Environmental, health and safety (EHS) aspects of cellulose nanomaterials (CNM)
Kangas, Heli

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Heli Kangas
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Motivation

Due to their unique nano-specific properties, cellulose nanomaterials (CNM) have numerous potential applications.

- replacement of fossil-based materials in packaging, deodorizing material in adult diapers, cell growing media...

As bio-based materials, CNM are often assumed safe.

However, their nano-specific properties may potentially make them hazardous towards humans and the environment.
Motivation

- Biopersistence of long and thin high-aspect ratio fibers is known (case asbestos)
- Wood dust is a carcinogenic material
- Nanoscale features give rise to new material properties and biological behavior
  - Decreased particle size – improved penetration
  - Increased specific surface area – enhanced interactions with their biological surroundings
Examples of safety assessment at VTT
Case 1: Human health - Results on the toxicity of the smallest fraction of cellulose nanofibrils

Background & approach

In our previous studies, CNF materials as such showed no indications of toxicity.

However, with fractionated cellulose nanofibrils, the smallest fraction showed indications of toxicity/slight toxicity.

- Due to cellulose nanofibrils?
- Due to the bacteria present in the sample?

Further testing was needed to confirm/disprove the slight toxicity effects observed.

Finely fibrillated CNF was fractionated into separate size fractions ensuring that there was no bacterial contamination.
Fractionation of CNF

1. Finely ground CNF was fractionated using tube flow fractionation into four fractions
2. The finest material, FR3 and FR4, representing ~20 w-% of the original CNF, were collected
3. Fractions FR3+FR4 were combined and subjected to toxicity tests.
Toxicity testing of the nano-scale fibrils (FR3+FR4)

- Cytotoxicity *in vitro*
  - Highest tolerated dose (HTD)
  - Total protein content (TPC)
- Sublethality
  - RNA inhibition test
- Genotoxicity *in vitro*
  - Ames test
- *In vivo* testing with nematode model
- Biocide addition before testing (10 mg/l)
Summary – case 1

Cytotoxicity
- No indication of cytotoxic effects in HeLa229 cells were observed in HTD test
- Some indication of cytotoxicity with the highest concentration (0.24 mg/ml)

Sublethal effects
- No sublethal toxicity in RNA inhibition test

Genotoxicity
- No indication of genotoxicity

Nematode model
- No systemic effects tested in vivo using Nematode

FR3+FR4 tested can be considered non-toxic at concentrations lower than 0.12 mg/ml
- The material should not be judged toxic based solely on cytotoxicity data, but should be addressed in relation to other toxicity test results and the intended use of the product.
Case 2: Environmental safety


The aim of the work was to obtain more information on the biodegradability and environmental safety of CNF and CNF-based products by

- Studying the biodegradability of CNF gels
- Studying the biodegradability and compostability of CNF films and papers containing CNF
- Studying the ecotoxicity during biodegradation in the composting environment.
Studied materials

- Cellulose nanofibrils (CNF)
- CNF films
  - Vacuum filtration
  - Casting
- CNF Papers
  - CNF as an additive in the pulp furnish
  - CNF in the coating formulation
Methodology used

- Biodegradability of CNF gels - OECD 301B Ready Biodegradability – CO\textsubscript{2} evolution (Modified Sturm Test)
- Compostability of CNF films and papers: EN 14045 Packaging. Based on the visual evaluation of the disintegration.
- Ecotoxicity during disintegration of CNF films and paper (in the composting environment): ISO 21338 standard method (Kinetic luminescent bacteria test).
Summary – case 2

Fibrillation degree had an effect on biodegradability of CNF samples

- the finer CNF material degraded to a larger extent during the test period.

- CNF films and papers were biodegradable according to criteria in the standard and also suitable for composting.

- Papers containing CNF even degraded further than reference paper during the 65 d test period.

- No acute ecotoxicity was observed during biodegradation of CNF films and papers.
Selection of right toxicity testing methods crucial!
- Not all suitable for gel-like materials, e.g. restriction of movement
- ECHA’s recommendations
  - E.g. bacterial testing not recommended for nanomaterials

Contamination
- False positives

Addition of biocides
- Need to know the correct dose that does not affect the test result
Case 3: Risk assessment of polymer composites containing CNF
Background and motivation

CNF offer sustainable alternative for manufacturing of light-weight composites with reduced carbon footprint.

However, little is known about the behavior of CNF at the different phases of the composites’ life cycle.

Exposure to CNFs during production, use or end-of-life may lead to e.g.

