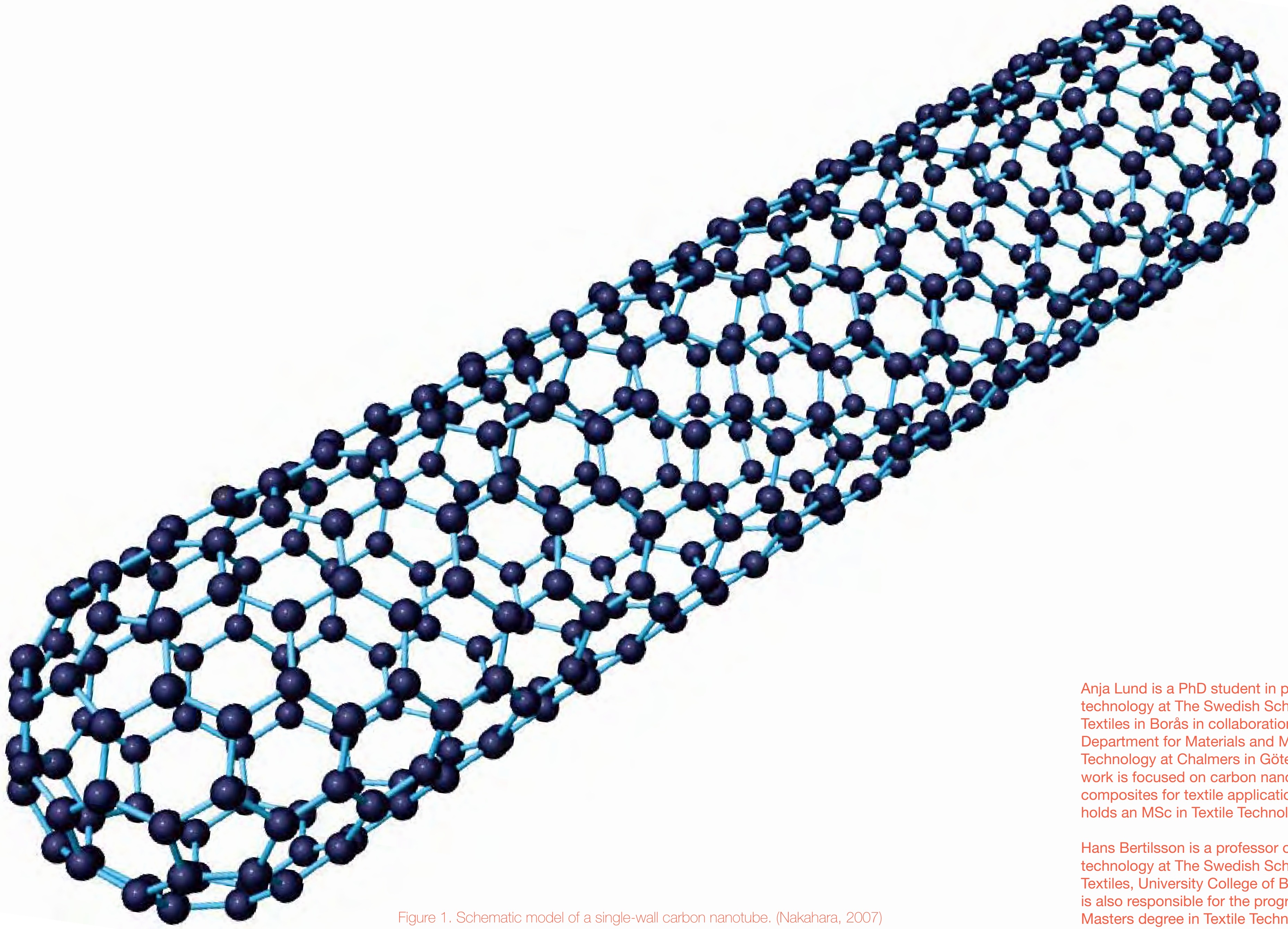

Figure 1. Schematic model of a single-wall carbon nanotube. (Nakahara, 2007)

Anja Lund is a PhD student in polymer technology at The Swedish School of Textiles in Borås in collaboration with The Department for Materials and Manufacturing Technology at Chalmers in Göteborg. Her work is focused on carbon nanotube-composites for textile applications. She holds an MSc in Textile Technology.

Hans Bertilsson is a professor of fibre technology at The Swedish School of Textiles, University College of Borås. He is also responsible for the programme for Masters degree in Textile Technology

Nanotechnology for textile applications – or how to make something from nothing

Anja Lund
PhD student, The Swedish School of Textiles, THS
University College of Borås
The Department for Materials and Manufacturing Technology at Chalmers University of Technology in Gothenburg
anja.lund@hb.se

Hans Bertilsson
Professor, The Swedish School of Textiles, THS, University College of Borås

In September 2006 a research project was started at The Swedish School of Textiles, with the broad aim of finding use for carbon nanotube/polymer composite[1] materials in textile applications. This article gives a background to the project and presents preliminary results.

Carbon nanotubes – what are those?

Carbon nanotubes (CNT) are closed cylinders consisting only of carbon atoms, with diameters of just a few nanometers[2] (nm) and lengths ranging from 100 nm to tens of micrometers. As properties of CNTs started to be explored in the early 1990's, it was found that they showed flexibility combined with excellent mechanical and thermal properties, and a variety of electrical properties. While thermal conductivity is high, electrical conductivity depends on the atomic structure, and ranges from conductive to semiconductive. These properties in combination with the small size, have encouraged scientists as well as the industry to explore the possibilities of putting carbon nanotubes into practicable use. Fig. 1 shows a single-wall carbon nanotube. There are also double-wall and multi-wall carbon nanotubes, having two or more concentric layers.

[1] A composite material consists of two different constituents (matrix and filler/reinforcement) which brought together create a material yielding attractive properties from both matrix and reinforcement.
[2] One nanometer (nm) is 10^{-9} meters or one millionth of a millimeter. One micrometer (µm) is 10^{-6} meters. This can be compared to a human hair which is roughly 50 µm in diameter.

Carbon nanotube composite materials – great potential but not without difficulties

The great interest for nanotechnology in general has very much to do with the nano-size of the materials. When a filler is added to a polymer with the purpose of enhancing mechanical properties, it is important not only that the filler itself has good mechanical properties, but also that it will interact with (bond to) the polymer matrix. This interaction will increase if the filler has a large surface area (area-to-volume ratio) to interact with. Fillers in nano-size can give a very large surface area related to their volume or mass, for example 1500 m^2/g. It can be shown that for optimum shape the reinforcing phase should have an aspect ratio (length divided by diameter) much higher than 1 (fibre-shape) or much less than 1 (platelet-shape), as illustrated in Fig. 2.

The small size also has potentially great advantages for enhancing electrical properties. Theoretically even a small amount of electrically conductive particles such as CNT can form a network inside a polymer matrix, thus forming a conductive path. The low concentration of reinforcement gives the great advantage of adding new properties without affecting the attractive properties of the polymer material itself, such as flexibility and soft touch in a textile fibre.