- inflammatory effects of employees
- unwanted adverse effects in the environment

Risk assessment performed to control and minimize any unwanted effects.
Approach

Risk = Exposure × Hazard

Identified critical points
1. Occupational
2. Environment
3. Consumer use
4. End-of-life

Information from the literature
1. Human health
2. Environment

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</table>
Hazard – information from the literature
Reported effects of CNF exposure

To humans

- Dose-dependent cytotoxicity
- Inflammatory effects
  - Potential resolution over time
  - Driven by material surface chemistry
- Biodurability in lungs
- Toxicity induced by chemical modification
- Raw material dependency – fibril dimensions

To environment

- Generally not acutely toxic to test organisms
- Surface charge had minimal influence
- Restriction of movement
- Raw material dependency – shape
- Biodegradability dependent on surface chemistry and fibrillation degree (available surface area)

Critical points in nano-composite manufacturing

The pre-production state, where the nanomaterials are at powder state, is the one with the highest risk.
- carrying, handling and weighing

Critical operations during production are mixing and pouring

Exposure in the post-production stage during demolding, curing and cleaning of the equipment is also possible, but with lower probability.

The final nanocomposite is unlikely to present a direct risk because nanoparticles are trapped into the solid resin.

However, machining of the composite may lead to exposure – during manufacturing, cutting and milling of composites containing CNC, the the highest exposure was during cutting of the composite.

For carbon nanotubes (CNT), release was not observed from ductile composite materials, whereas from brittle materials release was observed.

Weathering: all the studied materials exposed CNTs to the environment when the matrix was degraded by UV-light.


Exposure
Composite production in EU INCOM

The top-down and bottom-up approaches of the INCOM project
Lab scale production @VTT

1. Raw materials’ addition
   - Epoxy

2. Grinding
   - Spills
   - Aerosols, if volatiles

3. Hardening agent is added
   - Potential exposure points marked with red

4. Pouring into container
   - Spills

5. Transportation to molding place
   - Spills

6. Application into mold by pressure

7. Treatment with pressure at elevated temperature

8. Composite material containing cellulose nanomaterial

9. Cleaning the equipment
   - Spills
Industrial production @ small scale

- Resin transfer molding – RTM
- Seed moulding compound – SCM
- Vacuum injection
- Filament winding
Main exposure routes

- Inhalation exposure
- Skin exposure
1. Potential occupational exposure – critical points

- Spills during mixing of CNF and polymer
- Pressure in the mould - RTM
  - Breakage or leakage of the piping
- Spills during winding
- Machining – cutting, sanding etc.
  - High probability for exposure according to previous studies
- Mitigation measures
  - Fume hood, fresh air hood
2. Potential environmental exposure during production

- Material waste
  - Raw materials
  - Finishing residues incl. dust
- Washing water
  - Containers
  - Floors, surfaces etc.
- Mitigation
  - Minimize raw material waste
  - Re-use of finishing residues
  - Minimize dust in the working space, fume hood
  - Suitable cleaning methods for spills
3. Consumer use

Potential exposure depends on the end use and could take place e.g. by
- Wear and tear
- Machining, drilling, sanding etc.

Case example: sport equipment
- Cutting into size – not probable
- Polishing – not needed
- Accidental snapping
4. End of life

- Depends on the end use
  - Recycling
  - Re-use
  - Waste disposal: inceniration, landfill
- In case of sport equipment, inceniration is the most probable route
  - CNFs burned forming carbon
Conclusions – risk assessment

- No major concern found in lab scale or industrial production @ small scale
- As typical for risk assessment, exposure during the production steps and hazard related to the materials should be evaluated case-by-case
  - Increasing knowledge of hazardous properties and behavior of nanomaterials calls for continual review of the risk assessment and management measures
Acknowledgements – case 3

The research leading to these results has received funding from the European Union Seventh Framework Programme under grant agreement no 608746.

Co-authors Marja Pitkänen and Lisa Wikström
Risk assessment according to European Commission Recommendation
Risk assessment based on European Commission’s \textit{Guideline on the protection of the health and safety of workers from the potential risks related to nanomaterials at work}.

A 7-step procedure

1. Identification
   - Do nanomaterials exist in the workplace?
   - Check the inventories of substances applied and supplied
   - Material safety data sheets (MSDS) as primary sources of information
   - Contact the supplier / manufacturer if in doubt
   - REACH, CLP, European Observatory for Nanomaterials
     https://euon.echa.europa.eu

2. Hazard assessment
   - Information about hazardous properties needed: labels, SDS, occupational exposure limit values and scientific publications.
A 7-step procedure

3. Exposure
   - Consider all the routine operations and other foreseeable events in detail
   - Some clarifying questions
     - Is the material dusty or the process likely to generate dusts or aerosols?
     - Does the process include cutting, shearing, grinding, abrasion, or other mechanical release?
     - How often is exposure likely to occur?
   - Four classes of potential exposure

4. Risk categorisation
A 7-step procedure

5. Detailed risk assessment
   › Needed for risk levels 3 & 4
   › Quantative assessment of exposure

6. Risk management
   1) elimination or substitution
   2) process modification
   3) isolation or enclosing
   4) engineering control
   5) administrative control
   6) personal protective equipment (PPE)

7. Review
   › Regular check-up
Recommendations & next steps

- The safety of cellulose nanomaterials and CNM-based products should be evaluated case by case
- Co-operation for the development of testing methods needed
  - Validation / standardisation
- Increased understanding of the knowledge gaps
  - Short-term / long-term
- Pro-active communication between academia, producers, authorities etc.
  - Data from actual production needed for risk analysis