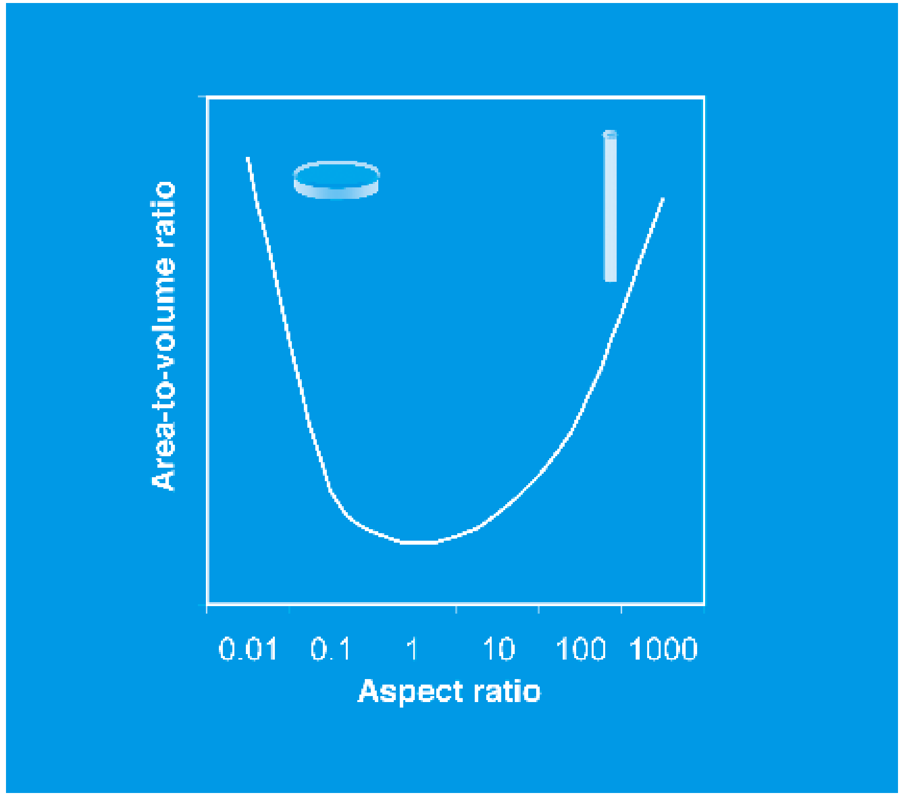

Figure 2. Principle of area-to-volume ratio as function of aspect ratio. (After Gustafsson, 2007)

However, to take advantage of nano-size reinforcements in practice, the nanoparticles must be separated into individuals and interact chemically with the surrounding matrix. This is where the problems start. The fact that carbon nanotubes consist only of carbon atoms, makes them highly non-reactive to most polymers. Instead they are highly prone to clinging to each other, forming large bundles or agglomerates. Researchers have spent much time and effort on the de-agglomeration and dispersion (spreading) of CNT within various matrices, frequently using solvents, chemical treatments and mechanical treatments such as ultrasonication or milling. Many of the good results shown in scientific papers are difficult to realize in a larger scale industrial process.

The solution seems to be in companies focusing only on the dispersion of carbon nanotubes, producing master-batches of polymers with a high concentration of CNT which are then relatively easy to dilute, e.g. by melt-mixing with a larger amount of polymers. This business has led to a few commercial CNT-composite products being available today. An example where CNT are used for electrical properties is exterior vertical panels of cars (plastic wings/fenders) – CNT makes the plastic electrically conductive, which is necessary for the painting process used. CNT can also be used as filler for dissipation of electricity in fuel lines and connectors. Other products use CNT for enhancing mechanical properties at a low weight. These include a yacht mast, bicycles, baseball bats, and golf club shafts. Finnish company Montreal sports produce hockey sticks using nanotechnology, and claim that the use of CNT gives benefits of higher flexibility and clear improvement of durability compared to sticks produced with carbon fibres. (Mapleston, 2007)

Carbon nanotubes in textiles?

To the author's knowledge there are to date no commercial products containing carbon nanotubes available in the textile area. There are however some scientific publications and these might give an idea about future applications in the area of smart textiles. One group of researchers has been able to produce composite fibres of about 50 µm in diameter, with an energy-to-break much higher than that of both Kevlar fibre and spider silk. In turn, the toughness (energy needed to rupture) of a fibre is five times higher for spider silk than for the same mass of steel wire. The polymer used was polyvinyl alcohol (PVA) with a high content of CNT. The same fibres were coated with electrolyte and could be used as capacitors woven into textiles. (Dalton, 2003)

Figure 3. Polymer granules for melt-processing. Right: pure Poly(vinylidene fluoride) (PVDF) supplied from Solvay Solexis. Left: PVDF containing 5 % by weight carbon nanotubes, commercial masterbatch purchased from Hyperion Catalysis, Inc.

Another group has shown it is possible to produce electrically conductive yarns by a wet-spinning process, also using PVA. The electrical resistance was however quite high – several tens of kΩ/cm for as much as 40 wt% of CNTs to PVA. Better results were achieved by adding CNT/PVA in the form of a coating to fibres such as cotton, silk and polyester. A coating with 30 wt% content of CNT of the mentioned fibres, resulted in a resistance of only 0.25-2.87 kΩ/cm. (Xue, 2007)

As a third example, an ongoing project at the University of Massachusetts at Dartmouth explores the possibilities of creating a conducting ink by adding carbon nanotubes to a solution of PEDOT-PSS[3]. Printing will be done on textile fabrics such as nylon 6, polyester and silk, and may be used to replace metallic components in wearable antennas. (NTC Online, 2006)

Carbon nanotubes have also been explored as a means to create an "artificial lotus leaf structure" on cotton fibres. It was found that the addition of CNT onto the surface of cotton substrates, created a cotton material which was highly hydrophobic. The authors expect that by also making use of the CNT's mechanical and electrical properties, these CNT-coated cotton fibres can find applications in sensing and conducting textiles. (Liu, 2007)

[3] PEDOT-PSS is an electrically conductive polymer blend.

Our project – pressure-sensitive textile fibres

In the current project at the School of Textiles, the polymer poly(vinylidene fluoride) (PVDF) with an addition of carbon nanotubes is melt-spun to form filament fibres. These fibres will then be characterized with a focus on electromechanical (piezoelectric) properties.

PVDF is a material with well-documented piezo-, pyro- and ferroelectric[4] properties. Its piezoelectric properties in particular are well exploited and commercially available in the form of a film for sensor and actuator applications, e.g. in microphones or speakers. A fibre with piezo- or pyroelectric properties could be used for wearable sensors in medical applications, reporting and responding to e.g. heartbeat and changes in body temperature. The fibre form would give advantages such as processability, increased comfort and wearability, washability and shapeability.

The addition of nanotubes should give advantages such as enhanced stiffness, which in turn will enhance the mechanical response, and also CNT can act as a nucleating agent, increasing the highly important crystallinity. PVDF is a semi-crystalline polymorphic fibre, which means it can crystallize into several different phases. While α-phase crystallinity is the one most easily formed, it is the β-phase crystallinity which gives the polarity necessary for piezoelectric activity in the fibre.

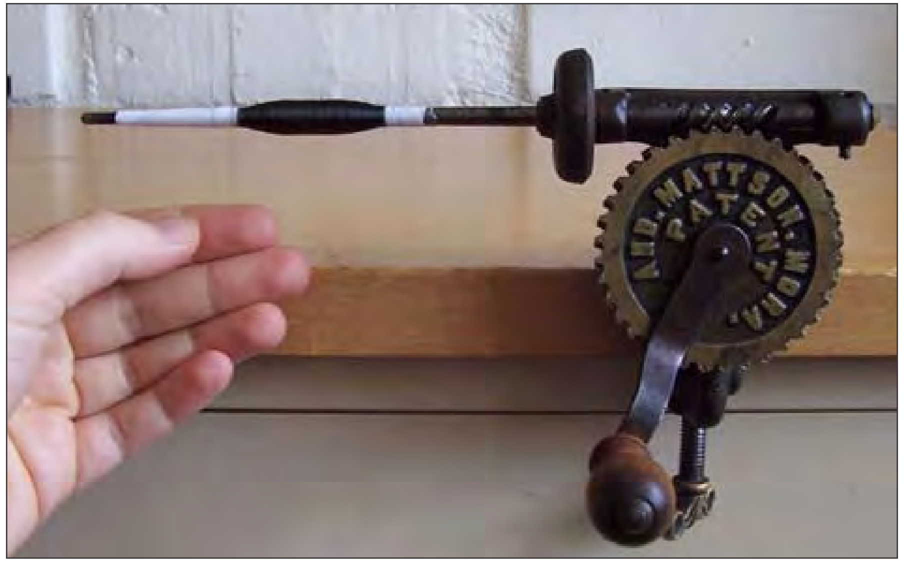

Figure 4. Old-fashioned technology has proven very useful in small-scale production for research purposes

PVDF as a piezoelectric sensor/actuator in continuous fibre form is to date not at all explored. Electrospinning[5] of PVDF has been done by IFP Research in Mölndal, among others, and there are some ten or so scientific papers describing PVDF in electrospun form for use as piezoelectric sensors. Some of these also add CNT, and one group has reported that the voltage output from such a sensor at a certain mechanical displacement increased from 2.4 mV using no CNT, to 84.5 mV at a loading of 0.05 wt% CNT. (Laxminarayana, 2005)

[4] A piezoelectric material is sensitive to mechanical deformation, such as pressure, and can produce a small voltage when deformed. A pyroelectric material is sensitive to changes in temperature, and can produce a small voltage in response to heating or cooling. A ferroelectric material has an electrically reversible polarity.

[5] In electrospinning an electrical charge is used to spin fibres from a polymer solution. The result is a non-woven mat of fibres approx. 100 nm in diameter.

First results show enhanced stiffness of fibres

The practical experiments so far have included mixing carbon nanotubes with polymer, fibre spinning, and characterisation of mechanical properties and crystallinity. The easiest way to blend CNT with polymer is melt-blending: CNT was added, in powder form, to polymer granules and mixed in a twin-screw extruder for a short time. Two kinds of CNT have been used for the experiments. Both are double-walled, and while one (denoted NH2) is functionalised by NH_2-groups attached to the surface, the other (denoted NF) was not functionalised. Functionalisation is expected to help de-agglomeration and dispersion of CNT as well as enhance interaction with the polymer.

Three different concentrations of CNT were chosen: 0.01%, 0.05% and 0.2% by weight. These concentrations were chosen from what has been shown in the literature to give a mechanical enhancement, but with no risk of adding electrical conductivity to the polymer (this would ruin piezoelectric activity). Fibres were then spun using a capillary rheometer. The same blending and spinning processes was performed using a composite where CNTs were first mixed with a small amount polymer with the help of a solvent (N-methyl-2-pyrrolidone).

Figure 5. Composite fibres melt-spun from PVDF with varying amounts of carbon nanotubes

Stress-strain tests where performed on all fibres. The equipment limits the maximum strain to 22%, none of the fibres broke at this elongation. Results show that while composite fibres prepared by melt-mixing in all cases end up with a lower stiffness than the pure PVDF-fibre (Fig. 6), the composite fibres prepared by solvent-aided dispersion show quite a high mechanical improvement (in this case meaning an increase in stiffness) at very low loadings of CNT (Fig. 7) (Gustafsson, 2007). The CNTs functionalised by NH_2-groups were much more efficient in enhancing mechanical properties, while non-functionalised CNTs at 0.05% and 0.2% instead gave a negative effect. The variation in mechanical properties is attributed to differences in dispersion, where a low concentration of solvent-mixed functionalised CNTs give the best dispersion, while larger amounts, no functionalisation and no solvent all are factors contributing to a less good dispersion. The addition of CNT showed no effects on processability or spinnability.

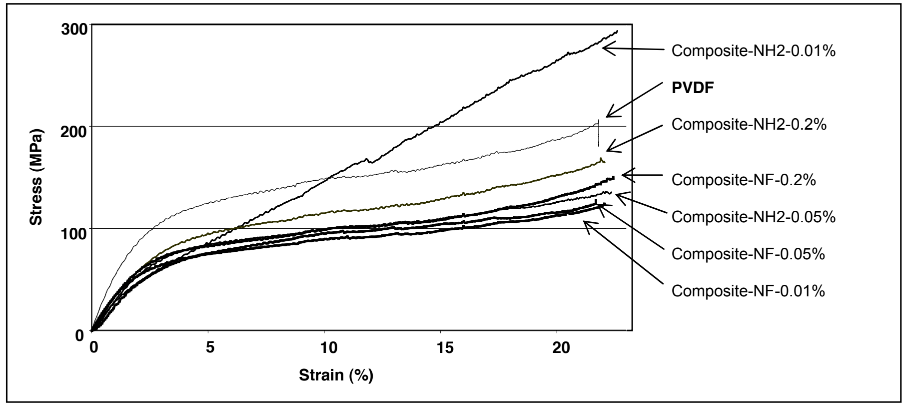

Figure 6. Stress-strain curves for composite fibres prepared by melt-blending and pure PVDF fibre

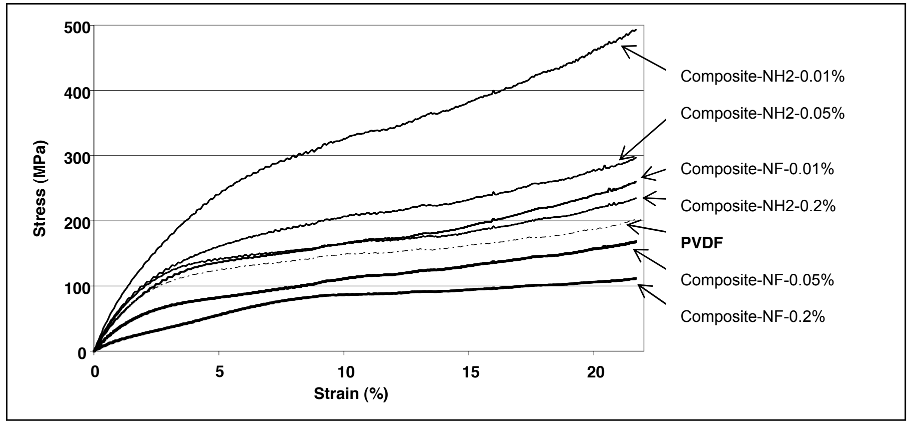

Figure 7. Stress-strain-curves for composite fibres prepared by solvent-aided mixing and pure PVDF fibre (After Gustafsson, 2007)

To be continued

This research will be continued with an investigation of the fibres' electromechanical properties. While CNTs so far did not show a positive effect on crystallinity, it is possible that the improvement in stiffness will still contribute to a good piezoelectric response. The first tests will be done using the fibres in different forms of woven structures.

References

[Nakahara, 2007] Figure 1 is published with permission from H. Nakahara, Nagoya University, Japan: *http://www.surf.nuqe.nagoya-u.ac.jp/index-e.html*. Accessed on 2007-11-21

[Gustafsson, 2007] Gustafsson, C. *The influence of carbon nanotube concentration on the mechanical properties and β-crystallite formation of melt spun carbon nanotubes/PVDF composite fibres* Thesis for the Masters degree in Textile engineering, University College of Borås – Swedish school of Textiles (2007)

[Mapleston, 2007] Mapleston, P. *Carbon nanotubes: Today's future technology?*, Plastics Engineering (2007)

[Dalton, 2003] Dalton, A. B. et al. *Super-tough carbon-nanotube fibres*, Nature 423, 703 (2003)

[Xue, 2007] Xue, P. et al. *Electrically conductive yarns based on PVA/carbon nanotubes*, Composite structures 78, 271-277 (2007)

[NTC Online, 2006] NTC Online Research Project Database (2006) *http://www.ntcresearch.org/projectapp/index.cfm?project=M06-MD01&topic=approach* Accessed on 2007-06-25

[Liu, 2007] Liu, Y. et al. *Artificial lotus leaf structures from assembling carbon nanotubes and their applications in hydrophobic textiles*, Journal of Materials Chemistry 17, 1071-1078 (2007)

[Laxminarayana, 2005] Laxminarayana, K. and Jalili, N., *Functional nanotube-based textiles: pathway to next generation fabrics with enhanced sensing capabilities.* Textile Research Journal 75, 670-680 (2005)